

**Highly Localised Surface Plasmon Polaritons
in Active Metallo-organic Multilayer Structures**

By Hong Yoon

Experimental Solid State Physics Group, Department of Physics
Imperial College London

May 2012

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy
of Imperial College London

Declaration of Originality

DECLARATION:

I certify that this assignment is my own work, except where indicated by referencing.

Abstract

Amplification of surface plasmon polaritons in plasmonic systems have been of great interest for realizing active nanophotonic devices. In this thesis, we present a study about optical gain of SPPs supported in planar metallo-organic multilayer structures based on the Kretschmann geometry. First, we present the effect of varying the geometry on behaviours of surface plasmon propagation, which appear as the change of angular reflectivity. A theoretical approach explains the characteristics well.

A kind of conjugated polymer material is introduced to the structures for obtaining gain. A film of this material with nanometer thickness is attached close to a metallic layer, being optically excited to supply energy. For understanding the interaction between surface plasmon polaritons and the active films, we experimentally investigate energy transfer channels from the active material to surface plasmons with an aid of a theoretical analysis. This result provides a strong evidence of being capable of exciting surface plasmon polaritons via dipole excitation.

We also report an experimental demonstration of optical gain properties in conventional waveguide structures where the active material acts as propagating channel by measuring amplified spontaneous emission phenomena, providing information of achievable optical gain.

Based on the strong evidences of both the active and passive properties, we demonstrate plasmonic gain in the structure incorporating the polymer film for the first time. For this, a double lock-in amplifier system is introduced. Plasmonic modal gain is explained with a support of theoretical estimates. The achieved modal gain is 9 cm^{-1} . This work suggests the design principle for active nano plasmonic devices.

Acknowledgements

This work would not have been possible without the support of many people. First, I heartily express my gratitude to my supervisors, Dr. Paul Stavrinou, Prof. Stefan Maier and Prof. Donal Bradley for their abundant guidance and encouragement. Their invaluable vision and knowledge has helped to open my eyes to look beyond science. I also thank Dr. Gihan Ryu for his helpful input and positive support. My discussions with him were always a pleasure and turned out to be critical to the progress of this work.

Special thanks go to Dr. Yannick Sonnefraud, Dr. Colin Belton, and Dr. Ruidong Xia in the group, for generosity in sharing ideas and for meticulous technical assistance in the lab, to my fellow graduates in the EXSS, especially Warren and Dangyuan for showing immense persistence and creativity. I also thank Carolyn and Bhavna in the group office for providing a supportive environment and helpful administrative work.

Finally, I thank my parents and sister for their deepest love and trust over the entire period of my study. I also thank my Korean fellows in Imperial for sharing life in London as well as discussions on various scientific issues.

If I have seen further, it is by standing on the shoulders of giants.
- Sir Isaac Newton, 1643-1727

Contents

Abstract	3
Contents.....	6
1 Introduction.....	9
1.1 Historical perspective on Surface Plasmons	9
1.2 SPP related research.....	10
1.3 Concepts: Towards Active Plasmonic devices.....	11
1.4 Outline of this thesis	12
References.....	14
2 Surface Plasmon Polaritons and Conjugated Polymers	23
2.1 Introduction.....	23
2.2 Characteristics of Surface Plasmon Polariton Propagation.....	23
2.2.1 Surface Plasmon Polaritons at a Single Interface	23
2.2.2 Plasmonic Excitation via Prism Coupling	27
2.2.3 Electric Permittivity of Silver	28
2.3 Optical Characterisation of Conjugated Polymers	32
2.3.1 Introduction	32
2.3.2 Absorption and Fluorescence	35
2.3.3 Photoluminescence lifetime.....	37
2.3.4 Photoluminescence Quantum yield	39
2.4 Summary	41
References.....	41
3 Surface Plasmon Polaritons in Prism-based Geometry	45
3.1 Introduction.....	45
3.2 The Attenuated Total Reflection (ATR) Method.....	46
3.2.1 Prism Coupling System	46
3.2.2 Operation	48
3.2.3 Angular Reflectivity Curves	49
3.3 Modeling of Surface Plasmon Propagations.....	51
3.3.1 Fresnel Formulae and Cavity Picture	51
3.3.2 Transfer Matrix Method.....	53
3.3.3 Dispersion Relation: Leaky Mode	56

3.3.4	Mode Behaviour with Geometrical Variation	58
3.3.5	Environment Change near Metal Layer	61
3.4	Summary	63
	References	64
4	Surface Plasmon Polaritons in Metallo-Organic Multi-layers	66
4.1	Introduction	66
4.2	Layer Fabrication	67
4.2.1	Silver Deposition	67
4.2.2	Polymer Film Formation.....	67
4.3	Surface Plasmon Polaritons in One-layer Structure.....	70
4.3.1	Geometric Dependence.....	70
4.3.2	Polarization Property	71
4.3.3	Spectral Dispersion.....	72
4.4	Surface Plasmon Polaritons in the Two-Layer Structures.....	74
4.4.1	Propagation Modes	74
4.4.2	Layer Thickness Dependence	77
4.4.3	SPP mode versus Photonic mode.....	80
4.5	Film Morphology Effect on SPPs	83
4.6	Summary	86
	References	87
5	Dipole Energy Transfer to Multi-layer Structures.....	89
5.1	Introduction.....	89
5.2	Surface Plasmon Coupled Emission (SPCE)	90
5.2.1	Energy Transfer to Surface Plasmon Polaritons	90
5.2.2	Setup	92
5.2.3	Modeling of Angular Emission Distribution	93
5.2.4	Directional Emission.....	95
5.2.5	Spectral Properties: SPP Dispersion	97
5.2.6	Sensitivity to Emission Spectrum	99
5.3	Excitation of Photonic Guided Modes	102
5.3.1	Photonic Modes in Asymmetric Slab Waveguides	103
5.3.2	Amplified Spontaneous Emission (ASE): Mirrorless Lasing.....	106
5.3.3	Variable Pump Intensity (VPI) Method	107
5.3.4	Variable Stripe Length (VSL) Method.....	110
5.4	Summary	114

References.....	114
6 Plasmonic Gain	120
6.1 Introduction: Amplification of Surface Plasmon Polaritons	120
6.2 Experimental Realization.....	122
6.2.1 Gain Effects in the ATR configuration	122
6.2.2 Optical Pumping Conditions	125
6.3 Setup	127
6.3.1 Double Modulation Technique	128
6.3.2 Photodetector Setting.....	129
6.3.3 Calibration Factors	130
6.3.4 Verification of the Detection Scheme	134
6.4 Results.....	136
6.4.1 Differential Angular Reflectivity	136
6.4.2 Other Effects.....	138
6.5 Extraction of Plasmonic Gain	140
6.6 Effect of Spacer Layer	142
6.7 Towards Active Plasmonic Devices	145
6.8 Summary	151
References.....	152
7 Conclusion	156
Appendix	160
A. Power Dissipation Density Calculation	160
B. Angular Radiation Distribution.....	162
C. Mathematical description of the signal process in dual-cascaded lock- in amplifiers for pump-probe experiments (faster probe modulation frequency: $\omega_e \ll \omega_p$)	164

1 Introduction

1.1 Historical perspective on Surface Plasmons

Nanophotonics, the study of optical phenomena that arise on subwavelength scales, has lately been receiving enormous attention by optical scientists due to many interesting features potentially present. Discoveries that deal with the interaction between light and matter on the nanoscale have been driven by growing interests of exploring new physics and supported by current advances in nanotechnology and nanoscience. A prime motivation of nanophotonics-related research lies in breaking the diffraction limit of light. New optical techniques capable of probing the sub-wavelength scale have been developed and employed to understand the characteristics of nanostructures of various kinds of materials, e.g. semiconductors, dielectrics and metals. Typical examples of methods are surface-enhanced Raman spectroscopy and near-field optical microscopy. Another important focus of nanophotonics was inspired by the rapid development of electronic chips (such as CPUs), which is positioned at the heart of the modern industrial revolution. This growing advancement, in terms of chip size and data processing speeds, is expected to face technical limits of fabrications, requiring new strategies in scientific and engineering viewpoints. Nanophotonic devices enabling to manipulate light signals in nano-engineered structures may be a potential alternative, which could make it possible to develop practical on-chip interconnectivity, reconciling the spatial gap with electronic devices.

Surface plasmon polaritons (SPPs), lying at the heart of nanophotonics, are unique optical phenomena that emerge at the interface between a metal and a dielectric. Metals as a main ingredient for SPPs support a quantum of plasma oscillation (plasmon). When plasmons couple with light, which is called polariton, the free electron gas in the metal oscillates resonantly with optical frequencies, leading to the propagation of an electromagnetic field on the metal's surface [1,2]. This resonance allows nanoscale light confinement and hence strong field enhancement. This gives SPPs unique optical properties, which stand out as a central part of nanophotonics field. SPPs, together with localised surface plasmons in three-dimensional metallic nanostructures, provide a physical background for the implementation of sub-wavelength optical devices. Because of their intriguing physical properties, the study of surface plasmon optics has been a rapidly growing field in nano-optics for over a decade. [3-5].

A brief historical perspective of surface plasmon polaritons is presented here. In 1909,

Sommerfeld provided an analytical description of radio frequency “surface waves” that arise at the boundary of hetero-materials (i.e. a lossy material) [6]. Fano, in 1936, suggested anomalies that appeared in the diffraction spectra of metallic gratings resulting in the surface’s electromagnetic waves [7]. In 1958, Ferrell was the first to predict the dispersion relation of electromagnetic waves of metal surfaces [8]. In 1960, Powell and Swan observed the excitation of surface plasmons at metal interfaces using electrons injected into aluminum foils [9], as it was theoretically predicted by Ritchie in 1957 [10,11]. These works confirmed the physical reality of surface plasmon waves.

The study of surface waves in the optical frequency region was initiated by Otto in 1968 [12]. Otto invented the attenuated-total-reflection (ATR) method that enables the direct coupling of bulk electromagnetic waves with surface waves at metallic interfaces. In the same year, Kretschmann and Raether devised a similar prism-based geometry [13] that many scientists have employed for SPP-related research. A few years later, Raether (1988) delivered an insightful review of the SPP studies [1]. The use of prisms for SPP excitation is a very simple and useful way to probe SPPs and allow their behaviour to be seen in momentum space. This technique is the main experimental tool in this thesis.

Scanning near-field optical microscopy (SNOM) is also an important tool for the study of plasmonic fields [14,15]. Since Fischer and Pohl (in 1989) first demonstrated the plasmonic effect in the near-field region [16], the technique has been extensively utilised to characterise propagating surface plasmons and localised plasmons, both of which have the evanescent nature of near fields [17-20]. This technique allows for the direct visualisation of SPP near-fields and proves the theoretical predictions of field behaviours.

1.2 SPP related research

New knowledge of the physical backgrounds of SPPs enables scientists to control light in different ways. They have started to discover unusual optical phenomena unobservable in normal optical materials and environments. Lewis reported the first experimental demonstration of light transmission through sub-micrometre metal holes in the microwave region in 1984 [21]. Ebbesen (in 1998) presented extraordinary transmission phenomena mediated by optical SPPs [22]. His work sparked enormous attention from scientists with the introduction of new optical materials termed ‘metamaterials’. Pendry in 2000 suggested a theoretical foundation of ‘superlens’ concept [23]. His work has shown a huge potential for creating new functional materials and devices before unimaginable, such as cloaking devices and the superlens with resolution beyond diffraction-limit [24-27].

Plasmonic metallic structures of one to three dimensions have been proven to have the

ability to sense low-level signal changes, due to enhancements of electromagnetic fields. This has been beneficial to nano-object and biological imaging, down to single-molecule level resolution [28,29]. One typical example is surface-enhanced Raman spectroscopy (SERS) [30, 31]. Raman signals enhanced over 10^{10} times in metal nanostructures can be attained [32]. This has led to amazing breakthroughs in sensor and diagnostic applications.

Studies of SPPs also developed applications in light manipulation beyond the diffraction limit, e.g. nano-waveguides [33-42] and nano-resonators [43-50]. Various plasmonic devices for telecommunication applications have been developed in combination with nanostructures, such as optical switches [51-55], polarisation controllers [56-59], and wavelength filters [60-63]. Improvement of the optical performance of optoelectronic devices using plasmonic effects also have been intensively studied; for example, the enhanced absorption and photocurrent generation for light energy harvesting [64-66] and improved out-coupling properties of light-emitting diodes [67-69]. Furthermore, studies of SPPs have explored quantum optic fields dealing with single photons that deliver quantum information [70-72].

The science and technology dealing with optical interaction with free electron oscillation are popularly named *plasmonics* [33,73]. Research into plasmonics has been facilitated by the development of nanofabrication technologies and advanced computing systems for numerical simulations and proven new optical techniques with high sensitivity and accuracy. As the study of metal optics rapidly extends to various applications by combining inorganic and organic semiconductors, plasmonics still demands novel measurement techniques and new concepts of materials.

1.3 Concepts: Towards Active Plasmonic devices

Active control of SPPs is a key issue in nanoplasmonic optics. Study of the dynamic effects of SPPs, termed ‘active plasmonics’, enables us to demonstrate optical functional circuits in nanostructures. Dynamic manipulation of optical signals in general lies in the use of active materials such as fluorescent materials. Photon (optical pumping) and current injections are typical examples of external energy methods for signal control. When energy is injected into a structure composed of an active material, the optical or physical properties of the material (such as electric permittivity) varies so that the signal light experiences different propagation conditions, thus showing modulation. This project is concerned with the optical pumping case because of its efficient generation of electron-hole pairs.

In addition to typical methods for SPP excitation such as prism coupling [74] and

grating coupling [75,76], dipole excitation can be addressed as an energy injection method into metallic interfaces [77]. Optical pumping uses an energy transfer process of oscillating dipoles in active materials. Energy transfer at the nanometre scale has been an important subject in nano-optic research since Forster addressed the effect of near-field interactions between closely spaced molecules [78]. Though energy transfer mechanisms between surface plasmons and electron-hole pairs in an optical gain medium have been investigated (including SPP enhanced emission [79,80], SPP enhanced absorption [82-83], and SPP enhanced electromagnetic field confinement), the mechanisms are not yet completely understood. However, as proven in many optoelectronic devices, it is expected that adopting the scheme of SPP-supported configuration enables active control of SPPs. Furthermore, especially for optical gain, the energy transfer process is an important step to realize amplification of SPPs.

To practically implement the demanding active functions of SPPs, one serious drawback has to be remedied: the short propagation length of SPP modes due to optical damping in metals. Since a theoretical background of stimulated emissions of surface plasmon polaritons was suggested by Stockman in 2003 [84], several experiments have attempted to compensate for the propagation loss of surface plasmons and to obtain gains to overcome the loss by using materials with optical gain, e.g., dye or semiconductors [85-89]. However, systematic studies for elucidating the possible mechanism must still be conducted in order to design concepts to incorporate the appropriate gain medium. Additional plasmonics research would provide a sound scientific understanding of optical interactions in nanostructures and can be directly expanded into a variety of subjects that deal with light on the nanometre scale.

1.4 Outline of this thesis

This thesis presents a study about optical gain of surface plasmon polaritons supported in planar metallo-organic multilayer structures. The main experimental approach is based on the Kretschmann geometry of prism coupling.

Chapter 2 describes the ingredients of the plasmonic multi-layer structures utilised in this study: the metallic layer and the active polymer layer. Optical characteristic of silver as a metallic layer is described, and its adaptability as a plasmonic layer is stressed. The optical properties of SPPs from the viewpoint of SPP mode and propagation loss, and how they are linked to optical behaviours that appear in the Kretschmann geometry are demonstrated. Additionally, conjugated polymer as an active gain medium is introduced

and its optical properties are explained in detail.

Chapter 3 presents a prism coupling system, which produces angular reflectivity spectra, and its measurement procedure. Passive plasmonic behaviours of the multilayer structures are investigated experimentally, and theoretical approaches examine the experimental output. Suggestions are made regarding how surface plasmon propagation emerging at those structures can be understood with an appropriate theoretical tool, the transfer matrix method, in terms of angular reflectivity spectra and the wave vector of SPP modes.

Chapter 4 describes the experimental and theoretical results of the plasmonic behaviour of silver/polymer multilayers. SPP modes are demonstrated to be strongly influenced and controlled by varying the dimensions of constituting layers. This layer configuration is a main platform for studying and proving the active functions of SPPs in combination with the active polymer.

Chapter 5 includes discussion of the experimental and theoretical investigation of the energy transfer from an optically excited dipole in the active material to surface plasmons. It is found that the results provide strong evidence for exciting surface plasmon polaritons via dipole excitation. An experimental demonstration of amplified spontaneous emission phenomena in conventional waveguide structures, where the active material acts as a propagating channel, is also reported.

In Chapter 6, plasmonic gain using a thin active polymer film is demonstrated for the first time. The experimental challenges of combining a pump-probe measurement scheme and a double lock-in amplifier technique are identified. The plasmonic gain is described by theoretical estimates in the SPP modal point of view.

Finally, Chapter 7 will summarise the overall results and discuss how the findings can be expanded to develop new nanophotonic devices.

References

- [1] Heinx Raether, Surface Plasmons on Smooth and Rough Surfaces and on Gratings, (Springer, Berlin, 1988)
- [2] Stefan A. Maier, Plasmonics: Fundamentals and Applications, New York, Springer, 2007, ISBN: 0387331506
- [3] E. Yablonovitch, "Inhibited spontaneous emission in solid-state physics and electronics," Phys. Rev. Lett. **58**, 2059–2062 (1987).
- [4] E. Chow, S. Y. Lin, S. G. Johnson, P. R. Villeneuve, J. D. Joannopoulos, J. R. Wendt, G. A. Vawter, W. Zubrzycki, H. Hou, and A. Alleman, "Three-dimensional control of light in a two-dimensional photonic crystal slab," Nature **407**, 983-6 (2000).
- [5] H.-G. Park, C. J. Barrelet, Y. Wu, B. Tian, F. Qian, and C. M. Lieber, "A wavelength-selective photonic-crystal waveguide coupled to a nanowire light source," Nature Photon. **2**, 622-626 (2008).
- [6] A. Sommerfeld, Partial Differential Equations in Physics, 4th ed. (Academic Press, 1967).
- [7] U. Fano, "Some theoretical considerations on anomalous diffraction gratings," Phys. Rev. **630**, 1936-1936 (1936).
- [8] R. Ferrell, "Predicted radiation of plasma oscillations in metal films," Phys. Rev. **111**, 1214-1222 (1958).
- [9] C. Powell and J. Swan, "Effect of oxidation on the characteristic loss spectra of aluminum and magnesium," Phys. Rev. **118**, 640 (1960).
- [10] R. Ritchie, "Plasma losses by fast electrons in thin films," Phys. Rev. **106**, 874 (1957).
- [11] R. Ritchie, "Surface plasmons in solids 1," Surf. Sci. **34**, 1–19 (1973).
- [12] A. Otto, "Excitation of nanradiative surface plasmon waves in silver by the

method of frustrated total reflection," *Zeitschrift fur Physik* **216**, 398-410 (1968).

[13] E. Kretschmann and H. Raether, "Radiative decay of non-radiative surface plasmons excited by light," *Z. Naturforsch* **23a**, 2135 (1968).

[14] Pohl, D. W. 1982 Optical near-field scanning microscope. US Patent no. 4 604 520.

[15] Pohl, D. W. 1991 Scanning near-field optical microscopy (SNOM). In *Advances in optical and electron microscopy*, vol. 12, pp. 243–312. London: Academic.

[16] F. Republic, "Observation of single-particle plasmons by near-field optical Microscopy," *Phys. Rev.* **62**, 2-6 (1989).

[17] D. Tsai, J. Kovacs, Z. Wang, M. Moskovits, V. M. Shalaev, J. Suh, and R. Botet, "Photon scanning tunneling microscopy images of optical excitations of fractal metal colloid clusters," *Phys. Rev. Lett.* **72**, 4149–4152 (1994).

[18] S. I. Bozhevolnyi, B. Vohnsen, I. I. Smolyaninov, and A.V. Zayats, "Direct observation of surface polariton localization caused by surface roughness," *Opt. Commun.* **117**, 417–423 (1995).

[19] P. Dawson, B. Puygranier, and J.-P. Goudonnet, "Surface plasmon polariton propagation length: A direct comparison using photon scanning tunneling microscopy and attenuated total reflection," *Phys. Rev. B* **63**, 1-10 (2001).

[20] L. Salomon, G. Bassou, H. Aourag, J. Dufour, F. de Fornel, F. Carcenac, and A.V. Zayats, "Local excitation of surface plasmon polaritons at discontinuities of a metal film: Theoretical analysis and optical near-field measurements," *Phys. Rev. B* **65**, 1-5 (2002).

[21] A. Lewis, M. Isaacson, A. Harootunian, and A. Muray, "Development of a 500 Å spatial resolution light microscope: I. light is efficiently transmitted through $\lambda/16$ diameter apertures," *Ultramicroscopy* **13**, 227–231 (1984).

[22] T. W. Ebbesen, H. Lezec, H. Ghaemi, T. Thio, and P. Wolff, "Extraordinary optical transmission through sub-wavelength hole arrays," *Nature* **391**, 667–669 (1998).

[23] J. Pendry, "Negative refraction makes a perfect lens," *Phys. Rev. Lett.* **85**, 3966-9

(2000).

[24] N. Fang, H. Lee, C. Sun, and X. Zhang, "Sub-diffraction-limited optical imaging with a silver superlens," *Science* **308**, 534 (2005).

[25] J. B. Pendry, D. Schurig, and D. R. Smith, "Controlling electromagnetic fields," *Science* **312**, 1780-2 (2006).

[26] W. Cai, U. K. Chettiar, A. V. Kildishev, and V. M. Shalaev, "Optical cloaking with metamaterials," *Nature Photon.* **1**, 224-227 (2007).

[27] X. Zhang and Z. Liu, "Superlenses to overcome the diffraction limit," *Nature Mater.* **7**, 435-41 (2008).

[28] K. Kneipp, Y. Wang, H. Kneipp, L. Perelman, I. Itzkan, R. Dasari, and M. Feld, "Single molecule detection using surface-enhanced Raman scattering (SERS)," *Phys. Rev. Lett.* **78**, 1667-1670 (1997).

[29] S. Nie, "Probing single molecules and single nanoparticles by surface-enhanced Raman scattering," *Science* **275**, 1102-1106 (1997).

[30] J. Tsang, J. Kirtley, and J. Bradley, "Surface-enhanced Raman spectroscopy and surface plasmons," *Phys. Rev. Lett.* **43**, 772-775 (1979).

[31] S. Ushioda and Y. Sasaki, "Raman scattering mediated by surface-plasmon polariton resonance," *Phys. Rev. B* **27**, 1401 (1983).

[32] J. A. Dieringer, B. Robert, I. Lettan, K. A. Scheidt, and R. P. Van Duyne, "A frequency domain existence proof of single-molecule surface-enhanced Raman spectroscopy," *J. Am. Chem. Soc.* **129**, 16249-16256 (2007).

[33] S. A. Maier, M. L. Brongersma, P.G. Kik, S. Meltzer, A.A. G. Requicha, and H. A. Atwater, "Plasmonics-A route to nanoscale optical devices," *Adv. Mater.* **13**, 1501-1505 (2001).

[34] S. A. Maier and H. A. Atwater, "Plasmonics: Localization and guiding of electromagnetic energy in metal/dielectric structures," *J. Appl. Phys.* **98**, 011101 (2005).

- [35] S. I. Bozhevolnyi, V. S. Volkov, E. Devaux, J.-Y. Laluet, and T. W. Ebbesen, "Channel plasmon subwavelength waveguide components including interferometers and ring resonators," *Nature* **440**, 508-11 (2006).
- [36] J. Dionne, L. Sweatlock, H. Atwater, and A. Polman, "Plasmon slot waveguides: Towards chip-scale propagation with subwavelength-scale localization," *Phys. Rev. B* **73**, 1-9 (2006).
- [37] B. Wang and G. P. Wang, "Planar metal heterostructures for nanoplasmonic waveguides," *Appl. Phys. Lett.* **90**, 013114 (2007).
- [38] Y. Matsuzaki, T. Okamoto, M. Haraguchi, M. Fukui, and M. Nakagaki, "Characteristics of gap plasmon waveguide with stub structures," *Opt. Express* **16**, 16314-25 (2008).
- [39] A. L. Pyayt, B. Wiley, Y. Xia, A. Chen, and L. Dalton, "Integration of photonic and silver nanowire plasmonic waveguides," *Nature Nanotech.* **3**, 660-5 (2008).
- [40] N. Berkovitch, M. Orenstein, and S. G. Lipson, "Novel complex modes in asymmetrical nanoscale plasmonic waveguides," *Opt. Express* **16**, 17842-7 (2008).
- [41] R. F. Oulton, V. J. Sorger, D. A. Genov, D. F. P. Pile, and X. Zhang, "A hybrid plasmonic waveguide for subwavelength confinement and long-range propagation," *Nature Photon.* **2**, 496-500 (2008).
- [42] X. Guo, M. Qiu, J. Bao, B. J. Wiley, Q. Yang, X. Zhang, Y. Ma, H. Yu, and L. Tong, "Direct coupling of plasmonic and photonic nanowires for hybrid nanophotonic components and circuits," *Nano Lett.* **9**, 4515-9 (2009).
- [43] H. Ditlbacher, A. Hohenau, D. Wagner, U. Kreibig, M. Rogers, F. Hofer, F. Aussenegg, and J. Krenn, "Silver nanowires as surface plasmon resonators," *Phys. Rev. Lett.* **95**, 1-4 (2005).
- [44] A. Hosseini and Y. Massoud, "Nanoscale surface plasmon based resonator using rectangular geometry," *Appl. Phys. Lett.* **90**, 181102 (2007).

- [45] M. Ringler, A. Schwemer, M. Wunderlich, A. Nichtl, K. Kürzinger, T. Klar, and J. Feldmann, "Shaping emission spectra of fluorescent molecules with single plasmonic nanoresonators," *Phys. Rev. Lett.* **100**, 1-4 (2008).
- [46] E. J. R. Vesseur, R. de Waele, H. J. Lezec, H. A. Atwater, F. J. García de Abajo, and A. Polman, "Surface plasmon polariton modes in a single-crystal Au nanoresonator fabricated using focused-ion-beam milling," *Appl. Phys. Lett.* **92**, 083110 (2008).
- [47] J. Jung, T. Søndergaard, and S. Bozhevolnyi, "Gap plasmon-polariton nanoresonators: Scattering enhancement and launching of surface plasmon polaritons," *Phys. Rev. B* **79**, 1-8 (2009).
- [48] M. Nezhad, A. Simic, O. Bondarenko, B. Slutsky, A. Mizrahi, L. Feng, V. Lomakin, and Y. Fainman, "Room-temperature subwavelength metallo-dielectric lasers," *Nature Photon.* **4**, 395–399 (2010).
- [49] J. Petschulat, C. Helgert, M. Steinert, N. Bergner, C. Rockstuhl, F. Lederer, T. Pertsch, A. Tünnermann, and E.-B. Kley, "Plasmonic modes of extreme subwavelength nanocavities," *Opt. Lett.* **35**, 2693-5 (2010).
- [50] A. De Luca, M. P. Grzelczak, I. Pastoriza-Santos, L. M. Liz-Marzán, M. La Deda, M. Striccoli, and G. Strangi, "Dispersed and encapsulated gain medium in plasmonic nanoparticles: a multipronged approach to mitigate optical losses," *ACS Nano* **5**, 5823-5829 (2011).
- [51] T. Nikolajsen, K. Leosson, and S. I. Bozhevolnyi, "Surface plasmon polariton based modulators and switches operating at telecom wavelengths," *Appl. Phys. Lett.* **85**, 5833 (2004).
- [52] K. J. Chau, S. E. Irvine, and A. Y. Elezzabi, "A gigahertz surface magneto-plasmon optical modulator," *IEEE J. Quantum Elect.* **40**, 571-579 (2004).
- [53] J. J. Xiao, K. Yakubo, and K. W. Yu, "Optical switching in graded plasmonic waveguides," *Appl. Phys. Lett.* **88**, 241111 (2006).
- [54] J. A. Dionne, L. A. Sweatlock, M. T. Sheldon, A. P. Alivisatos, and H. A. Atwater, "Silicon-based plasmonics for on-chip photonics," *IEEE J. Sel. Top. Quant.* **16**, 295-306

(2010).

[55] D. Perron, M. Wu, C. Horvath, D. Bachman, and V. Van, "All-plasmonic switching based on thermal nonlinearity in a polymer plasmonic microring resonator," *Opt. Lett.* **36**, 2731-2733 (2011).

[56] J. Elliott, I. I. Smolyaninov, N. I. Zheludev, and A. V. Zayats, "Polarization control of optical transmission of a periodic array of elliptical nanoholes in a metal film," *Opt. Lett.* **29**, 1414-6 (2004).

[57] J. Elliott, I. I. Smolyaninov, N. I. Zheludev, and A. V. Zayats, "Polarization control of optical transmission of a periodic array of elliptical nanoholes in a metal film," *Opt. Lett.* **29**, 1414-6 (2004).

[58] A. V. Krasavin, A. S. Schwanecke, N. I. Zheludev, M. Reichelt, T. Stroucken, S. W. Koch, and E. M. Wright, "Polarization conversion and focusing of light propagating through a small chiral hole in a metallic screen," *Appl. Phys. Lett.* **86**, 201105 (2005).

[59] M. Sukharev and T. Seideman, "Phase and polarization control as a route to plasmonic nanodevices," *Nano Lett.* **6**, 715-9 (2006).

[60] V. S. Volkov, S. I. Bozhevolnyi, E. Devaux, J.-Y. Laluet, and T. W. Ebbesen, "Wavelength selective nanophotonic components utilizing channel plasmon polaritons," *Nano Lett.* **7**, 880-4 (2007).

[61] K. Diest, J. A. Dionne, M. Spain, and H. A. Atwater, "Tunable color filters based on metal-insulator-metal resonators," *Nano Lett.* **9**, 2579-83 (2009).

[62] A. Hosseini, H. Nejati, and Y. Massoud, "Design of a maximally flat optical low pass filter using plasmonic nanostrip waveguides," *Opt. Express* **15**, 15280-6 (2007).

[63] N. Talebi, A. Mahjoubfar, and M. Shahabadi, "Plasmonic ring resonator," *J. Opt. Soc. Am. B* **25**, 2116 (2008).

[64] K. R. Catchpole and A. Polman, "Plasmonic solar cells," *Opt. Express* **16**, 21793-800 (2008).

- [65] J. A. Schuller, E. S. Barnard, W. Cai, Y. C. Jun, J. S. White, and M. L. Brongersma, "Plasmonics for extreme light concentration and manipulation," *Nature Mater.* **9**, 193-204 (2010).
- [66] H. A. Atwater and A. Polman, "Plasmonics for improved photovoltaic devices," *Nature Mater.* **9**, 205-13 (2010).
- [67] P. A. Hobson, J. A. E. Wasey, I. Sage, and W. L. Barnes, "The role of surface plasmons in organic light-emitting diodes," *IEEE J. Sel. Top. Quant.* **8**, 378-386 (2002).
- [68] L. H. Smith, J. A. E. Wasey, and W. L. Barnes, "Light outcoupling efficiency of top-emitting organic light-emitting diodes," *Appl. Phys. Lett.* **84**, 2986 (2004).
- [69] P. Melpignano, V. Biondo, S. Sinesi, M. T. Gale, S. Westenhöfer, M. Murgia, S. Caria, and R. Zamboni, "Efficient light extraction and beam shaping from flexible, optically integrated organic light-emitting diodes," *Appl. Phys. Lett.* **88**, 153514 (2006).
- [70] E. Altewischer, M. P. van Exter, and J. P. Woerdman, "Plasmon-assisted transmission of entangled photons," *Nature* **418**, 304-6 (2002).
- [71] D. Chang, A. Sørensen, P. Hemmer, and M. Lukin, "Quantum optics with surface plasmons," *Phys. Rev. Lett.* **97**, 1-4 (2006).
- [72] D. E. Chang, A. S. Sørensen, E. A. Demler, and M. D. Lukin, "A single-photon transistor using nanoscale surface plasmons," *Nature Phys.* **3**, 807-812 (2007).
- [73] W. L. Barnes, A. Dereux, and T. W. Ebbesen, "Surface plasmon subwavelength optics," *Nature* **424**, 824–830 (2003).
- [74] J. J. Xu and J. F. Tang, "Optical properties of extremely thin films: studies using ATR techniques," *Appl. Opt.* **28**, 2925-8 (1989).
- [75] H. Raether, "Dispersion relation of surface plasmons on gold-and silver gratings," *Opt. Commun.* **42**, 217–222 (1982).
- [76] Y. Okuno, T. Suyama, R. Hu, S. He, and T. Matsuda, "Excitation of surface plasmons on a metal grating and its application to an index sensor," *IEICE transactions on*

electronics **90**, 1507–1514 (2007).

[77] R. R. Chance, A. Prock, and R. Silbey, "Molecular fluorescence and energy transfer near interfaces," *Adv. Chem. Phys.* **60**, 1-65 (1978).

[78] T. Forster, "Energiewanderung und fluoreszenz," *Naturwissenschaften* **33**, 166-175 (1946).

[79] P. A Hobson, S. Wedge, J. A E. Wasey, I. Sage, and W. L. Barnes, "Surface plasmon mediated emission from organic light-emitting diodes," *Adv. Mater.* **14**, 1393-1396 (2002).

[80] M.-K. Kwon, J.-Y. Kim, B.-H. Kim, I.-K. Park, C.-Y. Cho, C. C. Byeon, and S.-J. Park, "Surface-plasmon-enhanced light-emitting diodes," *Adv. Mater.* **20**, 1253-1257 (2008).

[81] K. Tvingstedt, N.-K. Persson, O. Inganäs, A. Rahachou, and I. V. Zozoulenko, "Surface plasmon increase absorption in polymer photovoltaic cells," *Appl. Phys. Lett.* **91**, 113514 (2007).

[82] P. N. Saeta, V. E. Ferry, D. Pacifici, J. N. Munday, and H. a Atwater, "How much can guided modes enhance absorption in thin solar cells?," *Opt. Express* **17**, 20975 (2009).

[83] Y. A. Akimov, K. Ostrikov, and E. P. Li, "Surface plasmon enhancement of optical absorption in thin-film silicon solar cells," *Plasmonics* **4**, 107-113 (2009).

[84] D. Bergman and M. Stockman, "Surface plasmon amplification by stimulated emission of radiation: quantum generation of coherent surface plasmons in nanosystems," *Phys. Rev. Lett.* **90**, 1-4 (2003).

[85] J. Seidel, S. Grafström, and L. Eng, "Stimulated emission of surface plasmons at the Interface between a silver film and an optically pumped dye solution," *Phys. Rev. Lett.* **94**, 177401 (2005).

[86] M. Noginov, V. Podolskiy, G. Zhu, M. Mayy, M. Bahoura, J. Adegoke, B. Ritzo, and K. Reynolds, "Compensation of loss in propagating surface plasmon polariton by gain in adjacent dielectric medium," *Opt. Express* **16**, 1385-92 (2008).

- [87] M. Ambati, S. H. Nam, E. Ulin-Avila, D. A. Genov, G. Bartal, and X. Zhang, "Observation of stimulated emission of surface plasmon polaritons," *Nano Lett.* **8**, 3998-4001 (2008).
- [88] I. Radko, M. G. Nielsen, O. Albrechtsen, and S. I. Bozhevolnyi, "Stimulated emission of surface plasmon polaritons by lead-sulphide quantum dots at near infra-red wavelengths," *Opt. Express* **18**, 18633-41 (2010).
- [89] J. Grandidier, G. C. des Francs, S. Massenot, A. Bouhelier, L. Markey, J.-C. Weeber, C. Finot, and A. Dereux, "Gain-assisted propagation in a plasmonic waveguide at telecom wavelength," *Nano Lett.* **9**, 2935-9 (2009).

2 Surface Plasmon Polaritons and Conjugated Polymers

2.1 Introduction

Active plasmonics is an emerging field in nanophotonics. Adding active functions to plasmonic media has been of immense interest due to its potential to introduce new applications. Nanolasers are one of those applications. Using surface plasmon polaritons makes it possible to control light in nanoscale space without occupying micrometre dimensions that conventional photonic waveguides typically require. The required ingredients for realising active plasmonics are specially designed plasmonic media and active materials, such as fluorescent polymers and semiconductor quantum dots.

In this chapter the key features of surface plasmon polaritons and light-emitting conjugated polymers as an active media are explained. Experimental demonstrations of active plasmonic behaviour in this thesis are based on the prism-coupling method. This chapter demonstrates the usefulness of the prism-coupling method to study optical properties of plasmonic nanostructures, with silver highlighted as a good plasmonic material as compared to other noble metals (such as gold and aluminum). Lastly, optical characterisations of conjugated polymers and related measurement methods are presented.

2.2 Characteristics of Surface Plasmon Polariton Propagation

2.2.1 Surface Plasmon Polaritons at a Single Interface

The basic understanding of surface plasmon polaritons (SPPs) comes from the simplest plasmonic structure, which is a single interface of a metal and a dielectric. Surface plasmon polaritons can be generated at the interface of two materials with the real values of electric permittivity of the opposite sign. For example, noble metals such as gold or silver have negative values of the real part of dielectric constants up to the ultraviolet frequency region, and dielectrics including glass and air have positive values. The combination of these two materials showing different optical properties makes light-guiding interfaces for SPP modes.

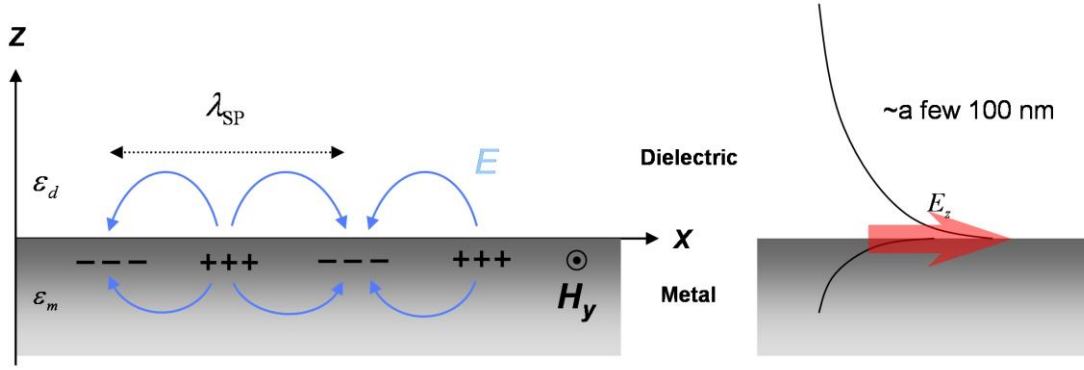


Figure 2.1 Description of the electric field and the charge distribution of surface plasmon polaritons at the metal/dielectric interface. The spatial period of electron gas oscillation is λ_{SPP} , which is shorter than the free space wavelength.

To understand the basics of surface plasmon polaritons, we begin with SPPs at a single metal/dielectric interface as shown in figure 2.1. In that planar interface, only transverse magnetic (TM) mode is taken into consideration for SPPs because there must be an electric field component oscillating parallel to the optical plane (x-z plane). Fields of TM polarization at the planar waveguide geometry (c.f. figure 2.1) can be described as follows.

$$\begin{aligned} E_d &= (E_{xd}, 0, E_{zd}) \exp i(k_{zd}x - k_{xd}z - \omega t) \\ H_d &= (0, H_{zd}, 0) \exp i(k_{zd}x - k_{xd}z - \omega t) \end{aligned} \quad (2.1)$$

For $z > 0$ (dielectric space),

$$\begin{aligned} E_m &= (E_{xm}, 0, E_{zm}) \exp i(k_{zm}x + k_{xm}z - \omega t) \\ H_m &= (0, H_{zm}, 0) \exp i(k_{zm}x + k_{xm}z - \omega t) \end{aligned} \quad (2.2)$$

For $z < 0$ (metallic space). ω is angular frequency of light, and k_{xd} and k_{xm} are the in-plane wavevectors and k_{zd} and k_{zm} are the out-of-plane wavevectors in the dielectric and the metal, respectively. The wave equation and governing equations derived from Maxwell's equations are given as,

$$\frac{d^2 H_{yi}(z)}{dz^2} + k_z^2 H_{yi}(z) = 0 \quad (2.3)$$

$$E_{xi}(z) = -\frac{i}{\omega \epsilon_0 \epsilon_i} \frac{dH_{yi}(z)}{dz} \quad (2.4)$$

$$E_{xi}(z) = \frac{k_x}{\omega \epsilon_0 \epsilon_i} H_{yi}(z) \quad (2.5)$$

where $i=d$ (dielectric) or m (metal).

We apply a boundary conditions that H_y and $\epsilon_i E_i$ are continuous at the interface, yielding

$$\frac{k_{zd}}{k_{zm}} + \frac{\epsilon_d}{\epsilon_m} = 0 \quad (2.6)$$

Fulfilling equation (2.3) for H_y produces

$$k_{zi}^2 = k_x^2 - \epsilon_i \left(\frac{\omega}{c} \right)^2 \quad (2.7)$$

Then combining equation (2.6) and (2.7) leads to the final dispersion equation.

$$k_x = \frac{\omega}{c} \sqrt{\frac{\epsilon_d \epsilon_m}{\epsilon_d + \epsilon_m}} = k_x' + i k_x'' \quad (2.8)$$

where $k_x' (= 2\pi/\lambda_{\text{SPP}})$ is the propagation constant, and λ_{SPP} is the spatial period of the SPP oscillation in metal as described in figure 2.1. SPPs propagate along the surface, exponentially decaying to both sides with different depths $\delta (= 1/[k_z])$. For instance, a silver/air interface has a decay depth of 23 nm at the silver side and 470 nm at the air side for a 675 nm wavelength. The evanescent fields with relative long decay depth at the dielectric side can be affected by a change in the environment.

The imaginary part of k_x , k_x'' determines the propagation length of SPPs, which is given by equation (2.9), as the intensity of SPPs decreases by internal damping loss due to its absorption in metal.

$$L_{\text{SPP}} = (2k_x'')^{-1} \quad (2.9)$$

L_{SPP} has a value of about 50 μm for a silver/air interface at 675 nm wavelength. In the lower frequency region, for instance THz [1, 2] and microwaves [3, 4], SPPs have longer propagation lengths than those in the visible region because fields extend into the dielectric region more and thus experience less absorption. This property could be useful for practical applications in this region.

Despite the short propagation length, other extraordinary characteristics of SPPs have been noticed. As compared to conventional waveguide structures, some important features of surface plasmon polaritons are pointed out: polarisation property, electric field (out-of-plane) discontinuity, and strong field confinement. Surface charge oscillations along the interface direction (x-axis) create the discontinuity of electric field E_z , the normal

component to the interface. Transverse Electric (TE) Polarisation waves that have only a E_y component cannot induce the surface in-plane oscillation of electrons, because the E_y field vector and SPP propagation vector are perpendicular each other. Planar multi-layer structures supporting plasmonic propagation generally show this polarisation dependence unless comprising materials have optical birefringence, whereas conventional waveguides can support both TE and TM polarisation modes. This polarisation property will be presented throughout this thesis.

Conventional waveguide structures relying on total internal reflection need to have at least one guiding layer, i.e. core layer (the electric permittivity ϵ_c), with a thickness that is comparable to or less than the wavelength of light, which is surrounded by a cladding material with a lower index of refraction $\sqrt{\epsilon_d}$, as seen in Figure 2.2(b). In those structures, for any guided fields fulfilling a phase-matching condition, a 2π round-trip phase shift of a transverse field in the core layer may be excited, but if the thickness of the layer decreases down to less than a cutoff thickness c.g. $\sim \lambda/10$ in planar silica/polymer waveguide with a index difference of 0.3, no guided modes can exist. On the other hand, the plasmonic single interface is not necessary to possess any layer at space. Instead, since metal has a negative sign of the real part of electric permittivity $\epsilon_m (< 0)$ and the dielectric has a positive sign of the real part of electric permittivity ϵ_d , the E_z field has a π phase-shift when crossing the interface and thus, a total round-trip phase of 2π around the interface can be satisfied. Hence plasmonic structures enable intense confinement of the electromagnetic field at the nanometre scale, thus leading to breaking the spatial limit of conventional optoelectronics devices.

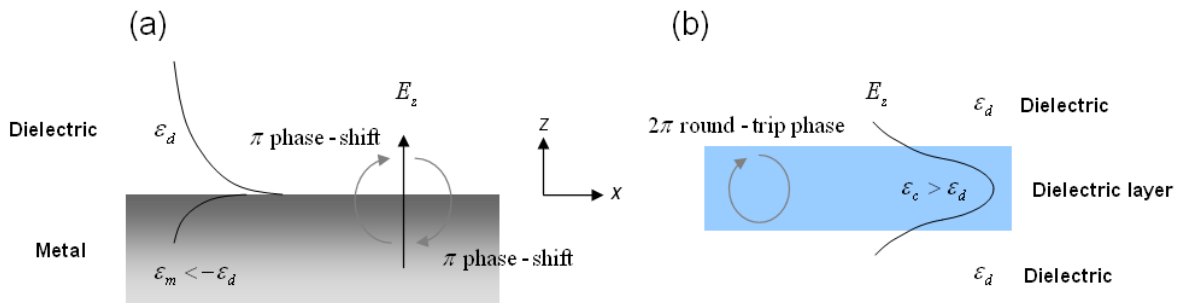


Figure 2.2 Comparison of phase-shift relations and field distributions for guiding conditions. Transverse field shapes of propagating modes are also depicted. (a) Surface plasmon polaritons at a single metal/dielectric interface (b) A conventional optical waveguide consisting of core dielectric region ϵ_c surrounded by clad dielectrics ϵ_d .

2.2.2 Plasmonic Excitation via Prism Coupling

Prism coupling is a useful technique to excite optical waveguide modes, including normal waveguide structures and surface plasmon polaritons (SPPs) multi-layer structures, and is known as the ‘attenuated total internal reflection (ATR)’ technique. The p- or s-polarised light that is inserted at an angle larger than the critical angle determined by a prism/air interface creates evanescent fields which can penetrate into a multi-layer structure through a tunneling gap if momentum matching is satisfied. The prism coupling method can be categorised by the type of its tunneling gap layer into two kinds of configurations (Figure 2.4). The Otto configuration includes a dielectric layer (e.g. air) as the tunneling layer [Ch1.12]; and the Kretschmann-Raether configuration includes a metal layer as the tunneling layer [Ch1.13].

As shown in Figure 2.2, the incoming light wave obtains higher momentum of light in the prism with electric permittivity ϵ_0 . The in-plane momentum (surface propagation momentum) of the incoming light is controlled by changing the incident angle in a way that the light line can be positioned to cross the dispersion curve for SPPs and the momentum of light can be matched to the in-plane momentum of SPP modes. The condition of equation (2.10) is fulfilled at a certain frequency:

$$k_{\text{SP}} = \frac{\omega}{c} \sqrt{\epsilon_0} \sin \theta \cong \text{Re} \left[k \sqrt{\frac{\epsilon_d \epsilon_m}{\epsilon_d + \epsilon_m}} \right] = \frac{\omega}{c} \left(\frac{\epsilon_d \epsilon_m'}{\epsilon_d + \epsilon_m'} \right) \quad (2.10)$$

where ϵ_d and $\epsilon_m (= \epsilon_m' + i\epsilon_m'')$ are the electric permittivity of dielectric and metal, respectively and we assume that $\epsilon_m'' < |\epsilon_m'|$. The SPP excitation is recognized as a minimum in the reflected light intensity. However, SPPs at the *metal/prism* interface cannot be excited because the interface mode has higher momentum than in prism.

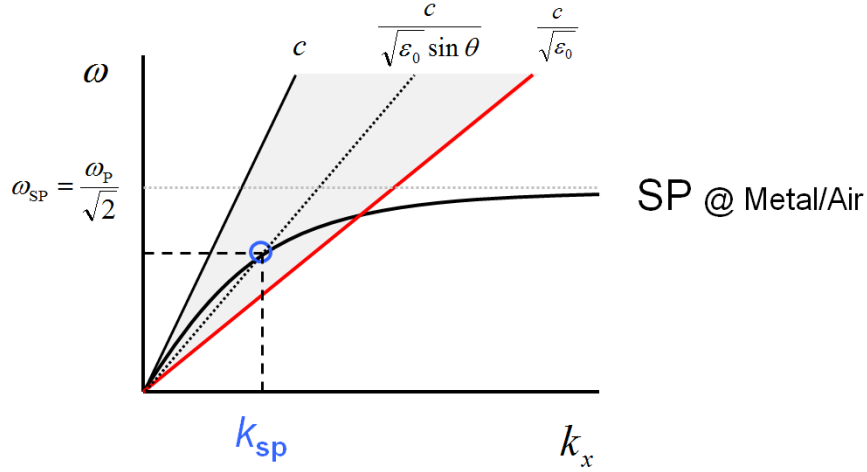


Figure 2.3 The dispersion relation for surface plasmon polariton propagation emerged at the metal/air interface via prism-coupling at certain incidence angle θ . At a given energy surface, plasmon momentum lies between the light line in air and in the prism with electric permittivity ϵ_0 .

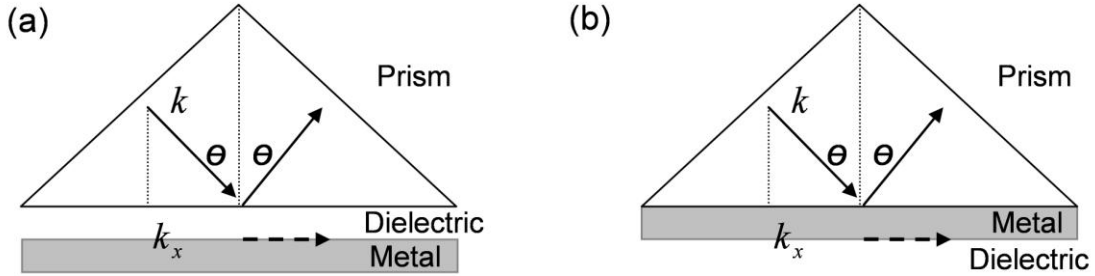


Figure 2.4 Configuration of the ATR method: (a) the Otto configuration (b) the Kretschmann-Raether configuration

By means of the prism coupler technique, we can precisely investigate the interactions between complex materials and light at the nanoscale by simply inserting propagating beam, and can study the control of light signals in a structure containing active layers.

2.2.3 Electric Permittivity of Silver

Materials capable of sustaining plasma-like behaviour of conducting electrons can be used for surface plasmon polariton media. For instance, various materials as well as noble metals have been demonstrated to support SPP propagation, including amorphous silicon [5], indium-tin-oxide (ITO) [6] that is widely used as a transparent electrode, and carbon-

based materials such as graphene [7].

In particular, the noble metals that behave like ideal plasma, e.g. copper, gold, and silver, have been preferred for studying surface plasmon polariton propagation, because noble metals have relatively smaller values of the imaginary part of dielectric constants than other metals, thus SPPs show less propagation loss. The optical characteristics of noble metals have often been studied via various experimental methods [8-15], including typical transmission and reflectance measurement [8, 9], ellipsometry [12] and the ATR method [13]. Theoretically, a plasma model known as the Drude model (equation (2.5)) can explain the optical properties of metals. This theoretical approach is a classical model that does not include quantum mechanical effects of the lattice potential and electron-electron interactions.

$$\varepsilon_m(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\omega/\tau_d} = \varepsilon_m'(\omega) + i\varepsilon_m''(\omega) \quad (2.11)$$

$$\varepsilon_m'(\omega) = 1 - \frac{\omega_p^2 \tau_d^2}{1 + \omega^2 \tau_d^2} \quad (2.12)$$

$$\varepsilon_m''(\omega) = \frac{\omega_p^2 \tau_d}{\omega(1 + \omega^2 \tau_d^2)} \quad (2.13)$$

where τ_d is the relaxation time of the electrons in the metal and ω_p is the plasma frequency, which is given by

$$\omega_p^2 = \frac{Ne^2}{\varepsilon_0 m_e} \quad (2.14)$$

where N is the electron density, e is the electron charge and m_e is the effective electron mass.

For metals, the interband absorption is associated with transitions from the Fermi surface to the next higher empty band or with transitions from a lower lying filled band to the Fermi surface. In the visible region of the spectrum, noble metals show Drude-like properties and silver is best fitted by the Drude model because its interband transitions are outside the visible region (at $\sim 4\text{eV}$).

As explained above, the ATR method has been used for studying dispersion relation of surface plasmons and also measuring dielectric constants, together with other techniques, including ellipsometry. Figure 2.5 shows the comparison of the experimental data of the electric permittivity of several observations and the fitted data from equations (2.12) and (2.13) of the Drude model with τ_d and ω_p taken from [11] as $1.30 \times 10^{16} \text{s}^{-1}$ and $4.28 \times 10^{-14} \text{s}$, respectively. The experimental observations include works of Johnson and Christy

(transmission and reflection method) [9], Dujardin & Theyeand (transmission and reflection method) [9], Nash and Sambles (SPP excitation using a metallic grating) [11] and U. Schroder [13] (the ATR method). Values are taken from Palik [14]. The Drude model does not describe the optical response of metals in the region at which electronic transitions to higher energy levels occur (the interband transitions).

In the visible wavelength range above approximately 500 nm, the experimental data of ϵ_m'' has a wide range of distribution. The ϵ_m'' values are more sensitive than ϵ_m' values regarding film deposition conditions and environment according to experimental conditions during measurement. In addition, the reason for the difference in ϵ_m'' is thought to be from the fact that the Drude theory deals with an ideal case of pure crystals, not a case of polycrystalline materials that would have a different τ_d [11]. Rasigni and Rouard [15] found a significant difference in measurement results between experiments conducted in air and in a vacuum. It is known that silver forms a silver sulphide layer and is more likely to be contaminated compared to gold. This kind of contamination causes an increase in $|\epsilon_m'|$ and $|\epsilon_m''|$ [11].

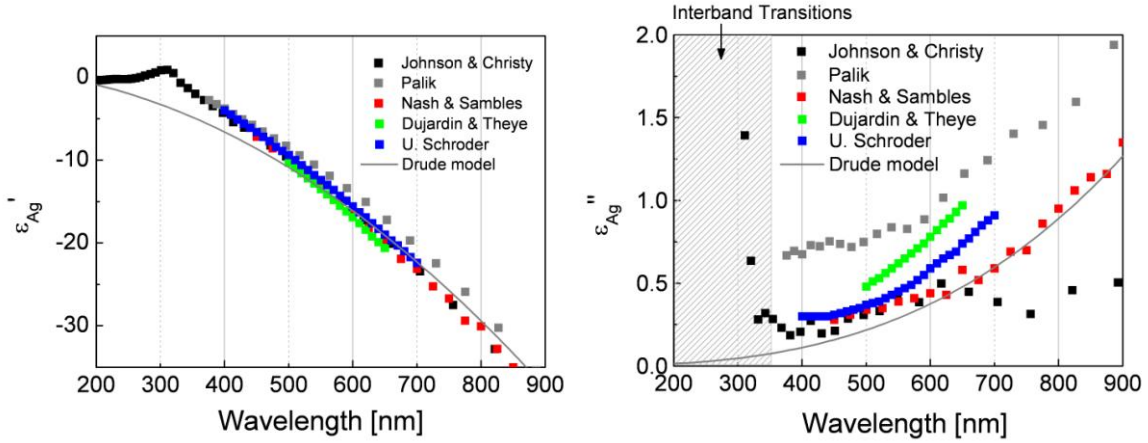


Figure 2.5 Comparison of real and imaginary part of silver permittivities taken from Johnson and Christy' [8], Dujardin and Theye' [9], Nash and Sambles' [11], U. Schroder's works [13], Palik's book [14], and the fitting data of the Drude model (grey solid line)

In this thesis, silver is mainly used as the metallic material as it presents the lowest optical loss at the visible range among the noble metals. This feature also appeared in its angular reflectivity behaviour in the prism-coupling case as the angular linewidth reflects the optical loss. Figure 2.6 shows the theoretical angular reflectivity curves from 40 nm-thick single films of silver, gold, and aluminum (in Kretschmann geometry), using the dielectric constants at 633 nm presented in Table 2.1. The reflectivity curve of the silver

film with respect to incidence angle in prism is much sharper than those of gold and aluminum. The sharpness of the dips is advantageous not only to investigate SPP characteristics against geometrical or environmental changes and excitation frequency, but also to apply to sensor applications that require high sensitivity.

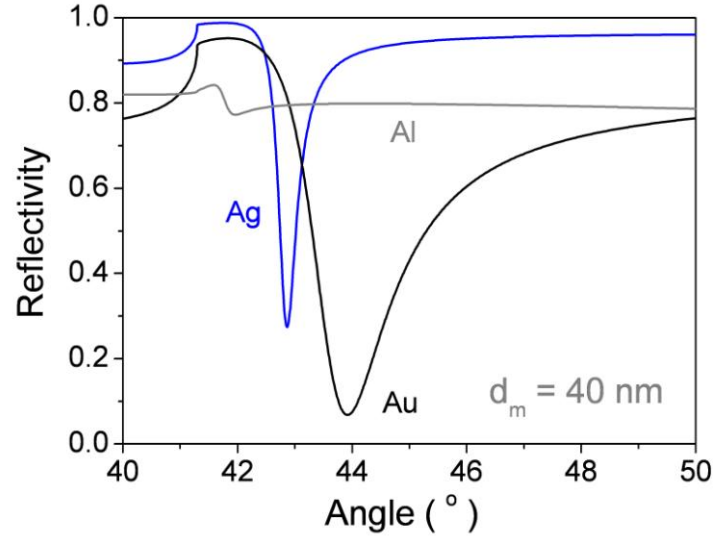


Figure 2.6 Theoretical angular reflectivity curves from 40 nm thick single films of silver, gold, and aluminum in the Kretschmann geometry using dielectric constants at 633 nm in Table 2.1

	$\varepsilon'_m(\omega)$	$\varepsilon''_m(\omega)$
Ag [8]	-18.4	0.48
Au [8]	-11.9	1.24
Al [15]	-47.0	18.0

Table 2.1 List of electric permittivities of silver, gold and aluminum at 633 nm. The values of silver and gold were taken from Ref. [8] and aluminum from Ref. [15]

2.3 Optical Characterisation of Conjugated Polymers

2.3.1 Introduction

Conjugated polymers have been recognized as promising active elements in organic light-emitting diodes (OLEDs) [17,18], photovoltaics (PVs) [19,20] and photo-pumped lasers [21,22]. Semiconducting conjugated polymers are a combination of repeated units of conjugated molecules that are based on a backbone of π -bonded carbon atoms. As an alternative of inorganic materials, conjugated polymers can offer active functions to current optoelectronic devices with fabrication advantages in terms of mass production and low cost. Optical properties of conjugated polymer are mainly subject to their electronic structures. This section will deal with chemical bonds that give rise to electronic and optical properties to organic materials.

As the essential building block for organic molecules, carbon has the ability to form long-chain molecules consisting of several repeat units. Semiconducting and metallic organic polymers are based on sp^2 hybridized linear carbon chains. The carbon atom has 6 electrons outside the nucleus, of which 4 are valence electrons; i.e. four (the 2s and the 2p electrons) take part in chemical bonds. By promoting one electron from 2s to 2p and taking a linear combination of s, p_x , p_y , and p_z orbitals, carbon can form two primary hybrid orbital structures in molecules or crystals; tetrahedrally directed covalent bonds (sp^3 hybridized) as in diamond and saturated polymers (plastic), and hexagonally directed covalent bonds (sp^2p_z hybridized) as in graphite and conjugated polymers. Ethane (C_2H_6) exhibits the simplest form of carbon-carbon double bonding that consists of three in-plane σ bonds and two π bonds (Figure 2.7).

In π -conjugated polymer chains, σ bonds create the 'backbone' while π electrons in π bonds are delocalized along the polymer chain. Thus, semiconducting and metallic behaviors of conjugated polymers originate from these overlapping of π bonds between sp^2p_z hybridized carbons. On the contrary, saturated polymers, where all of the valence electrons are bound in σ bonds, cannot transport electrons.

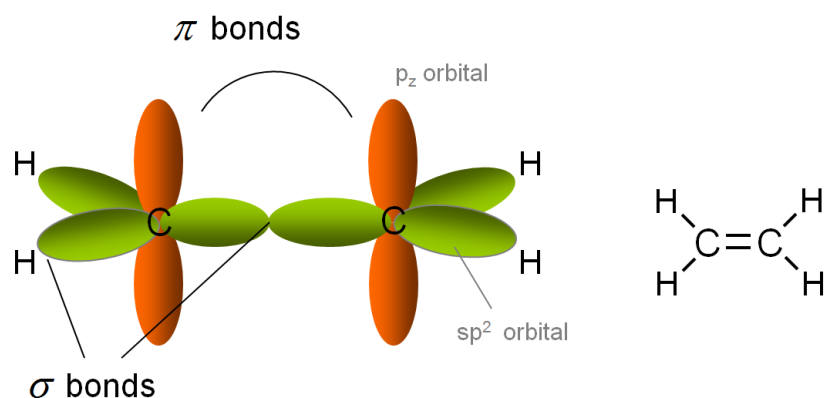


Figure 2.7 The σ and π bonding in ethene: the chemical double bonding between sp^2 hybridized carbons

π -conjugated molecules are created in a way where the carbon atoms are bonded by alternating single and double (or triple) bonds. The electronic structure of conjugated polymers with the bonding (π and σ) and antibonding (π^* and σ^*) band generated due to the overlap of orbitals band are sketched in figure 2.8. The π and π^* band is split into subbands according to the number of the carbon atoms in the repeat unit of conjugated polymers. Since each subband can hold two electron per atom (spin up and down), the lowest π subbands are filled and the highest π^* subband are empty. The highest π band state in electron-filled π bands is termed the highest occupied molecular orbit (HOMO) and the first unoccupied orbital (π^*) is designated the lowest unoccupied molecular orbit (LUMO) [23,24].

The energy difference between HOMO and LUMO defines a bandgap E_g and is determined by the length of conjugated segment. As length of combined molecules increases, more π states are admitted and the energy gap decreases as analogous to the quantum potential size effect. The HOMO level corresponds to the valence band in the inorganic semiconductors. The same analogy exists between the LUMO level and the conduction band.

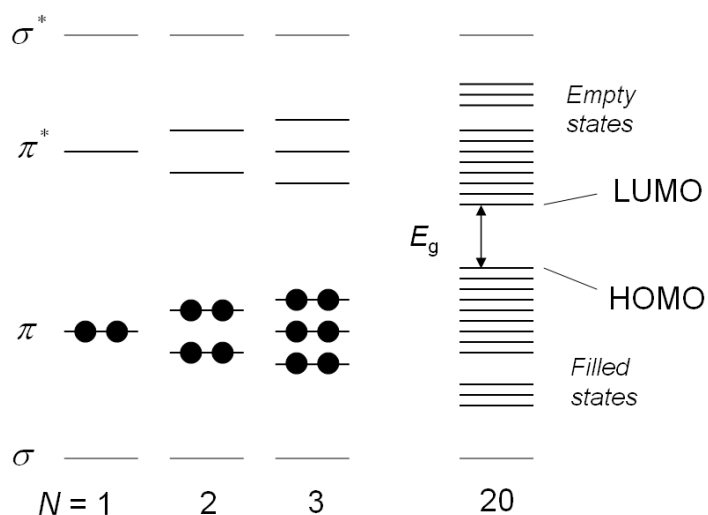


Figure 2.8 The energy band of semiconducting conjugated molecules according to the number of the carbon atoms involved in a chemical repeat unit in conjugated polymers

A large number of conjugated polymers are composed of different types of units attached together by chemical covalent bonds in a single repeat unit. They are known as **co-polymers** [24], and can comprise just two different units (binary copolymers) or three (ternary), and so on. It is one of the common strategies used by molecular engineers to manipulate the properties of polymers to gain the right combination of properties for a specific application. Figure 2.9 shows the chemical structures of poly(9,9)-dioctylfluorene-co-benzothiadiazole (F8BT) co-polymer [25] and a red chromophore (contributing to red emission) included in Lumogen Red (also known as Lumogen Red [21,25,26]) binary co-polymer incorporating the F8BT chemical unit. Both F8BT and Lumogen Red polymers are fluorene-based conjugated polymers with light-emitting property.

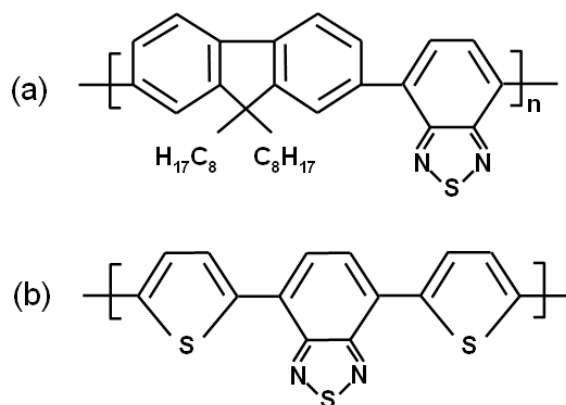


Figure 2.9 The chemical structures of (a) F8BT polymer and (b) Red chromophore in Lumogen Red copolymer

2.3.2 Absorption and Fluorescence

The photophysics and optical properties of conjugated polymers are important for optoelectronic devices. The part of the molecule containing the electrons involved in the electronic transition which gives rise to absorption is called chromophore. The conjugated polymers are molecular solids with localized conjugation units, which behave as chromophores and have strong interaction between conjugation units, leading to the dependence of the photophysics on the morphology. Combination of absorption and photoluminescence measurements are a basic process to understand the photophysics of conjugated polymers, determined by a number of factors from overall electronic transition levels and vibronic subbands to polymer conformation and morphology effects.

In this thesis, absorption measurements on polymer films were conducted using a transmittance measurement based UV-Vis spectrometer (Shimadzu UV Probe UV-2550) and photoluminescence was measured by using a spectrometer equipped by two monochromators (Spex FluoroMax-3 fluorimeter system); one is for selecting a pumping wavelength light from a white light source and the other is for scanning detection wavelengths.

In spectroscopy, absorbance (called optical density, OD) defined as $A = \log_{10}(I_0/I)$ is often used, where I_0 is the intensity of incoming light at a specific wavelength, and I is the intensity of light after a sample. From observed absorbance values in the UV-Vis transmittance measurement, the absorption coefficient α of a material can be estimated by Beer's law:

$$I / I_0 = 10^{-A} = \exp(-\alpha \cdot d) \quad (2.15)$$

where d is film thickness. The absorption coefficient α is a material property regardless of film geometry. Figure 2.10 shows the measured absorption coefficient and photoluminescence spectra of 100 nm thick Lumogen Red polymer film on glass. The absorption spectrum is broadly distributed over the measurement wavelength range and the spectrum has strong absorption coefficient of $\alpha_{\max} \sim 10^5 \text{ cm}^{-1}$ and as a result, the polymer is expected to have large stimulated emission section, which is desirable for optical gain property.

One expects that thicker films have higher OD values. The OD trend at 532 nm over film thickness is plotted in figure 2.11, which is nearly a linear relation. This relation could be used to estimate a film thickness for a given sample in case that topological analysis would be difficult e.g. films on flexible substrates.

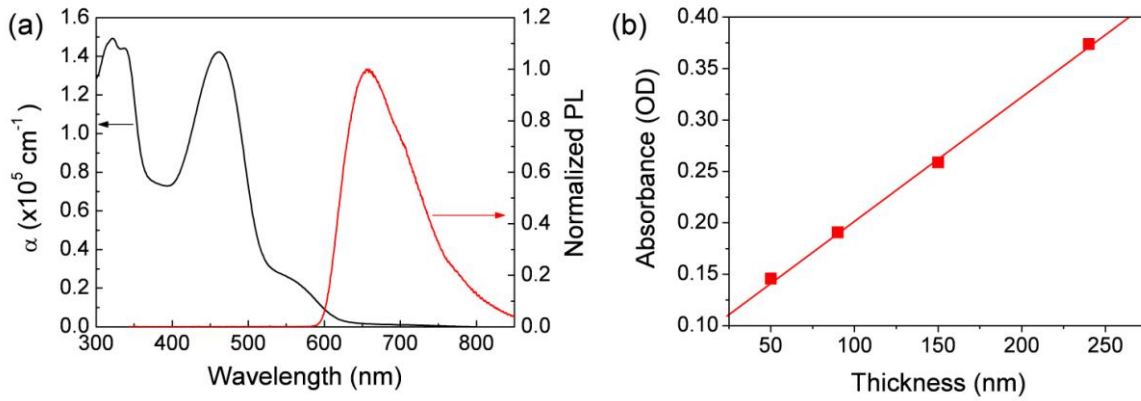


Figure 2.10 (a) Measured absorption (absorption coefficient α) and photoluminescence spectra of 90 nm thick Lumogen Red polymer film (b) Measured absorbance values from Lumogen Red films of 50 nm, 90 nm, 150 nm, and 240 nm; The OD trend at 532 nm over film thickness is nearly linear.

Conjugated polymers typically present 4-level laser system as described in figure 2.11, which is desirable for laser materials [27]. Optically pumped electrons from the valence band (π band) to the conduction band (π^* band) experience fast relaxation to the band edge in π^* band by structural relaxation and then radiative transition (fluorescence) occurs in nanosecond time scale at red-shifted wavelengths, which is known as ‘Stokes shift’, followed by non-radiative relaxation down to the ground state 0. Despite thermal distribution of electrons, in a certain pumping condition, the level 1 is more likely to be empty, resulting in more efficient population inversion process. The absorption spectrum does not overlap the spontaneous emission spectra due to the large Stokes shift as shown in figure 2.10. Accordingly, self-absorption at emission wavelengths is very small contrary to inorganic semiconductors.

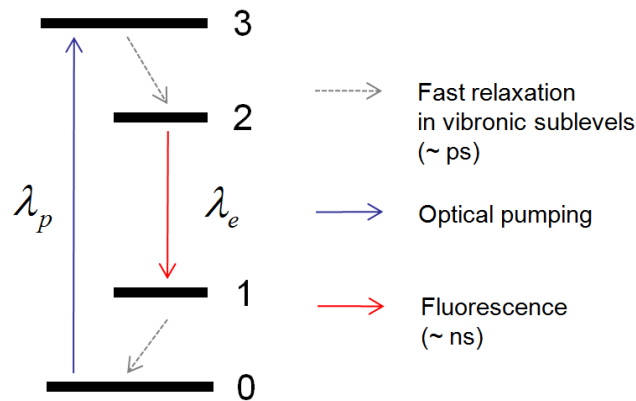


Figure 2.11 Four-level system of luminescent conjugated polymers

2.3.3 Photoluminescence lifetime

Measurements of photoluminescence (PL) lifetime and PL quantum yield (PLQY) are essential procedures to characterize the photophysics of luminescent semiconducting materials. The relaxation process between vibronic levels and energy transfer between chromophore can be understood via both measurements [27,28]. In this work, PL lifetime was measured via a streak camera system (Hamamatsu Photonics C4334) in combination with a spectrometer (Hamamatsu Photonics C5094) (c.f. Figure 2.12(a)). The pump source for exciting a sample was a 405 nm pulsed laser with 50 ps duration operating at 1 MHz. Fluorescence photons from an organic sample pass through the monochromator and the streak camera in sequence, and then photon-counting events were recoded with respect to both time and emission wavelength during a measurement. Figure 2.12(b) is a schematic of the operating principle of the streak camera. Incoming photons are converted into photo-electrons on the photocathode, and the electrons pass through between a pair of the electrodes applying sweeping voltages in a timing synchronized to the laser light and are deflected at different angles. The multiplied electrons via the micro-channel plate (MCP) are imaged on the phosphor screen, which finally maps a two-dimensional data of time and wavelength.

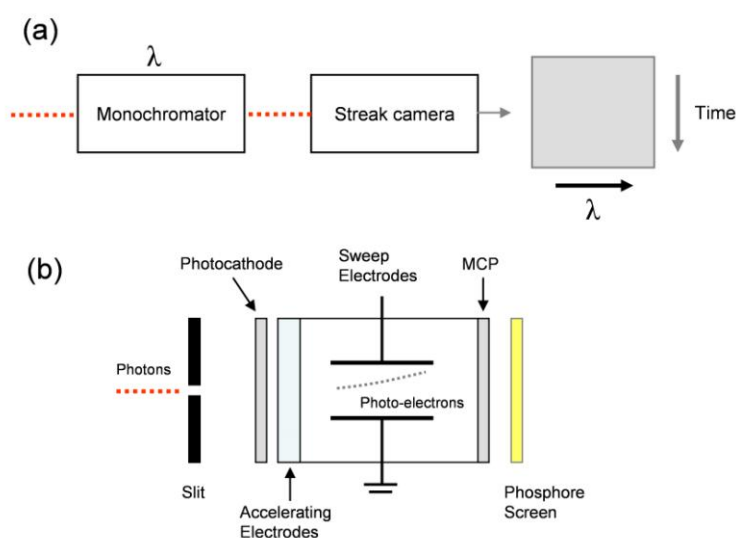


Figure 2.12 (a) Schematic of a time-resolved photoluminescence system employing the streak camera. Red dotted line is flows of photons passing through a monochromator and the streak camera in sequence. A final output data from the system is a two-dimensional plot of time and wavelength axis. (a) Operation of the streak camera.

Figure 2.13 shows a typical measurement data of PL dynamics for a Lumogen Red polymer film with 50 nm thickness coated on a Spectrosil B (synthetic vitreous silica) glass and cumulative photon-counting numbers over the whole detection wavelength in the time scale (c.f. normalized PL decay function on right). Experimental PL lifetime $\langle \tau \rangle$ is extracted by taking a statistical calculation as expressed by

$$\langle \tau \rangle = \frac{\int_T f_{PL}(t) \cdot t \cdot dt}{\int_T f_{PL}(t) \cdot dt} \quad (2.16)$$

where f_{PL} is normalized PL decay function and T is the time range to be integrated. The calculated τ_{PL} from the transient photoluminescence curve in Figure 2.13 is 1.84 ns. For light-emitting conjugated polymers, typical PL lifetimes are on the order of nanoseconds, reflecting strong transition.

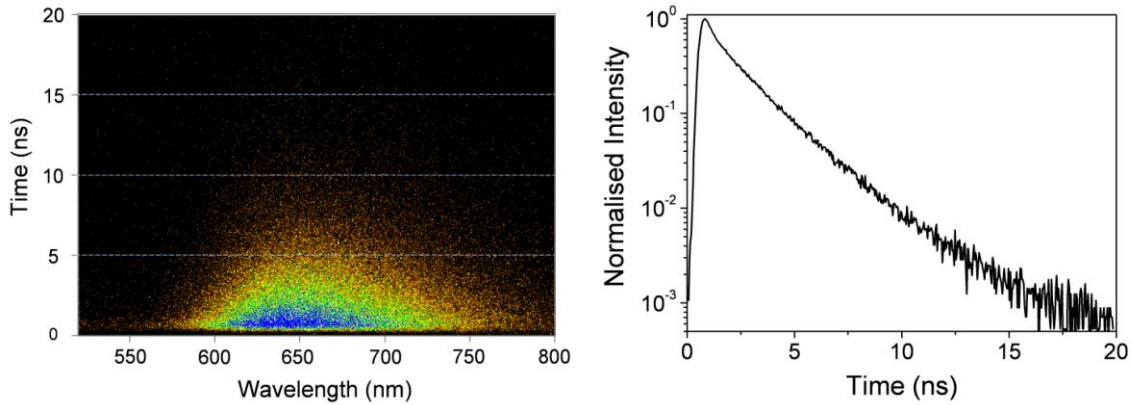


Figure 2.13 Streak camera measurement data and resulting transient photoluminescence dynamics from a 50 nm thick Lumogen Red copolymer film on Spec B substrate

Excited excitons in the polymer can depopulate into many possible decay channels including radiative decay. Total decay rates can be given as $\Gamma_{total} = \Gamma_{rad} + \Gamma_{nr}$ and PL lifetime reflects the total decay rates as expressed by

$$\tau = \frac{1}{\Gamma_{rad} + \Gamma_{nr}} \quad (2.17)$$

2.3.4 Photoluminescence Quantum yield

PL quantum yield is defined as a ratio of the number of absorbed photons to the number of emitted photons, meaning quantum efficiency of the radiative channel, i.e. fluorescence process. The measurement method is to use an integrating sphere [28-30], which is a hollow sphere. Its inner surface is coated with a highly reflective and diffuse material such as BaSO₄ so that photons emitted over the whole solid angle from a film sample can be counted. For this method, three spectral measurements are required (c.f. Figure 2.3): (a) a spectrum of the pump light intensity $I_p(\lambda)$ is measured in the absence of sample (b) the sample in the sphere is hit directly by the pump light and spectra of pump light and fluorescence $I_{em}(\lambda)$ are collected. (c) the measurement is conducted with the sample that is diffusely exposed by the pump light.

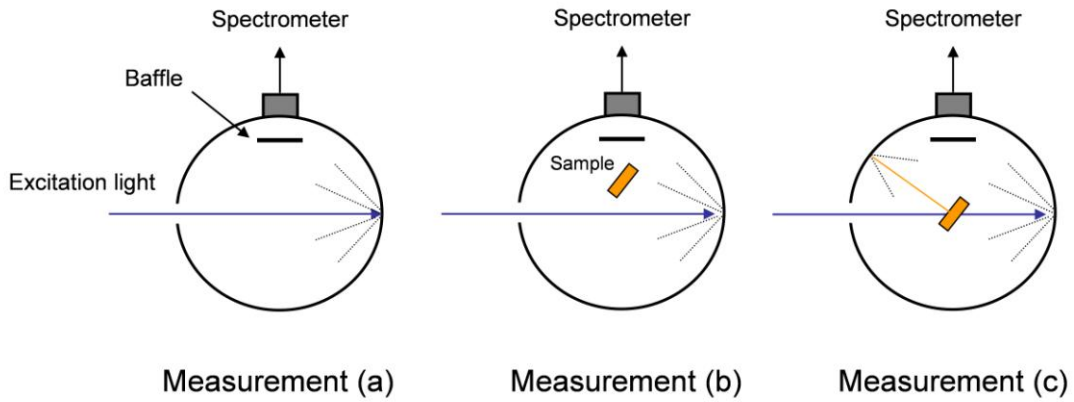


Figure 2.14 Illustration of three measurement configuration required for estimating photoluminescence quantum yield. (a) No sample in the sphere (b) the sample is in the sphere. scattered light (depicted as dotted lines) from the sphere wall excites the sample (c) input light directly shine the sample.

For the three measurements, photon numbers of pump light, L_a , L_b , and L_c and fluorescence P_b and P_c (the subscripts a, b, and c are related to the measurement (a),(b) and (c), respectively.) are obtained by integrating each spectral areas multiplied by λ/hc , where λ is the wavelength. Then finally, experimental PL quantum yield is calculated as the following equation [28].

$$\eta_{PL} = \frac{P_c - (1 - A)P_b}{L_a A} \quad (2.18)$$

where $A=(1-L_c/L_b)$ corresponds to the absorption coefficient at the pump wavelength. Figure 2.14 is an example of the three measurements of (a), (b) and (c) for 90 nm thick

Lumogen Red polymer film excited at 532 nm. The measured PLQY for the 90 nm thick Lumogen Red polymer film was $12 \pm 2\%$, considered quite fluorescent.

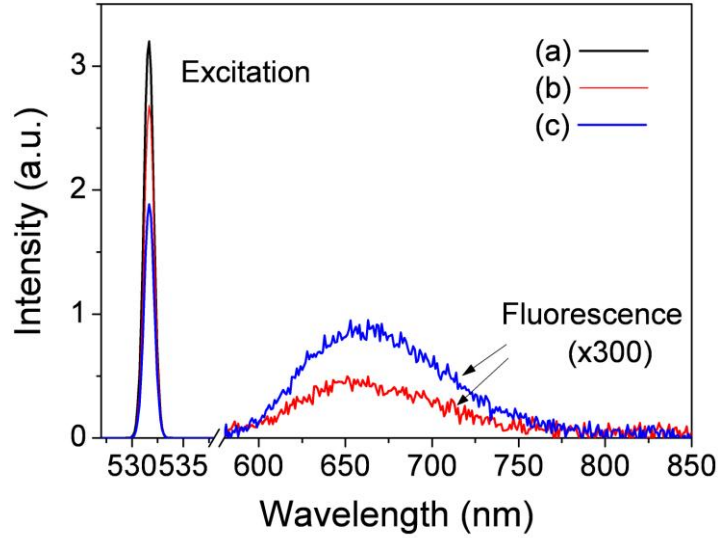


Figure 2.15 The spectra of pump light (532 nm wavelength) and corresponding fluorescence by three measurement configurations: (a) no sample (black line) (b) the sample diffusely exposed by the pump light (red line) (c) the sample directly exposed by the pump light (blue line). These spectra are collected from the sample with 90 nm thick Lumogen Red polymer film. The fluorescence spectra are enlarged by 300 for clarity.

In terms of the decay channels, PL quantum yield is given as

$$\eta = \frac{\Gamma_{rad}}{\Gamma_{rad} + \Gamma_{nr}} \quad (2.19)$$

Planar waveguide structures or plasmonic structures intrinsically provide additional decay channels of in-plane propagation modes. The waveguide coupling effect also varies with geometrical variation, consequently leading to the change of both PL lifetime and PL quantum yield. Therefore, it can be stated that the combination of PL lifetime and quantum yield measurements may give valuable information about energy transfer mechanisms related to radiative and non-radiative decay for active layer structures and further benefit us to design optimum optoelectronics devices.

2.4 Summary

The basic features of surface plasmon polaritons were explained together with prism-coupling method. SPPs in a single metal/dielectric interface were compared with photonic mode of conventional waveguide structures. Pros and cons of silver as a plasmonic medium have been discussed, and the physical and optical characteristics of conjugated polymers as a optical gain material were introduced together with the explanation of their electronic structures, suggesting that conjugated polymers is a good laser material.

References

- [1] J. Rivas, M. Kuttge, P. Bolivar, H. Kurz, and J. Sánchez-Gil, "Propagation of surface plasmon polaritons on semiconductor gratings," *Phys. Rev. Lett.* **93**, 1-4 (2004).
- [2] C. R. Williams, S. R. Andrews, S. A. Maier, A. I. Fernández-Domínguez, L. Martín-Moreno, and F. J. García-Vidal, "Highly confined guiding of terahertz surface plasmon polaritons on structured metal surfaces," *Nature Photon.* **2**, 175-179 (2008).
- [3] S. A. Maier, M. L. Brongersma, and H. A. Atwater, "Electromagnetic energy transport along arrays of closely spaced metal rods as an analogue to plasmonic devices," *Appl. Phys. Lett.* **78**, 16 (2001).
- [4] A. P. Hibbins, B. R. Evans, and J. R. Sambles, "Experimental verification of designer surface plasmons," *Science* **308**, 670-2 (2005).
- [5] V. Giannini, Y. Zhang, M. Forcales, and J. Gómez Rivas, "Long-range surface polaritons in ultra-thin films of silicon," *Opt. Express* **16**, 19674 (2008).
- [6] F. Michelotti, L. Dominici, E. Descrovi, N. Danz, and F. Menchini, "Thickness dependence of surface plasmon polariton dispersion in transparent conducting oxide films at 1.55 microm," *Opt. Lett.* **34**, 839-41 (2009).
- [7] M. Jablan, H. Buljan, and M. Soljačić, "Plasmonics in graphene at infrared

frequencies," Phys. Rev. B **80**, 1-7 (2009).

[8] P. Johnson and R. Christy, "Optical constants of the noble metals," Phys. Rev. B **6**, 4370–4379 (1972).

[9] M. Dujardin and M.-L. Theye, "Investigation of the optical properties of Ag by means of thin semi-transparent films," J. Phys. Chem. Solids **32**, 2033-2044 (1971).

[10] M. A. Ordal, L. L. Long, R. J. Bell, S. E. Bell, R. R. Bell, R. W. Alexander, and C. A. Ward, "Optical properties of the metals Al, Co, Cu, Au, Fe, Pb, Ni, Pd, Pt, Ag, Ti, and W in the infrared and far infrared," Appl. Opt. **22**, 1099-20 (1983).

[11] D. J. Nash and J. R. Sambles, "Surface plasmon-polariton study of the optical dielectric function of silver," J. Mod. Opt. **43**, 81-91 (1996).

[12] C. Fragstein and H. Kampermann, "Eine neue, einfache, polarimetrische Methode zur Bestimmung der optischen Konstanten von Metallen," Z. Physik **173**, 39 (1963).

[13] U. Schroder, "Der einfluss dünner metallischer deckschichten auf die dispersion von oberflächenplasmaschwingungen in gold-silber-schichtsystemen," Surf. Sci. **102**, 118 (1981).

[14] E. D. Palik, *Handbook of Optical Constants of Solids* (Academic Press, 1985).

[15] G. Rasigni and P. Rouard, "On the variation with wavelength of the optical constants of thin metallic films," J. Opt. Soc. Am. **53**, 604 (1963).

[16] C. Kennedy and D. E. Gray, *American Institute of Physics Handbook* (McGraw-Hill, 1972), p. 409.

[17] J. Burroughes, D. Bradley, A. Brown, R. Marks, K. Mackay, R. Friend, P. Burns, and A. Holmes, "Light-emitting diodes based on conjugated polymers," Nature **347**, 539–541 (1990).

[18] R. Friend, R. Gymer, and A. Holmes, "Electroluminescence in conjugated polymers," Nature **80**, 119-124 (1999).

- [19] C. J. Brabec, N. S. Sariciftci, and J. C. Hummelen, "Plastic solar cells," *Adv. Funct. Mater.* **11**, 15-26 (2001).
- [20] S. Günes, H. Neugebauer, and N. S. Sariciftci, "Conjugated polymer-based organic solar cells," *Chem. Rev.* **107**, 1324-38 (2007).
- [21] R. Xia, G. Heliotis, and D. D. C. Bradley, "Fluorene-based polymer gain media for solid-state laser emission across the full visible spectrum," *Appl. Phys. Lett.* **82**, 3599 (2003).
- [22] B. H. Wallikewitz, M. de la Rosa, J. H.-W. M. Kremer, D. Hertel, and K. Meerholz, "A lasing organic light-emitting diode.," *Adv. Mater.* **22**, 531-4 (2010).
- [23] R. Anderson, D. Bendell, and P. W. Groundwater, *Organic Spectroscopic Analysis* (Royal Society of Chemistry, 2004).
- [24] G. Hadziioannou, *Semiconducting Polymer: Chemistry, Physics and Engineering, Volume 1*, Chapter 1 (Wiley-VCH, 2007).
- [25] M. Campoy-Quiles, G. Heliotis, R. Xia, M. Ariu, M. Pintani, P. Etchegoin, and D. D. C. Bradley, "Ellipsometric Characterization of the Optical Constants of Polyfluorene Gain Media," *Adv. Funct. Mater.* **15**, 925-933 (2005).
- [26] G. Heliotis, R. Xia, D. D. C. Bradley, G. A. Turnbull, I. D. W. Samuel, P. Andrew, and W. L. Barnes, "Two-dimensional distributed feedback lasers using a broadband, red polyfluorene gain medium," *J. Appl. Phys.* **96**, 6959 (2004).
- [27] A. Heeger, N. Sariciftci, and E. B. Namdas, *Semiconducting and Metallic Polymers* (Oxford University Press, 2010).
- [28] J. de Mello and H. Wittmann, "An improved experimental determination of external photoluminescence quantum efficiency," *Adv. Mater.* **6**, 107 (1997).
- [29] N. Greenham, "Measurement of absolute photoluminescence quantum efficiencies in conjugated polymers," *Chem. Phys. Lett.* **241**, 89-96 (1995).
- [30] G. Samal, A. Tripathi, A. Biswas, S. Singh, and Y. Mohapatra, "Photoluminescence

quantum efficiency (PLQE) and PL decay characteristics of polymeric light emitting materials," *Synthetic Met.* **155**, 344-348 (2005).

3 Surface Plasmon Polaritons in Prism-based Geometry

3.1 Introduction

Optical excitation is essential for the study of complex structures that support any light propagation modes. Using certain optical excitation methods e.g. prism-coupling and grating coupling, light waves from free space can be transformed into propagating modes. The prism-coupling method, called the attenuated total reflection (ATR) method, has typically been used to investigate conventional waveguide modes and has also been realised as being a powerful tool to study plasmonic structures with subwavelength confinement. For example, the ATR method has been adopted to demonstrate improved light-emitting or photovoltaic functions in a specially engineered diode geometry with the help of surface plasmon polaritons or localised surface plasmons [1,2]; additionally, a number of studies about active plasmonics [3-8] have been conducted using the ATR method. It offers simple and efficient optical excitation without the loss of incoming light, and also it enables the examination of propagation characteristics in momentum space, which leads to the construction of dispersion relations. Here we mainly adhere to the Kretschmann-Raether geometry, in which a metal layer acts as a tunnelling channel for evanescent fields. The main reason for this is that directly attaching the metal layer to the prism surface does not require an additional apparatus to control the distance between the prism and a multi-layer sample, eliminating experimental uncertainty.

This chapter will present the prism coupling system based on the Kretschmann-Raether configuration and related theoretical backgrounds conducted throughout this thesis. We successfully demonstrate its basic operation for plasmonic multi-layer structures. Both cavity descriptions, derived from the Fresnel formulae method and the transfer matrix method (TMM), are used to help understand the behaviour of surface plasmon propagation thoroughly and to estimate the experimental results precisely.

3.2 The Attenuated Total Reflection (ATR) Method

3.2.1 Prism Coupling System

A basic prism coupling system was designed to perform reflectivity measurement with respect to light incidence angles from any multi-layer structures that reside on the hypotenuse surface of the right-angle prism. Using information including the resonance angle, minimum reflectivity and angular line width obtained from angular reflectivity curves, a test structure can be analysed. The following are the key requirements of a prism coupling system:

- Optical source with narrow spectral line width
- Polarisation selection
- Angular accuracy

In general, waveguide structures show different propagation properties on light wavelengths. Propagation vector and field distribution are important parameters determined by any given waveguide structure, showing wavelength dependence [9,10]. In order to examine light-guiding behaviour in any photonic structure, power stable optical sources with narrow spectral line width are essential. We can select lasers with selected wavelengths or monochromator-equipped broadband sources. The preferred sources in this study are continuous wave (CW) single frequency lasers because of their output stability, inherent narrow spectrum and good spatial coherence. Accurate selection of the polarisation of light is important in any optical measurement system. An optical medium could have anisotropy such as birefringence and polarisation-sensitive absorption and emission. Most plasmonic structures are also extremely sensitive to the polarisation of light. Lastly, angular accuracy is an important factor in determining a system's ability to resolve angular reflectivity curves. Light beam size, the minimum angle step of rotation stage, and physical variations of the prism limit angular accuracy.

As shown in Figure 3.1, a prism coupler system consists of many optical components such as a source part, polarisation part, rotation stage part that includes a photodetector and operation program. Three laser diodes emitting light at wavelengths of 473 nm, 532 nm and 675 nm are selected according to the spectral regions at which plasmonic structures need to be examined. The polarisation part consists of a polariser and a $\lambda/2$ wave plate covering the visible frequency regime. The polariser filters the polarisation direction of light from the sources and then the $\lambda/2$ wave plate tunes the polarisation state to

transverse magnetic (TM) or transverse electric (TE) modes. An optical arm, on which a silicon photodetector and a focusing lens are positioned, is attached to the rotation stage controlled by a computer program based on a LabVIEW communication platform.

Light from the laser diodes is polarised by passing through a Glan-Thompson polariser and enters the sample prism to hit a waveguide layer structure. To excite surface plasmon polaritons, the prism is rotated on a rotation stage with an angle resolution of 0.05 degree, thus the incident angle of p-polarised light varies in such a way that the photon momentum in the prism matches the momentum of the SPP while the photodiode detects the reflected light, thereby recording the reflectance curve with respect to the incident angle. The polarisation state of an incident light selected by the Glan-Thompson polariser is adjusted as TE or TM states by rotating the $\lambda/2$ wave plate.

If surface plasmon modes are excited, the angular reflectance curve exhibits a dip whose width is related to total attenuation the excited SPPs experience and whose angle position of minimum reflectivity corresponds to the momentum of SPPs. Its behaviour depends on the refractive indexes of metal and dielectrics, the thicknesses of the materials and the degree of loss at the interface. By adjusting the rotation stage to the resonance angle showing minimum reflectivity, surface plasmon polaritons are excited and their electric fields at the interface are several times more enhanced than incoming fields, which means that the interaction between light and materials around the plasmonic interface is enhanced.

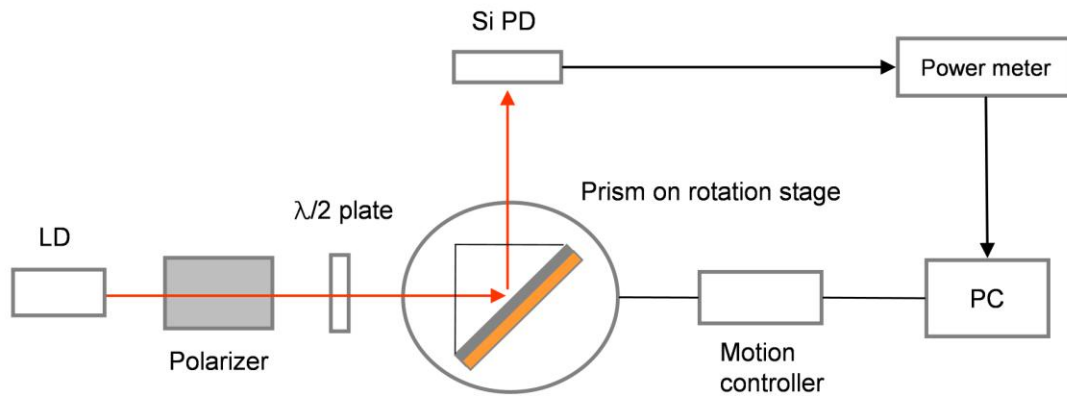


Figure 3.1 Basic configuration of a prism coupler system

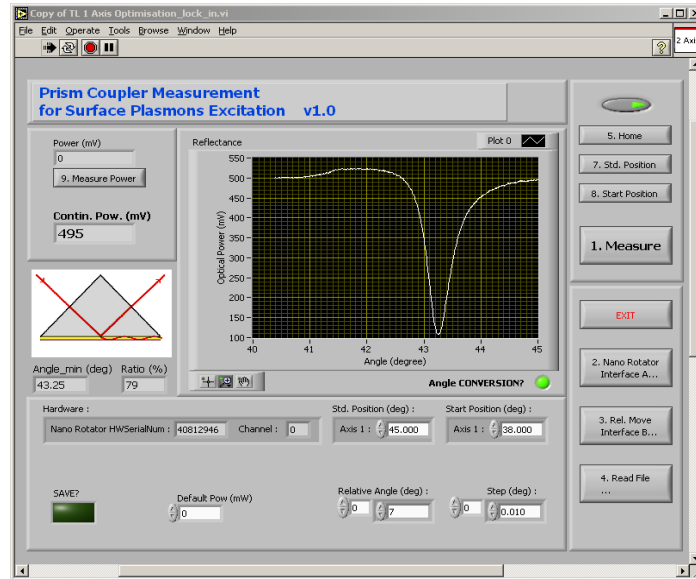


Figure 3.2 LabVIEW program for operation of the prism coupling system; the program contains rotation stage control, data display and logging and data analysis functions

3.2.2 Operation

The measurement procedure has two steps. First, after a prism sample is loaded on a mount installed on the rotation stage, a standard angle, which is an incident angle of 45 degrees with respect to the metal surface (0 degree with respect to the entrance surface of a prism), is determined in order to define the incident angle of light accurately and in a way that the reflected light spot becomes located at the slit hole through which the incident light passes, as described in Figure 3.2(b). As light is refracted at the entrance surface of the prism, as shown in Figure 3.2(a), the rotation angle of the rotation stage must be transformed into the angle inside a prism using a simple equation (3.1) from the Snell's law.

Second, the prism is rotated at the centre axis of the metal surface during measurement. An angle-dependent reflectance is recorded within a certain angle scan range from an initial angle, and is automatically converted into data with respect to the angle inside the prism and then analysed in terms of a resonance angle, reflectance and angular line width.

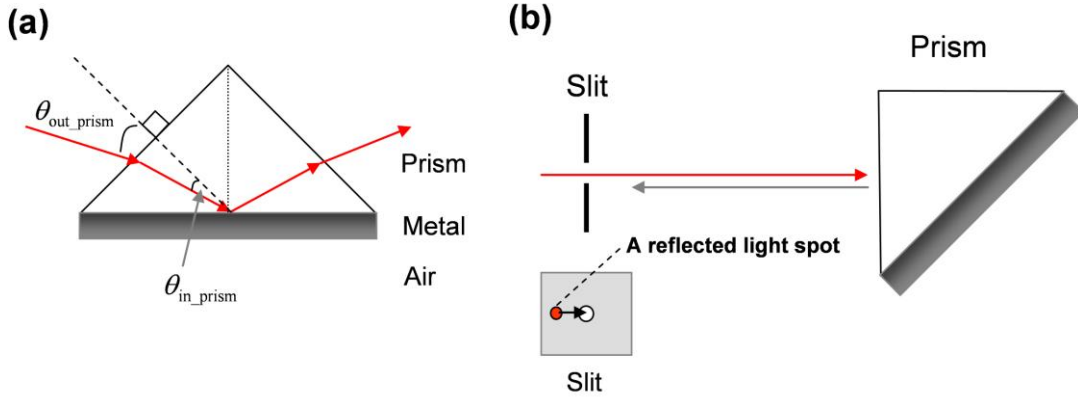


Figure 3.3 (a) Schematic of light path for prism-coupling (b) Description of the path of reflected light for discriminating a reference angle

$$\sin \theta_{\text{in_prism}} = \frac{1}{n_{\text{prism}}} \sin \theta_{\text{out_prism}} \quad (3.1)$$

$$\theta = \theta_{\text{in_prism}} + 45^\circ$$

where n_{prism} is the refractive index of prism material. The following facts bringing uncertainty to the measurement are taken into consideration: as described in Figure 3.2(b), the angular tolerance of a BK7 prism (Thorlabs Co., Ltd) of three arcmin and the other spot from the opposite surface, as well as the entrance surface for defining the reference angle, create an angle uncertainty of ± 0.05 degree, and refraction at the entrance face of the prism makes the light beam profile elliptical, which means there are additional propagation momentum vectors generated.

3.2.3 Angular Reflectivity Curves

The operation of the prism coupling system gives rise to angle-dependent reflectivity data that contains physical information regarding plasmonic resonances as well as total internal reflection between the substrate and superstrate, which are resonance angle θ_{res} , angular line width $\Delta\theta$ and critical angle θ_c . If the superstrate and substrate are given as in our case, BK7 prism and air, respectively, the critical angle at which evanescent fields can be created above is determined by Equation 3.1.

$$\theta_c = \arcsin\left(\frac{n_{\text{air}}}{n_p}\right) \quad (3.2)$$

where n_p and n_{air} are refractive indices of prism and air, respectively. The measured angular

reflectivity (from a 50 nm thick silver layer) at 675 nm in Figure 3.1 shows that the critical angle appears at the angle point we expected. It should be noted that the resonance angle of the angular reflectivity curves is larger than the critical angle. It provides direct evidence that evanescent fields couple to surface plasmon polaritons with a higher in-plane momentum than in air. The resonance angle and angular line width may be expressed by the following equations [Ch1.1]:

$$\theta_{\text{res}} = \sin^{-1} \left(\frac{k'_x}{k_0 n_p} \right) \quad (3.3)$$

$$\Delta\theta = \frac{2k''_x}{k_0 n_p \cos \theta_{\text{res}}} \quad (3.4)$$

where $k_0 = 2\pi/\lambda$, λ is the wavelength in vacuum and $k_0 (=k'_x + ik''_x)$ is the complex propagation constants supported by a certain plasmonic layer structure. The resonance angle θ_{res} increases as k'_x increases, meaning that the effective index of a propagation mode gets higher, while the angular line width $\Delta\theta$ is proportional to k''_x which determines propagation attenuation length.

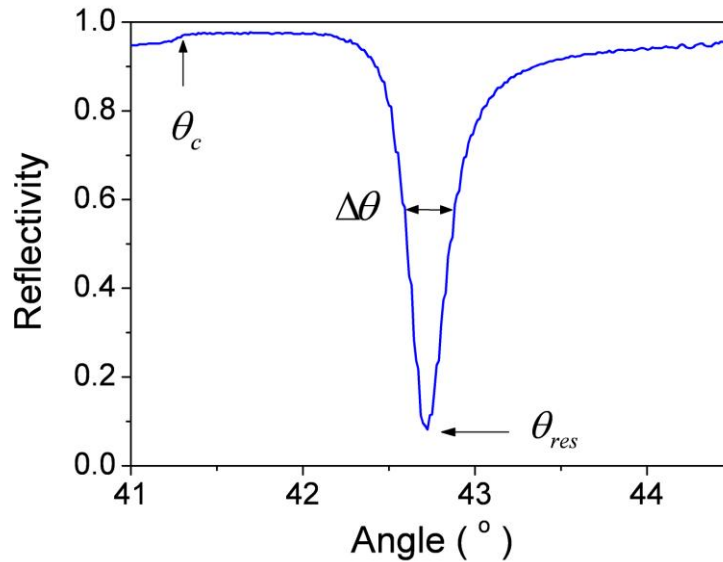


Figure 3.4 Measured angular reflectivity curve from the 53 nm silver film at the wavelength of 675 nm; resonance angle θ_{res} , angular line width $\Delta\theta$ and critical angle θ_c are indicated in the graph

3.3 Modeling of Surface Plasmon Propagations

3.3.1 Fresnel Formulae and Cavity Picture

Surface plasmon polaritons can be supported at an interface that includes at least two media with dielectric constants of opposite sign. The quantitative description of the reflected intensity R from a multi-layer structure can be predicted by the Fresnel equations [11]. We start with the simplest plasmonic structure based on Kretschmann geometry in which only the metal layer has a finite thickness, that is, thickness d_1 , thus called a ‘one-layer structure’. Figure 3.3 shows a schematic of a Kretschmann-Raether one-layer structure configuration, including two infinite regions of prism material (superstrate) and air (substrate) and one metal layer.

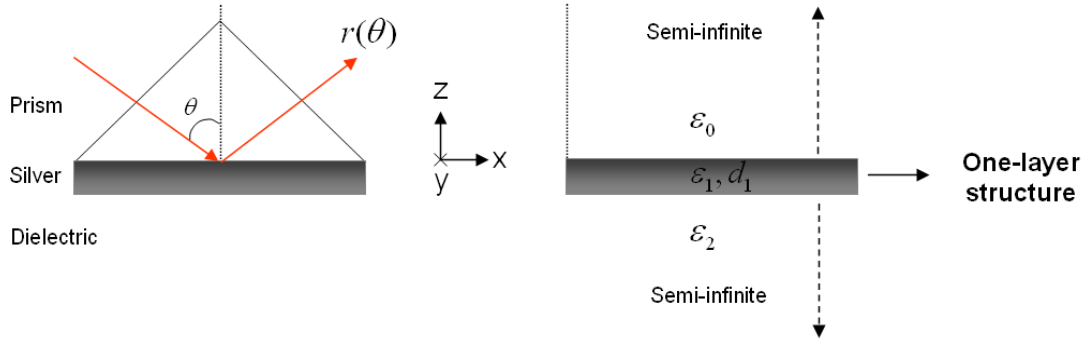


Figure 3.5 One-layer structure of Kretschmann-Raether configuration

The angle-dependent reflectivity R for p-polarized light, with E_0 incoming and E_r the reflected field, is given by [Ch1.1]

$$R(\theta) = \left| \frac{E_r}{E_0} \right|^2 = \left| \frac{r_{01}^p + r_{12}^p \exp(2ik_{z1}d_1)}{1 + r_{01}^p r_{12}^p \exp(2ik_{z1}d_1)} \right|^2 \quad (3.5)$$

where $r_{ik}^p = (k_{zi}\epsilon_k - k_{zk}\epsilon_i) / (k_{zi}\epsilon_k + k_{zk}\epsilon_i)$ and $k_{zi} = \pm \sqrt{\epsilon_i \left(\frac{\omega}{c} \right)^2 - k_x^2}$, $i = 0, 1, 2$.

The real part of k_x , k_x' is the propagation vector of SPP guiding modes and the imaginary part of k_x , k_x'' corresponds to the inverse of propagation length, while the parameter k_z describes the field distribution along the z direction, which gives the skin depth of surface plasmon modes.

Resonances appear in many physical systems. Dipole energy transition and light cavity

structures are typical examples exhibiting a resonant behaviour of optical fields [12]. The intensity distribution of resonant oscillations may be described by a Lorentzian function, in which resonance position (or resonant frequency) and the degree of damping are the main factors. Prism-coupled surface plasmon polaritons is a form of light confinement at single or multiple metal/dielectric interfaces. Hence, we could treat a multi-layer structure supporting the SPP as an optical resonator. Equation 3.6 is the approximated expression of Equation 3.5 in the vicinity of surface plasmon resonance by the Lorentzian type relation under the special conditions, $|\epsilon_1'| \gg 1$, $|\epsilon_1''| \gg |\epsilon_1'|$ and $\exp(2ik_x d_1) \ll 1$.

$$R(\theta) \approx |r_{01}^0|^2 \left(1 - \frac{4\gamma_i \gamma_r}{(k_x - k_x^0)^2 + (\gamma_i + \gamma_r)^2} \right) \quad (3.6)$$

where k_x^0 is the propagation constant at resonance and r_{01}^0 is reflectivity at the interface between the prism and silver. For a one-layer structure, radiation loss and internal propagation loss are given by [1-1]

$$\gamma_r = \text{Im}(\text{constr}_{01}^p(k_x^0)) \quad (3.7)$$

$$\gamma_i = \text{Im}(k_x^0) \approx \frac{\omega}{2c} \left(\frac{\epsilon_1' \epsilon_2'}{\epsilon_1' + \epsilon_2'} \right)^{3/2} \left(\frac{\epsilon_1''}{\epsilon_1'^2} \right) \quad (3.8)$$

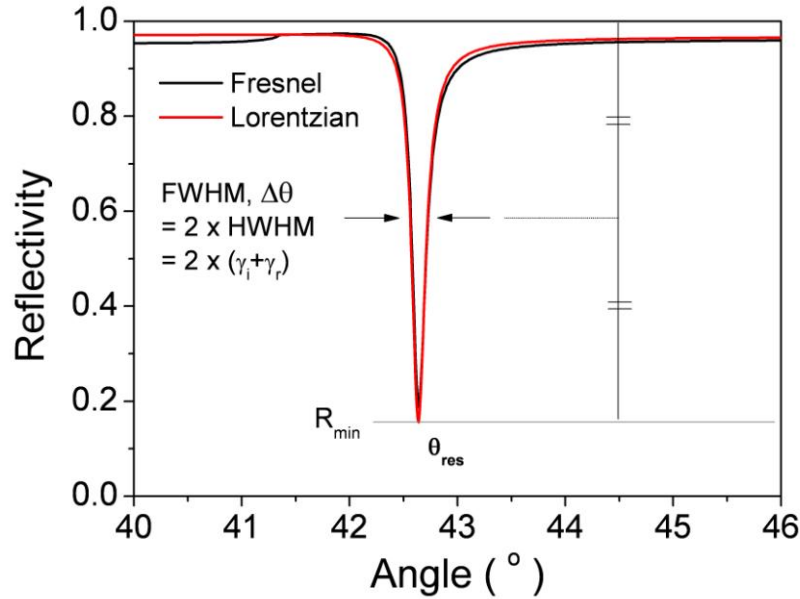


Figure 3.6 Reflectivity curves from the layer structure of BK7 prism/ Silver (55 nm) / Air by Fresnel equations (3.5) and the Lorentzian function (3.6)

Figure 3.6 shows the coincidence of the calculated reflection curves of the layer structure of BK7 prism/silver (55 nm)/Air by both the Fresnel equation and the Lorentzian equation. The angular line width is defined as the width of a reflectivity curve at which half the difference of $R=1$ and $R_{\min}$ is located. The term $\gamma_i + \gamma_r$ corresponds to the half-width at half-maximum (HWHM) of the Lorentzian function, and we can say that two times $(\gamma_i + \gamma_r)$ is the full-width at half-maximum (FWHM) or angular line width, which implies a propagation length of,

$$L_i = [2(\gamma_i + \gamma_r)]^{-1} \quad (3.9)$$

Reflectivity is affected by the interference between partial fields E_1 that are reflected from incoming fields and the out-coupled fields E_2 from the enhanced electric fields of SPP excitation (Figure 3.7). Fulfilling the condition of the equation (3.10) in the Lorentzian function gives rise to a minimum value of a dip ($R=0$). This may be viewed as the destructive interference between both fields that are completely out of phase of each other (optimum coupling).

$$\gamma_i = \gamma_r \quad (3.10)$$

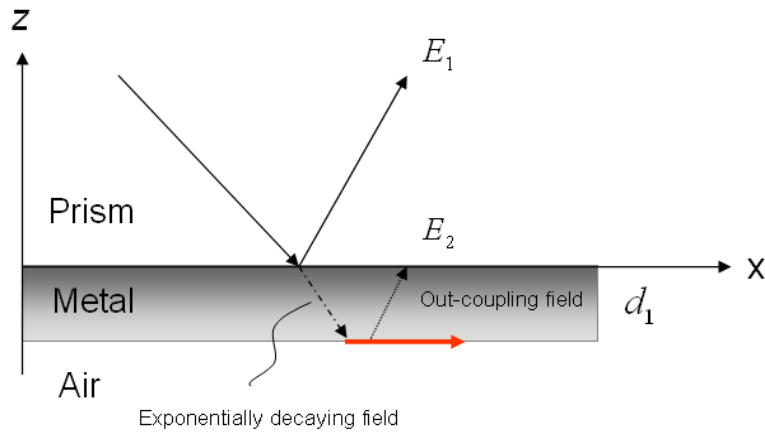


Figure 3.7 Schematic of the ATR process through a metal film

3.3.2 Transfer Matrix Method

The transfer matrix method is a useful tool for planar multi-layer analysis [9,11]. One of advantages of the TMM is that the basic optical properties of reflectance and transmittance for complex multi-layer structures can be obtained easily by multiplying each layer's

matrices in a straight-forward calculation. Various physical situations such as loss, gain and birefringence can be handled using the TMM [13,14]. The method can also generate the dispersion equation of the TE and TM modes supported by multi-layer structures, the solutions of which are propagation constants of guided or leaky modes, and the corresponding electric and magnetic field profiles around the layer geometry can be obtained. It is also possible for active guiding modes to be analysed. Therefore, the transfer matrix method is essential to the understanding of surface plasmon properties in one-dimensional metallic multi-layers.

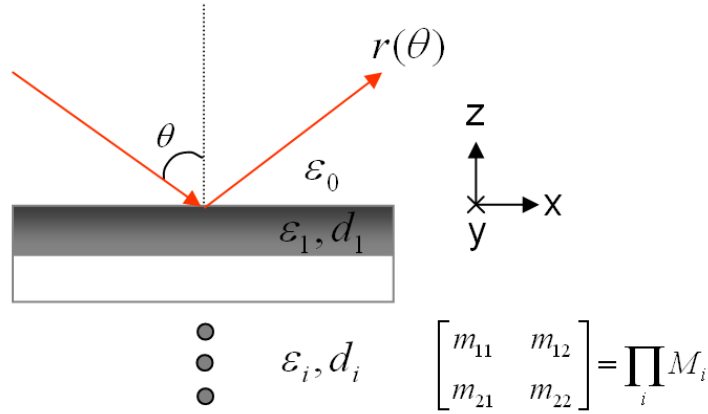


Figure 3.8 An example of a multi-layer structure supporting SPP modes

As taken for the Fresnel equation method, the same coordinate system is used where the x axis is parallel to the upper boundary of the ATR configuration and whose $+z$ direction points into the substrate. For a parallel polarised (TM) plane wave, the magnetic vector has a single component H along the y direction, which is perpendicular to this paper. Assuming that a plane wave is incident in the prism in the form,

$$H_i = \exp[i(k_{xi}x - k_{zi}z)] \quad (3.11)$$

The reflection coefficient $r(k_x)$, defined as the ratio of the amplitude of the reflected field to that of the incident field at the prism base, is given by

$$r(k_x) = \frac{m_{12} - (Z_s m_{22} - Z_0 m_{11}) - Z_0 Z_s m_{21}}{m_{12} - (Z_s m_{22} + Z_0 m_{11}) - Z_0 Z_s m_{21}} = \frac{N(k_x)}{D(k_x)} \quad (3.12)$$

where the coefficients $m_{qr}(q, r = 1, 2)$ are elements of the overall transfer matrix of the structure.

$$\begin{bmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{bmatrix} = M_{s-1} M_{s-2} \dots M_1 M_0 \quad (3.13)$$

Here M_j is a 2 X 2 matrix written for each layer as,

$$M_j = \begin{bmatrix} \cos(k_{zi} z_i) & -Z_i \sin(k_{zi} z_i) \\ \frac{1}{Z_i} \sin(k_{zi} z_i) & \cos(k_{zi} z_i) \end{bmatrix} \quad (3.14)$$

with $Z_i = k_z / (k_0 \epsilon_i)$ and $k_z = \pm (\epsilon_i k_0^2 - k_x^2)^{1/2}$ where $k_0 = 2\pi/\lambda$, λ is the wavelength in vacuum and 0 and s designate the superstrate (prism) and the substrate regions, respectively. The dispersion equation of SPPs is given by the denominator $D(k_x)$ of equation (3.12). For the TM modes, we get the field distributions of H_y , E_x and E_z , around a multi-layer structure using equations (2.4) and (2.5).

Figure 3.9 shows the calculated angle-dependent reflectivity at 675 nm light from a structure with a 50 nm thick silver layer by means of the transfer matrix method and the calculated magnetic field profile with respect to the amplitude of the incident magnetic field at the resonance angle θ_{res} indicated in Figure 3.9(a). The transfer matrix method is very advantageous for analysing optical characteristics of the complex multi-layer structures in terms of various factors of reflectance, transmittance, propagation modes and electric and magnetic field distributions of the modes.

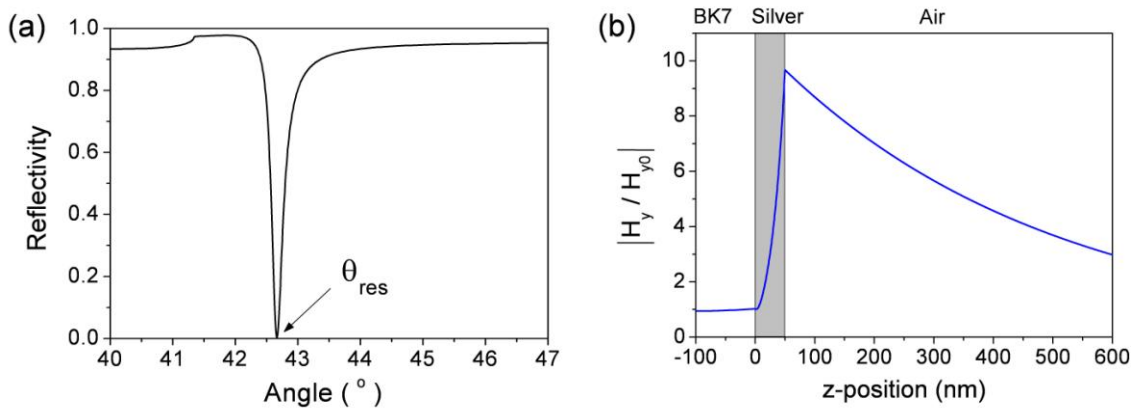


Figure 3.9 (a) The calculated angle-dependent reflectivity from the structure of BK7 Prism/silver (50 nm)/Air at 675 nm by means of the transfer matrix method; (b) The corresponding magnetic field distribution along the optical axis (z-axis) calculated at the resonance angle θ_{res}

3.3.3 Dispersion Relation: Leaky Mode

Here we present the mode behaviour of SPPs that occur in the prism-coupling geometry, which is directly linked to angular reflectivity curves discussed at the previous sections. Layer structures attached to prism could have a variety of modes, including guided modes and leaky modes, in terms of transverse field patterns [15] because a single thin metal film has two plasmonic interfaces that form coupled propagation modes. Here, only the asymmetric case in which the refractive indices of surrounding materials of metal layer are not equal were studied because of the excitation requirement of the phase-matching condition of the incoming photon through the prism. Figure 3.10 shows the schematic description of the magnetic field profiles of a leaky mode in the prism and a bound mode, which could occur in the one-layer structure. The one-layer structure with a single metal layer could have both leaky modes whose fields in prism or dielectric are radiative and bound modes whose fields in prism and dielectric are decaying. In the Kretschmann geometry, however, only leaky modes are observable because they can be decoupled to the prism in the form of a photon. Thus, we are mainly interested in the behaviour of the modes. The leaky mode radiating into the prism, fulfilling the condition of Equation 3.18, is taken into consideration for the plasmonic mode analysis.

$$\sqrt{\varepsilon_d} < n_{leaky} < \sqrt{\varepsilon_0} \quad (3.18)$$

where ε_d and ε_0 are electric permittivities of prism layer and dielectric layer, respectively.

In order to understand surface plasmon mode behaviours from a more general structure configuration and under any physical changes, the related dispersion relation must first be analysed. Generally, surface plasmon propagation constants are complex numbers that have imaginary term k_x'' determining propagation length $L_i=1/(2k_x'')$ due to lossy metals. Complex dispersion equations of any metallic multi-layer structure supporting any surface plasmon modes can be deduced by the TMM and then their complex solutions can be solved using numerous zero searching algorithms [16] or a rigorous mathematical technique based on the contour integral in the complex plane [17].

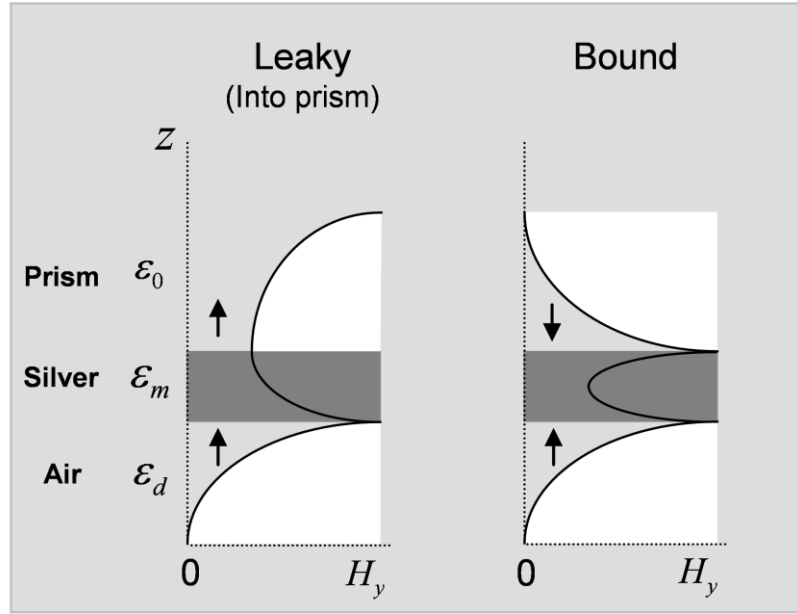


Figure 3.10 Field distribution of bound and leaky modes guided by thin metal films ϵ_m . The arrows indicate transverse energy flow in the surrounding dielectrics including prism ϵ_0 .

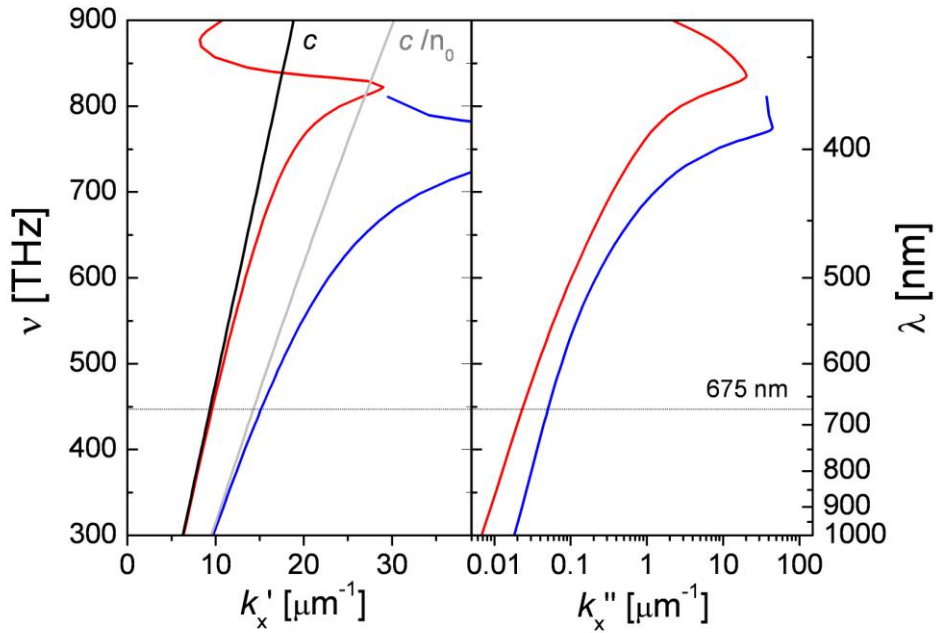


Figure 3.11 Dispersion relationship of leaky (red line) and bound (blue) surface plasmon polariton modes supported by the layer structure of BK7 Prism/silver (50 nm)/Air, which was calculated by the Newton-Raphson root searching algorithm. The light lines in vacuo (labelled c , black line) and in the prism (labelled c/n_p , grey line) are also shown.

In detail, propagation constants k_x of SPP modes are numerically calculated from the denominator $D(k_x)$ of Equation 3.12. For the calculation of leaky modes, in particular, a sign of out-of-plane momentum k_z in a prism must be set as negative since the field diverges into the prism. Figure 3.11 shows the dispersion relation of BK7 Prism/silver (50 nm)/Air layer configuration. Numerical calculation of complex propagation constants $k_x (=k_x' + ik_x'')$ was implemented using the Newton-Raphson root searching algorithm of a Mathematica built-in function called *FindRoot* [18]. The calculated propagation constants of the leaky mode lie between the light line in the BK7 prism and in the air throughout most of the visible region; their propagation losses increase as optical frequency goes higher, which can be attributed to the increased mode propagation momentum k_x' that results from the SPP mode confined more strongly around the silver/air interface.

3.3.4 Mode Behaviour with Geometrical Variation

We discuss the geometrical dependence of a leaky SPP mode in terms of its propagation vector. In the Kretschmann-Raether configuration, the prism layer not only acts as a momentum provider for the photon to couple into surface plasmon polaritons (SPPs), but it also allows SPPs to decouple out in photon form. In a prism/silver/air configuration, the corresponding complex propagation constants against silver thickness d_{Ag} are shown in Figure 3.12. As the silver thickness increases more than the skin depth of SPPs in silver, e.g. $\delta \sim 30$ nm at 675 nm, k_x' and k_x'' converge into values that are exactly equal to the real and imaginary parts of $k_x = k_0(\epsilon_{Ag}\epsilon_{Air}/(\epsilon_{Ag} + \epsilon_{Air}))^{1/2}$, respectively, where $k_0 = 2\pi/\lambda$, λ is the wavelength in the vacuum, which corresponds to the momentum of the SPP mode at the silver/air interface.

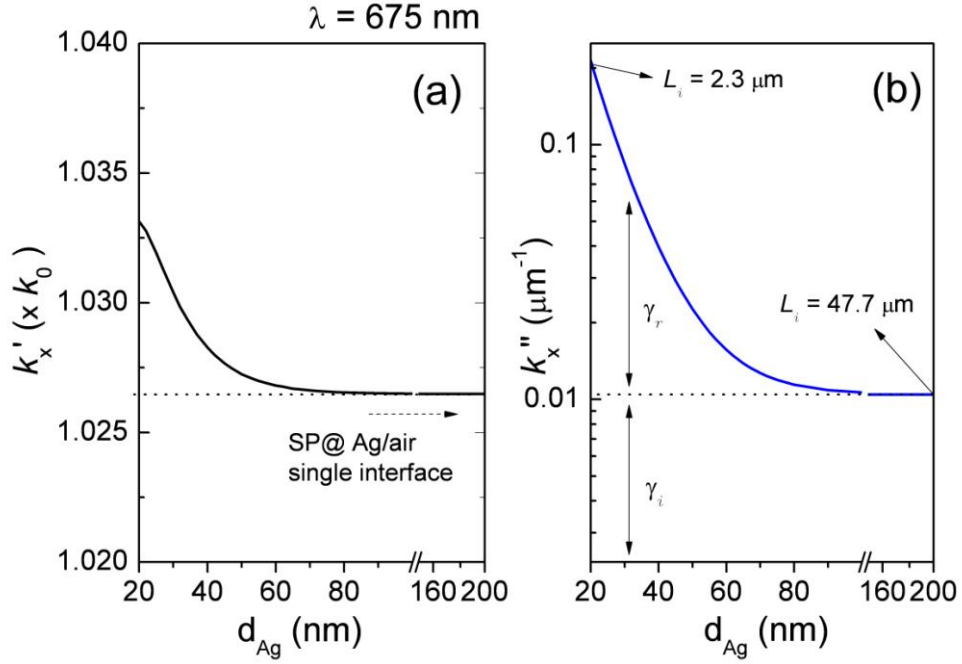


Figure 3.12 Silver layer thickness dependence of propagation constants of prism/silver film/air configuration at 675 nm wavelength: (a) Variation of the real part of the corresponding complex propagation constants; (b) The imaginary part of the corresponding complex propagation constants containing γ_i and γ_r . Propagation lengths for two extreme silver thicknesses, 20 nm and 200 nm, are displayed.

The imaginary part of propagation constants k_x'' may be categorised into both radiation loss γ_r and internal loss γ_i according to the concept introduced from the cavity picture in the previous section. The internal loss can be defined by $\gamma_i = k_x''(d_{Ag} \gg \delta)$ and relies on only the metal/dielectric interface (potentially metal/multi-dielectric layer interfaces), excluding the prism semi-infinite layer, but the radiation loss γ_r is strongly dependent on d_{Ag} . Therefore, in short, numerically calculated mode propagation momentum k_x'' can be defined by the total loss of γ_r and γ_i , also determining the angular line width of reflectivity correspondingly.

$$2k_x'' = 2(\gamma_i + \gamma_r) \approx \Delta\theta \quad (3.19)$$

In practice, angular reflectivity curves from prism-coupling experiments are measured to evaluate SPP properties in a specific structure. Here we show the correlation of angular reflectivity curves and the theoretical approaches by examining the trend of internal loss γ_i and radiation loss γ_r with respect to the thickness d_{Ag} of silver films. Figure 3.13 shows the trend of minimum reflectivity and angular line width in a function of d_{Ag} and angular reflectivity curves at three distinctive silver thicknesses of 34 nm, 53 nm and 76 nm around

optimum thickness (insets in Figure 3.13). For a thinner silver thickness (~ 50 nm, yielding optimum coupling of $R=0$), radiation loss γ_r becomes dominant, thus increasing reflectivity. As d_{Ag} increases, γ_r becomes weak because the metal thickness becomes too thick for SPP fields to escape out, also resulting in increased reflectivity. The thinner silver thickness leads to the higher total propagation loss. The variations of internal loss γ_i and radiation loss γ_r as a function of d_{Ag} , which were numerically calculated, were plotted in Figure 3.13 (b). It is evident that the $\Delta\theta$ trend is consistent with the trend of total loss k_x'' (blue solid lines in Figures 3.13 (a) and (b)), confirming the nature of the leaky modes in the prism-based structures.

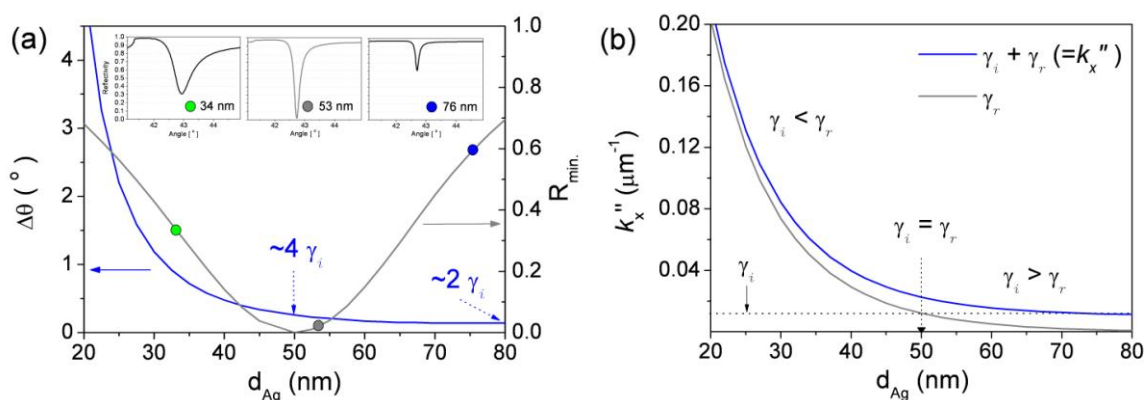


Figure 3.13 (a) Reflectivity and angular line width with respect to the thickness of Ag films. The three insets display angular reflectivity curves at three silver thicknesses of 34 nm, 53 nm and 76 nm, which are indicated in the $\Delta\theta$ trend. (b) The trends of internal loss γ_i and radiation loss γ_r with respect to the thickness of Ag films. They were obtained by the numerical calculation of the dispersion equation.

d_{Ag}	$\gamma_i (cm^{-1})$	$\gamma_r (cm^{-1})$
34 nm	104.66	504.87
53 nm	104.66	94.27
76 nm	104.66	11.41
200 nm	104.66	0

* $\lambda=675$ nm

Table 3.1 Calculated internal loss γ_i and radiation loss γ_r for four silver thicknesses 34 nm, 53 nm, 76 nm, and 200 nm with a 38 nm thick Lumogen Red film and without Lumogen Red

To evaluate whether the two loss factors obtained from the numerical calculation can reflect angular reflectivity curves well, a reflectivity curve drawn by inputting γ_i and γ_r values into the equation (3.6), which were calculated as displayed in Table 1, are compared with the curves by the transfer matrix method for the 76 nm thick silver film. Both curves have a good agreement with each other.

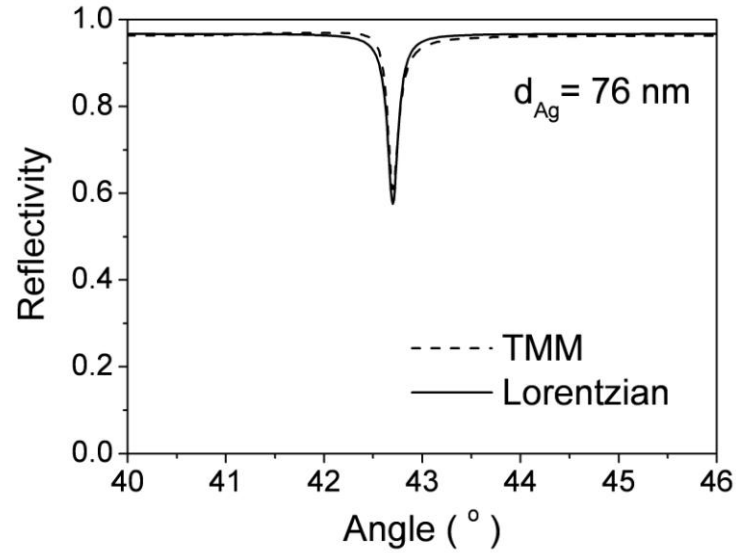


Figure 3.14 Comparison of angular reflectivity curves by the Transfer Matrix Method and a Lorentzian function for the 76 nm thick silver film

3.3.5 Environment Change near Metal Layer

In this section, the theoretical analysis of the effects of environment change near a metal/dielectric interface on SPP modes is presented. So far, the case that dielectric is air ($\epsilon_d=1$) has been discussed. We move to higher dielectric medium cases ($\epsilon_d>1$). Figure 3.15 shows the change of angular reflectivity curves from one-layer structures when the dielectric is assumed to have a range of dielectric constants from $\epsilon_d=1$ to $\epsilon_d=n_d^2=(1.3)^2$ (n_d : refractive index). For both the 34 nm and 76 nm thick silver films, reflectivity curves move to larger resonance angles as their dielectric constants increase because of correspondingly increased propagation constants; their angular widths also become broader, which means propagation loss is increased. It is noted that critical angles move to larger positions as can be expected from Equation 3.2.

Both the 34 nm and 76 nm thick silver films have the same sensitivity on environment as about 6° per 0.1 of Δn_d in terms of resonance angle movement; however, propagation lengths (numerically calculated) for the 76 nm thick silver films are more sensitive than the

34 nm thick ones.

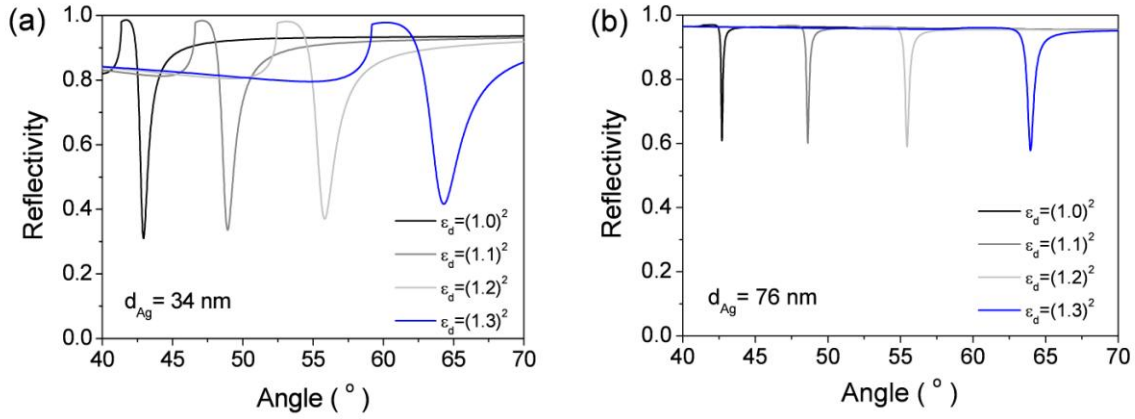


Figure 3.15 Angular reflectivity curves from different dielectric constants of the dielectric semi-infinite layer (a) 34 nm thick silver film case (b) 76 nm thick silver film case

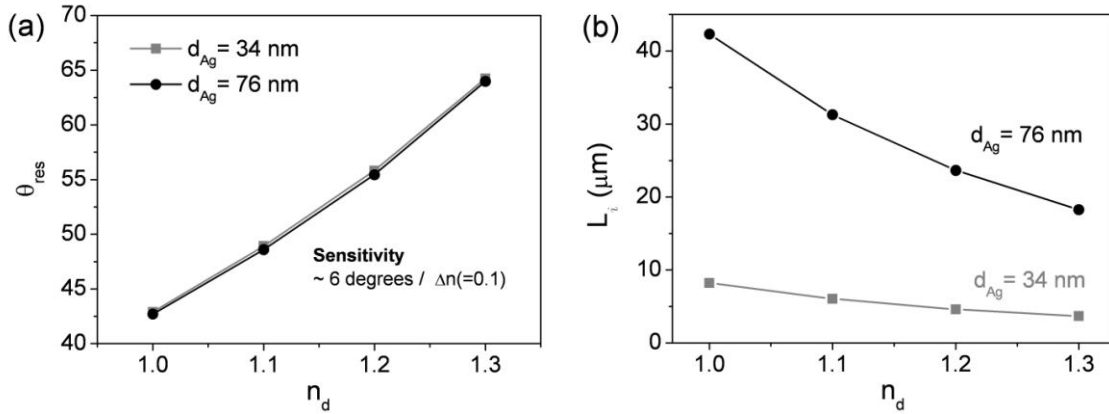


Figure 3.16 (a) Changes of resonance angles of 34 nm and 76 nm thick silver films according to a refractive index of the dielectric semi-infinite layer, which were obtained in figure 3.15 (b) Propagation lengths for 34 nm and 76 nm thick silver films in a function of refractive index of the dielectric semi-infinite layer

The effect of refractive indexes of the films on SPP modes is more clearly understood by the observation of the SPP field distributions around layer structures. Figure 3.17 shows the plasmonic magnetic field distributions of the 34 nm thick silver film cases with $n_d=1$ and $n_d=1.3$. The field in the dielectric layer of $n_d=1.3$ is more tightly confined near the silver/dielectric interface than the field in air. A high dielectric semi-infinite layer, e.g. SiO_2 , LiF and PMMA, in the vicinity of the silver film leads to a higher propagating constant (slower phase velocity), which means there is more strong confinement near the metal layer and also results in more propagation loss than the case without a dielectric film.

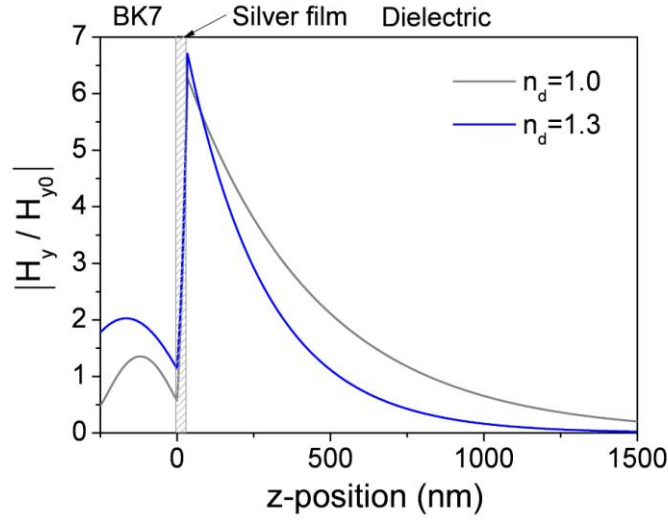


Figure 3.17 Comparison of magnetic field profiles of surface plasmon polaritons in the dielectric layer of $n_d=1.0$ and $n_d=1.3$, being supported by BK7 prism/silver (34 nm)/Dielectric layer configuration

3.4 Summary

In this chapter, the Kretschmann geometry based prism coupling measurement system has been demonstrated for use in the study of plasmonic multi-layer structures. We provided evidences of the basic features of surface plasmon polaritons supported by a one-dimensional layer configuration. To help understand the phenomena, two main theoretical approaches—cavity picture and propagation mode picture—were suggested. We have shown how they can describe plasmonic propagation properties related to angular reflectivity curves and what physical factors exist behind the experimental curves. It was proven that the plasmonic properties displayed via the prism-coupling method are well explained by the theoretical approaches. They will be fully used throughout the remaining chapters. The prism coupling system in conjunction with the analytical backgrounds plays a main role in examining metallo-organic multi-layer structures thoroughly and can be used to prove gain effects on the structures, which are the topics of Chapters 6.

References

- [1] D. M. Koller, A. Hohenau, H. Ditlbacher, N. Galler, F. R. Aussenegg, A. Leitner, J. R. Krenn, S. Eder, S. Sax, and E. J. W. List, "Surface plasmon coupled electroluminescent emission," *Appl. Phys. Lett.* **92**, 103304 (2008).
- [2] J. K. Mapel, M. Singh, M. A. Baldo, and K. Celebi, "Plasmonic excitation of organic double heterostructure solar cells," *Appl. Phys. Lett.* **90**, 121102 (2007).
- [3] T. Sanbongi, S. Katano, Y. Uehara, and S. Ushioda, "Time-Resolved Spectroscopy of laser-induced light emission from an evaporated Au film in the Kretschmann geometry," *Jpn. J. Appl. Phys.* **47**, 6114-6116 (2008).
- [4] A. S. Vengurlekar and T. Ishihara, "Surface plasmon enhanced photon drag in metal films," *Appl. Phys. Lett.* **87**, 091118 (2005).
- [5] O. Popov, V. Lirtsman, and D. Davidov, "Surface plasmon excitation of amplified spontaneous emission from laser dye molecules embedded in polymer matrix," *Appl. Phys. Lett.* **95**, 191108 (2009).
- [6] M. Righini, G. Volpe, C. Girard, D. Petrov, and R. Quidant, "Surface Plasmon Optical Tweezers: Tunable Optical Manipulation in the Femtonewton Range," *Phys. Rev. Lett.* **100**, 8-11 (2008).
- [7] R. Naraoka, H. Okawa, K. Hashimoto, and K. Kajikawa, "Surface plasmon resonance enhanced second-harmonic generation in Kretschmann configuration," *Opt. Commun.* **248**, 249-256 (2005).
- [8] S. E. Yalcin, Y. Wang, and M. Achermann, "Spectral bandwidth and phase effects of resonantly excited ultrafast surface plasmon pulses," *Appl. Phys. Lett.* **93**, 101103 (2008).
- [9] J. Chilwell and I. Hodgkinson, "Thin-films field-transfer matrix theory of planar multilayer waveguides and reflection from prism-loaded waveguides," *J. Opt. Soc. Am. A* **1**, 742 (1984).
- [10] E. Anemogiannis, E. N. Glytsis, and T. K. Gaylord, "Determination of guided and

leaky modes in lossless and lossy planar multilayer optical waveguides: reflection pole method and wavevector density method," J. Lightwave. Technol. **17**, 929-941 (1999).

[11] E. Hecht, *Optics* (Addison-Wesley, 2002).

[12] A. Yariv, *Optical Electronics in Modern Communications* (Oxford University Press, 1997).

[13] T. Visser, H. Blok, and D. Lenstra, "Modal analysis of a planar waveguide with gain and losses," IEEE J. Quantum Elect. **31**, 1803–1810 (2002).

[14] I. Avrutsky, "Guided modes in a uniaxial multilayer," J. Opt. Soc. Am. A **20**, 548-56 (2003).

[15] J. Burke, G. Stegeman, and T. Tamir, "Surface-polariton-like waves guided by thin, lossy metal films," Phys. Rev. B **33**, 5186–5201 (1986).

[16] Jing Chen, Gennady A. Smolyakov, Steven R. J. Brueck and Kevin J. Malloy, "Surface Plasmon modes of finite, planar, metal-insulator-metal plasmonic waveguides," Opt. Express **16**, 14902 (2008)

[17] Chengkun Chen, Pierre Berini, Dazeng Feng, Stoyan Tanev and Velko P. Tzolov, "Efficient and accurate numerical analysis of multilayer planar optical waveguides in lossy anisotropic media," Opt. Express **7**, 260 (2000)

[18] R. D. Kekatpure, A. C. Hryciw, E. S. Barnard, and M. L. Brongersma, "Solving dielectric and plasmonic waveguide dispersion relations on a pocket calculator," Opt. Express **17**, 24112-29 (2009).

4 Surface Plasmon Polaritons in Metallo-Organic Multilayers

4.1 Introduction

In this chapter our interest is to study the surface plasmon polaritons (SPPs) supported in a planar layer geometry, comprising either one or two layers, e.g. metal and a polymer material. The SPP mode properties are governed by the optical properties of the materials, e.g. dielectric permittivity, and the geometry or film thickness, see e.g. [1-4]. While these planar or one-dimensional structures are very simple in terms of geometry, compared to three-dimensional confinement structure like metal nanoparticles, they provide us with an excellent platform from which to study the basic properties of SPPs. A Prism-coupling method, in conjunction with theoretical analysis, is used extensively to probe SPP characteristics through angular reflectivity curves. Experimentally obtained reflectivity curves are analyzed in terms of layer thickness, polarization, and excitation wavelength. The Prism-coupling method itself is a well-known technique for examining film conditions such as film thickness and dielectric constants [5,6]. In the later parts of the chapter we highlight just how sensitive the technique is when we examine the response from polymer/metal structures where the polymer film has been applied from different solvents. These results highlight the importance and impact that the solvent used has on the SPP properties and, to our knowledge, are the first time the technique has been applied in this way.

Overall the chapter demonstrates several key aspects of SPP mode propagation in metallo-organic structures that is used for the later studies in Chapters 5 and 6. Perhaps more widely it serves to reaffirm how SPPs can be utilized in a diverse range of fields, for example, in organic light-emitting devices with metallic contacts [7,8] to quantum control of single plasmons [9,10].

4.2 Layer Fabrication

4.2.1 Silver Deposition

Generally forming a silver film on a glass flat substrate or directly onto a prism can be produced via thermal or sputtering evaporation. However silver deposited by these methods can have a tendency to develop into islands particularly on substrates such as glass and silicon. This is especially the case for example at lower evaporation speeds since the atoms have enough time to arrange themselves on the surface and form rough surfaces. For thicker films, surface roughness is somewhat reduced because of bigger grain size [11]. Therefore the main approach to obtain a better quality surface (lower roughness) is often to use a higher evaporation speed.

Clearly the surface quality in our samples will be important, especially in view of the strong surface confinement of SPPs, therefore a high evaporation speed over 0.5 nm/s was maintained throughout. Under these conditions fabricated silver films, of around 70 nm in thickness, show a surface roughness rms value less than 0.7 nm. Prior to the silver deposition, the flat substrate and prisms were cleaned by ultrasonic treatment in acetone. The silver films were produced by thermal evaporation, under high vacuum conditions. Shot-type silver sources of 1-3 mm size with 99.99% purity (purchased from Sigma Aldrich) were kept in nitrogen environment to maintain purity and prevent contamination. The evaporation conditions for silver films are summarised in Table 4.1.

Vacuum pressure	< 5.0×10^{-6} mbar
Rate	> 0.5 nm/s
Ag source	99.99% pure

Table 4.1 The silver film deposition conditions using a thermal evaporator

4.2.2 Polymer Film Formation

Conjugated polymers are soluble in many common solvents and forming polymer films can easily be produced, from solution, by a spin-coating technique. The resulting quality of the polymer film produced by the spin-coating method is subject to a number of factors,

such as crystalline orientation, surface energy of substrate and solubility to name a few (see e.g. [12,13]). To make the solutions, the polymer is mixed with an adequate solvent to ensure the solute is well dissolved at a certain concentration ratio. For the Lumogen Red conjugated polymer, Chlorobenzene or toluene were used as the solvents. The *Wettability* of the solution on the substrate is an important factor for arriving at a high quality glassy film. The Wettability can be straightforward to estimate by observing the contact angle at which the liquid/vapour interface meets the surface line of the substrate before film formation. Typically if the contact angle found is less than 40° the solution should spread well on the surface. Figure 4.1 shows an image of a droplet of Chlorobenzene-based Lumogen Red polymer solution formed on a silver surface, itself deposited on Spectrosil B substrate (an arrangement typical of all metallo-dielectric structures investigated in this thesis). The measured contact angle of the solution was as low as 20° thus the solution is expected to spread well on the surface and make uniform films. For comparison, a water droplet on the surface has a contact angle of around 90° .

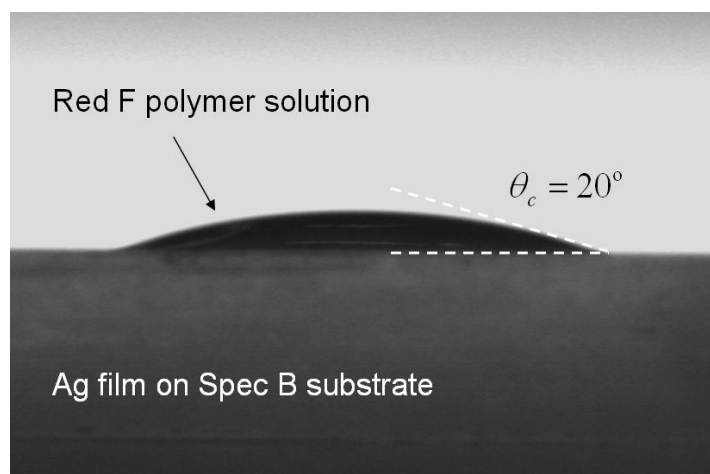


Figure 4.1 Contact angle measurement of the Lumogen Red conjugated polymer solution dissolved in Chlorobenzene. The picture shows a droplet of the solution on silver film deposited on Spec B glass substrate. The diameter of the droplet is on a millimetre scale. The measured contact angle is $\theta_c=20^\circ$ indicating the solution is fairly wet on the surface.

Two main factors largely determine the film thickness, they are the concentration of the solutions and the spin speed. In Figure 4.2, the resulting thickness of Lumogen Red films, determined using a stylus profiler, are shown according to different spin speeds (rpm) and different solution concentrations. The four concentrations comprised 12.5 mg/ml, 16.5 mg/ml, 20 mg/ml, 24 mg/ml in Chlorobenzene and the spin speed ranged from 1000 rpm to 7000 rpm (Figure 4.2). As expected, higher concentrations produced thicker films for the same spin-speed, while for the same concentration a lower spin speed tended to produce

thicker film. We also noticed that for spin speeds less than 2000 rpm the resulting surface appeared quite rough therefore, to produce the high quality glassy films required for our studies spin speeds >2000 rpm were used.

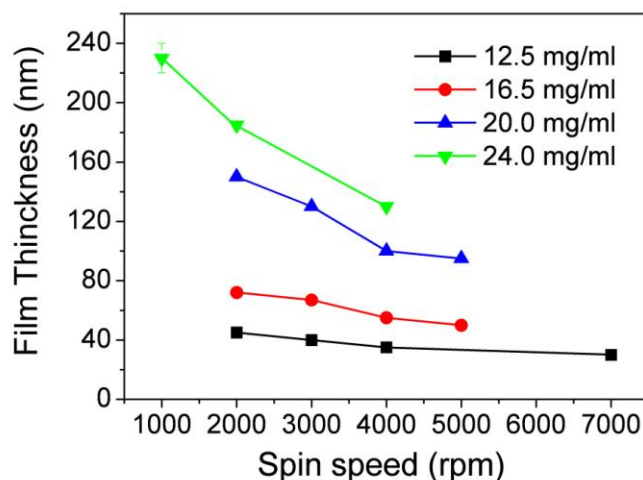


Figure 4.2 The thickness dependence of spin-casted Lumogen Red films as a function of spin speed from Chlorobenzene-based solutions of 12.5 mg/ml, 16.5 mg/ml, 20 mg/ml and 24 mg/ml concentrations

In Figure 4.3 we show optical constants of a Lumogen Red film obtained via ellipsometry. The value k_{extc} , the extinction coefficient indicates the amount of absorption loss and has similar spectrum with the absorption spectrum of Figure 2.9. For the modeling of multi-layer structures, the values of n and k_{extc} are converted into the dielectric functions used by the equations (3.9-3.15) using $\epsilon' = n^2 - k_{\text{extc}}^2$ and $\epsilon'' = 2nk_{\text{extc}}$.

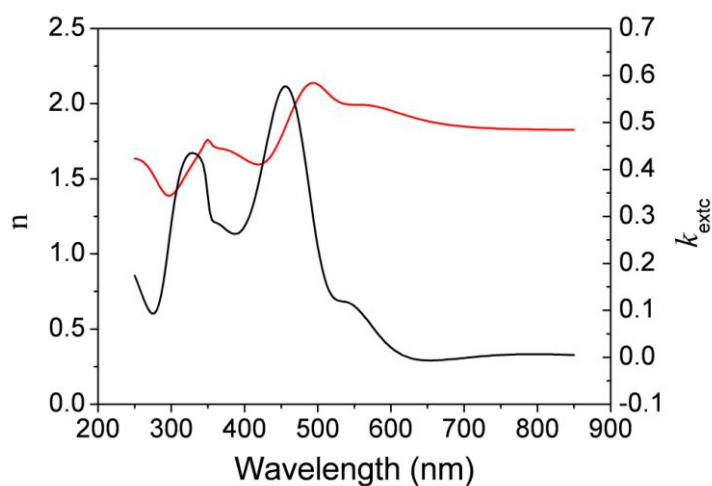


Figure 4.3 Optical constants of a Lumogen Red polymer film measured by ellipsometry (Courtesy of Dr. Mariano Campoy-Quiles, Imperial College London)

4.3 Surface Plasmon Polaritons in One-layer Structure

4.3.1 Geometric Dependence

To first understand and demonstrate surface plasmon propagation in the Kretschman geometry, a *one-layer* structure was examined. Thin silver films with a thicknesses typically between 30-70 nm were deposited via thermal evaporation directly onto the surface (*hypotenuse*) of a right angle prism. In this respect the one layer structure possesses two interfaces of silver/prism and silver/air, but only the SPP localised at the silver/air interface is accessible in the Kretschman geometry as the mode behaviour of leaky SPP modes whose in-plane momentum is in the momentum in prism was discussed in chapter 3 (see e.g. §3.3.3).

Experimentally obtained angular reflectivity curves (solid lines), along with theoretical curves (dotted lines), are displayed in Figure 4.4(a). For the case with a Ag thickness of 53 nm the reflectivity minimum is almost zero and indicates near perfect optimum coupling to the SPP. All measured curves are seen to be in excellent agreement with the theoretical curves. To further analyze the film thickness dependence, information on the resonance angle, minimum reflectivity and angular linewidth is extracted from the angular reflectivity curves of Figure 4.4(a) and are plotted as a function of silver film thickness d_{Ag} in Figures 4.4 (b), (c) and (d) respectively. For all Figures (a-d) the dotted lines are from the TMM calculation using a silver dielectric constant of $\epsilon_{Ag} = -19.6 + i0.8$. We see that all the properties (i.e. resonance angle, reflectivity minimum and linewidth) are very well reproduced using our theoretical (TMM) approach. Considering now the overall trends, we find as the silver thickness increases from 20 nm to 90 nm, the resonance angle decreases and converges to an angle 42.7° (Fig. 4.3(b)). In other words, the propagation momentum approaches that of a single silver/air interface. The angular linewidth reflects the propagation loss of SPPs as was previously mentioned (see eqn (3.19)). Our results show as the silver thickness increases, the angular linewidth dramatically decreases (Fig. 4.3(d)). For example for a 70 nm thick film the angular linewidth is seven times as small as that found for a 30 nm thick film, implying a much lower propagation loss. These observations reaffirm that even for these simple structures the key properties of SPP (such as propagation loss) can be very effectively tuned and controlled through the geometry (i.e. thickness).

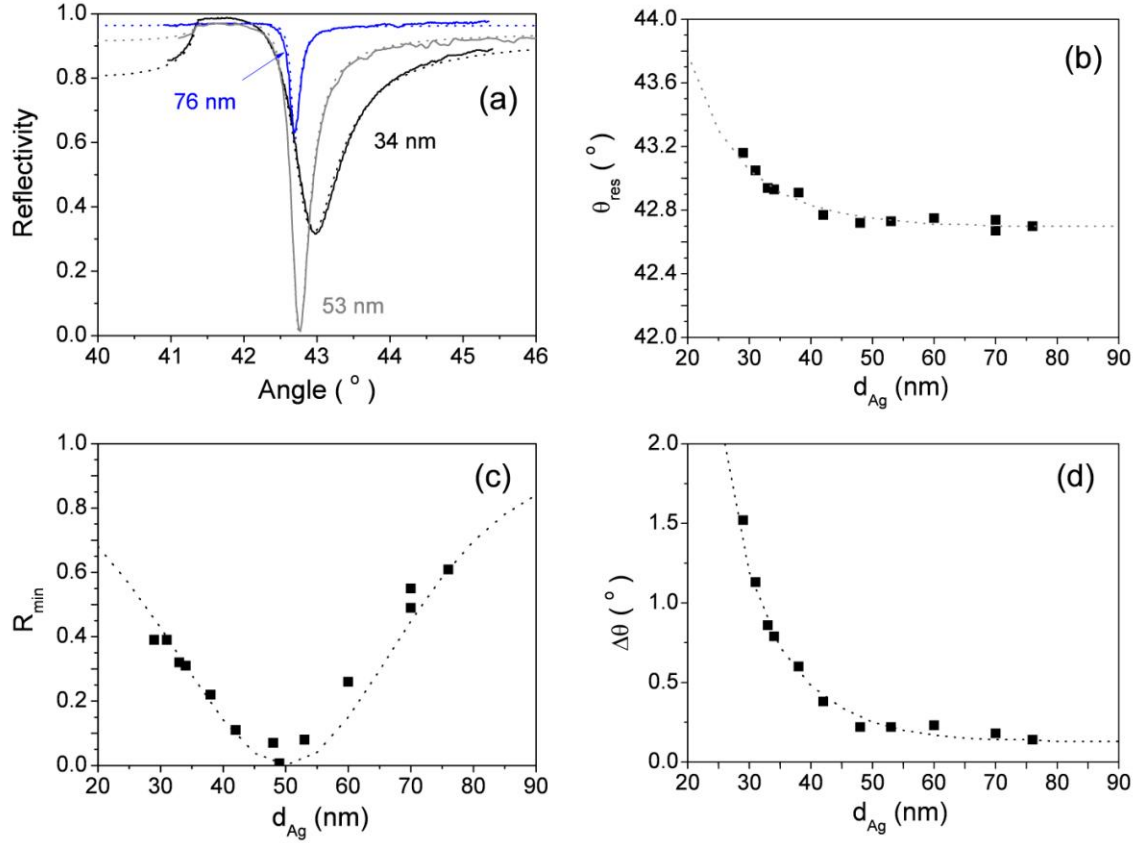


Figure 4.4 Silver thickness dependence of angular reflectivity curves in the one-layer structures: (a) experimentally measured angular reflectivity curves (solid lines) from different silver films of 34 nm, 53 nm, and 76 nm thickness, which are fitted with theoretical curves (dotted lines). Each silver thickness is indicated as different colours of black, gray, and blue, respectively. From a number of silver thicknesses the (b) Resonance angle (c) Minimum angular reflectivity and (d) Angular line width are extracted from the reflectivity spectra. The experimental data (square dots) were taken from the angular reflectivity curves in figure (a) and the dotted lines describe theoretical trends using a silver dielectric constant $\epsilon_{Ag} = -19.6 + 0.8i$.

4.3.2 Polarization Property

A distinguishing feature of SPPs in general, and particularly for a planar structure, is the sensitivity to polarization that can be used to provide unambiguous evidence of SPP excitation. As explained in chapter 2, only p-polarized light (or TM mode) can excite the SPP modes in planar metallic structures, with the SPP excitation clearly identified by a dip observed in the reflection curves (cf. Fig.4.3(a)). This unique feature of SPPs can be

demonstrated for a 34 nm thick silver film shown in Figure 4.5, where the polarization state of an incident light is selected using a $\lambda/2$ wave plate in the prism coupling system.

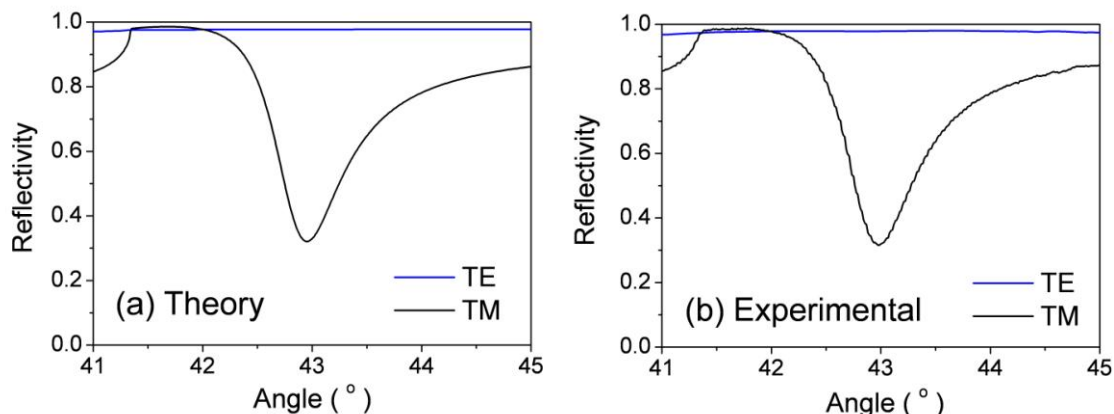


Figure 4.5 Angular reflectance curves from a 34 nm thick silver film in the Kretschmann geometry at TE-polarized and TM-polarized light (a) TMM calculation (b) Experiment

Figure 4.5 displays both modeling and the measurement of angular reflectivity curves for TE (s-polarised) and TM mode (p-polarised) incident light corresponding to an incident wavelength of 675 nm. Both the calculated and experimental reflectance curves show no resonance dip when incident light is TE polarized, in contrast to the case for TM polarization that clearly shows the SPP induced dip.

4.3.3 Spectral Dispersion

The spectral dispersion behavior of angular reflectivity curves in planar structures can be attributed to the underlying dispersion of the SPPs supported by the structure. (Also associated with the plasmonic mode behaviour analyzed in chapter 3.) Experimental investigations into the spectral dispersion were conducted by using three different laser sources of 473 nm, 532 nm and 675 nm, which usefully span the visible frequency region.

The two samples chosen for the study used silver thickness layers of 33 nm and 70 nm. Figure 4.6 (a) and (b) displays the measured angle-dependent reflectance curves recorded under the three separate incident wavelengths. In both structures, the reflectivity dip is seen to move to larger angles with the linewidths becoming wider for shorter incident wavelengths. Both of these observations may be understood from the characteristic dispersion of the SPP (Figure 4.7) where the SPP exhibits a higher propagating momentum (larger angle) for higher optical frequencies (shorter wavelengths) and a corresponding higher propagation loss (i.e. larger angular linewidth) due to increased confinement in the

silver layer.

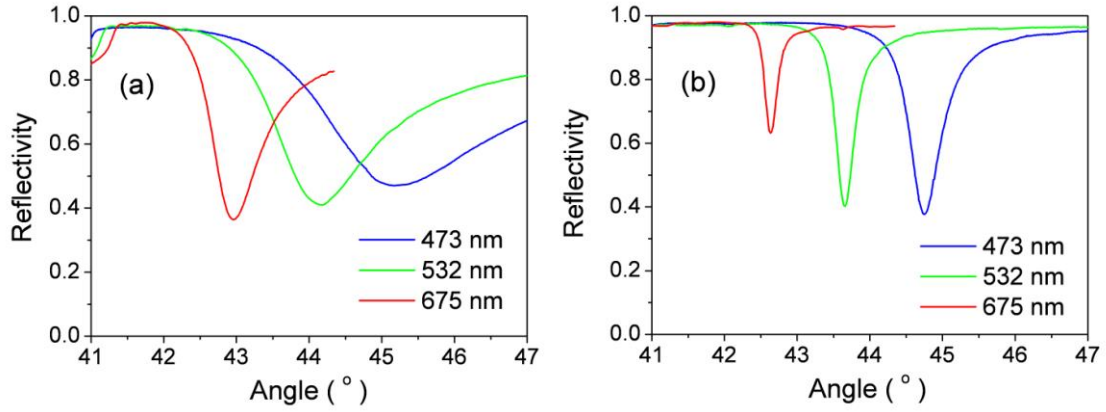


Figure 4.6 (a) Experimental data of reflectance curves from 33 nm thick silver layer at three wavelengths of 473 nm, 532 nm and 675 nm (b) Experimental data of reflectance curves from 70 nm thick silver layer at three wavelengths of 473 nm, 532 nm and 675 nm

Figure 4.7 shows an angular reflectivity *map* for the structure comprising a 33 nm thick silver layer calculated for a range of incident frequencies and angle of incidence. The map, or specifically the dark region represent the reflectance dip and essentially describes the underlying dispersion of the SPP supported in the structure. Experimental data from the curves in Figure 4.6(a) for the three different wavelengths are also plotted on the map and can be seen to match with the expected positions.

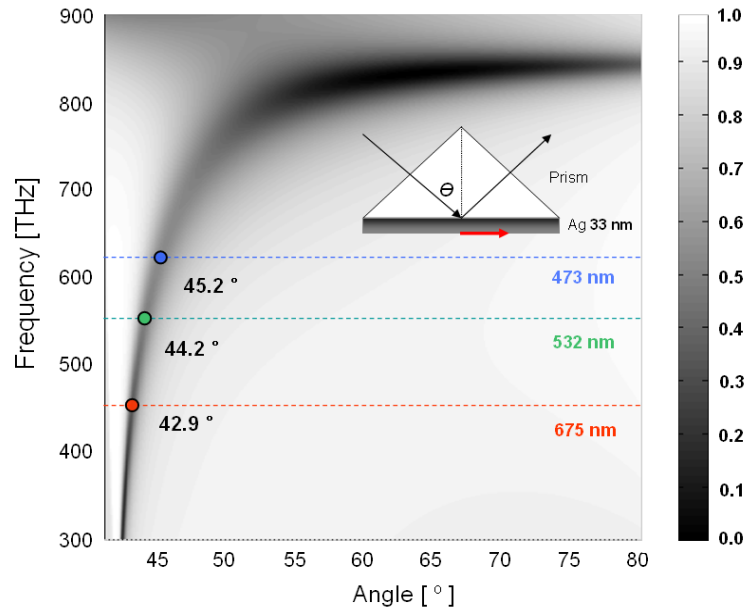


Figure 4.7 Angular reflectivity map in a function of angle of incidence and frequency of light for the one-layer structure with a 33 nm thick silver layer. Dark regions indicate the reflectivity minima and essentially represent coupling to the SPP.

4.4 Surface Plasmon Polaritons in the Two-Layer Structures

4.4.1 Propagation Modes

In this section we turn to a *two-layer* structure, which comprises a silver layer and a thin dielectric layer (a fluorescent conjugated polymer namely the Lumogen Red copolymer). Many of the properties identified in the previous section concerning the spectral response will also be investigated here but with the added emphasis on the possibility of using the polymer layer as an active material; a subject further developed in chapters 5 and 6. Our initial investigations here will focus on the passive properties, i.e. the role of the polymer as an additional dielectric layer in the Kretschmann arrangement.

A schematic illustration of the resulting samples under study and the relation to a two-layer configuration is shown in Figure 4.8. The polymer layer is situated (deposited) directly onto the silver layer. The thickness of polymer layer will be examined in relation to the modes that are supported but typically, for the experimental investigations, is on the order of 50 nm. In the two-layer structure, SPPs can still be excited at the silver/dielectric (herein, polymer film) interface. However, we will show there can be some subtle (and not so subtle) differences in the SPP properties compared to the one-layer structure, particularly in relation to the propagation momentum of a SPP mode and its field distribution.

To first examine the SPP propagation behaviour for the two-layer structure we turn to the numerical approach, solving for a complex propagation wavevector, as discussed in the chapter 3. We first start with a 50 nm thick silver film and display the real and imaginary components of the calculated complex propagation wavevector as the incident optical frequency is varied (the black curves in Figure 4.9). The real part of the propagation wavevector is in phase with the incoming light and represents the dispersion relation of the SPP mode. The imaginary part, shown in the right plot of Fig. 4.4, is directly related to propagation loss of the mode.

To clarify the effect of including a polymer layer, two different polymer thicknesses were then considered; specifically a 20 nm and 38 nm layers shown as green- and blue-lines in Figure 4.9. The results indicate that the addition of a polymer layer increases the propagation constant and results in a higher propagation loss, presumably due to the higher overall refractive index of the structure and subsequently a tighter confinement of the SPP mode within the metal. Significantly we find that for frequencies over 500 THz (600 nm),

the propagation wavevector of the SPP mode in the structures appears outside the region of the vacuum light-line and the prism light-line. Thus for these incident wavelengths, the SPP mode cannot be excited by the prism configuration and no reflectivity dips would appear. This shows the choice of film thickness (and overall thickness of the structure) must be carefully considered for experimental studies.

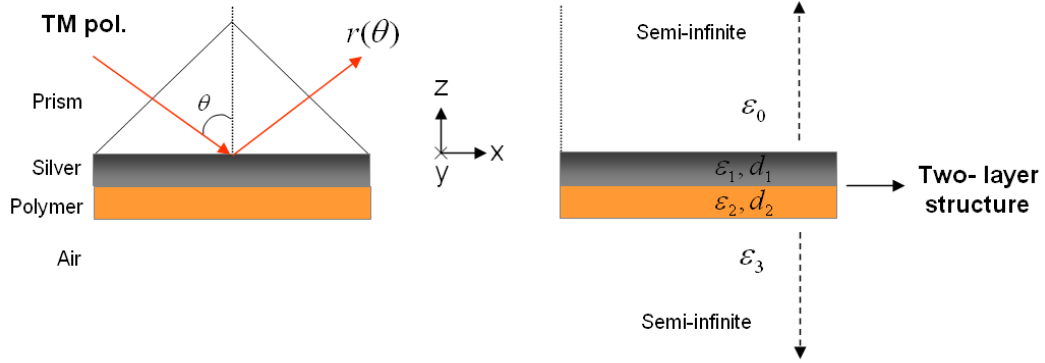


Figure 4.8 The schematic of layer configuration of the two-layer structure: prism/silver film/polymer film/air configuration

In Figure 4.10 we examine the silver thickness dependence on the modal properties for structures with and without a polymer layer. Some common trends can be identified; the real and imaginary parts of the propagation constant are seen to converge to fixed values as the silver thickness increases. As noted earlier, the main effect of adding the polymer layer is to increase both the propagation constant (real part) and the propagation loss (imaginary part) as the fields are increasingly confined near the interface. Propagation lengths for two extreme silver thicknesses are indicated in the right hand plot of Figure 4.10. For thicknesses of 20 nm and 200 nm we find propagation lengths of 0.5 μm and 8.5 μm . These results may be understood by noting that thinner silver films will tend to exacerbate the propagation length because of the dominant contribution of the radiation loss γ_r (see e.g. Fig. 3.12). Whereas when the silver thickness is larger than the skin depth of SPPs, the radiation loss γ_r is suppressed and only the intrinsic propagation loss γ_i contributes to total propagation loss resulting in a lower overall propagation loss (and longer propagation length).

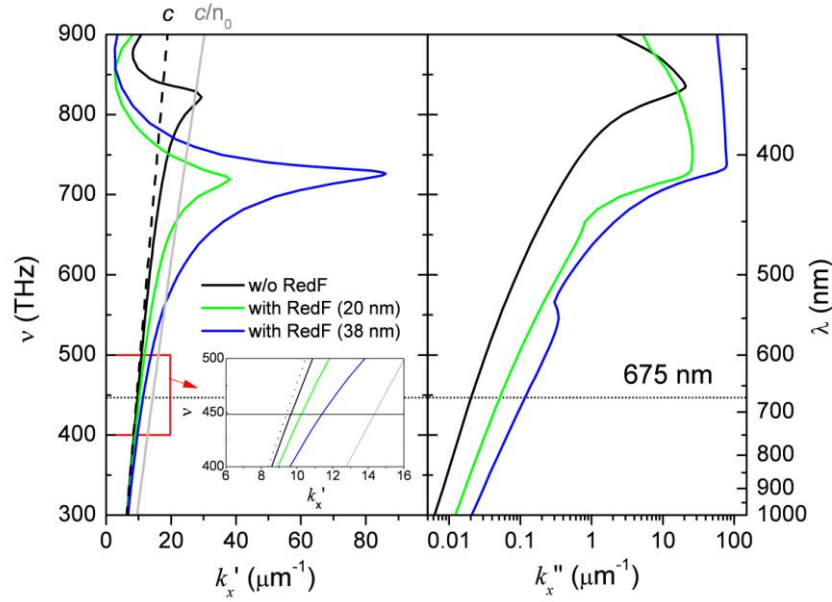


Figure 4.9 Calculated dispersion relations of the surface plasmon propagation mode supported by a two-layer structure of BK7 Prism/50 nm thick silver film/ thin polymer (Lumogen Red) film /air structure, calculated by a Newton-Raphson root searching algorithm. The inset shows the close-up view of the rectangle section shown in the real part of propagation momentum for a wavelength 675 nm.

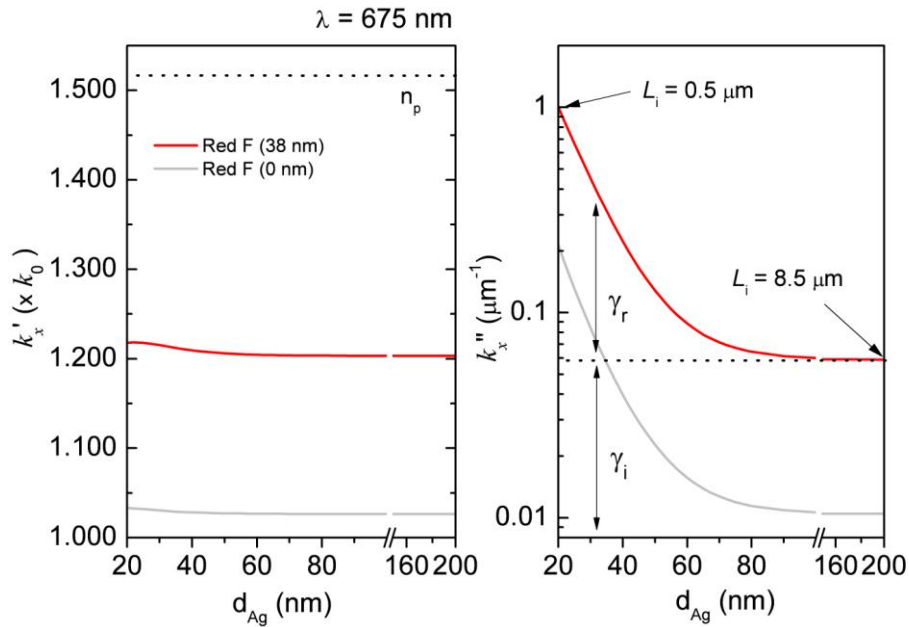


Figure 4.10 Silver layer thickness dependence of propagation constants of prism/silver film/polymer film/air configuration at 675 nm wavelength: (Left panel) Variation of the real part of corresponding complex propagation constants. (Right panel) the imaginary part of corresponding complex propagation constants containing γ_i and γ_r . Propagation lengths for two extreme silver thickness 20 nm and 200 nm are displayed.

4.4.2 Layer Thickness Dependence

Ahead of the later studies (Chapters 5 and 6) where the interest will be on the active (emissive properties) of SPPs, we first turn to some preliminary experimental studies on the two-layer structure consisting of a BK7 prism, a silver film, a Lumogen Red polymer layer (the active layer). Lumogen Red films were fabricated by spin-coating from solution onto silver surfaces, which were already deposited onto the prism. Our initial interest is with the changes to the reflectivity response as the silver layer is varied. Comparisons with the single-layer structure examined in §4.3 will also be made.

To begin the investigations on the thickness of the silver layer, three structures with silver thicknesses of 33nm, 53 nm, and 76 nm were fabricated. The thickness of spin-coated Lumogen Red film was nominally 38 nm. As with the previous studies, angular reflectivity spectra were taken from each sample for 675 nm incident wavelength and the resonance angle position, angular linewidth, minimum reflectivity were extracted. The results are shown in Figure 4.11 along with theoretical spectra obtained from the transfer matrix method. For the calculations we took the dielectric permittivity of the Lumogen Red film at 675 nm, from Figure 4.3, to be $\epsilon_{Ag}=(n_p)^2=(1.8618)^2$, and (as before) used $\epsilon_{Ag} = -19.8+0.8i$ for the silver dielectric constants.

Compared to the results from the one-layer structures in Figure 4.4, the resonance angles appear larger and the linewidths have become broader; entirely consistent with the conclusions drawn from Figures 4.9 and 4.10. Nevertheless, the overall trends, in terms of varying the silver thickness, are broadly similar to those found for the one-layer structure; as the silver thickness increases, resonance angle and linewidth converge to smaller values. The other point worth mentioning is that all the two-layer results are extremely well described by the TMM calculations, as was also found for the one-layer case. As well as validating our model and, to a certain extent, the input parameters we are using, it also highlights how the mode behaviour of surface plasmon polaritons in the one and two layer structure are closely linked to the angular reflectivity curves appeared in the Kretschmann geometry.

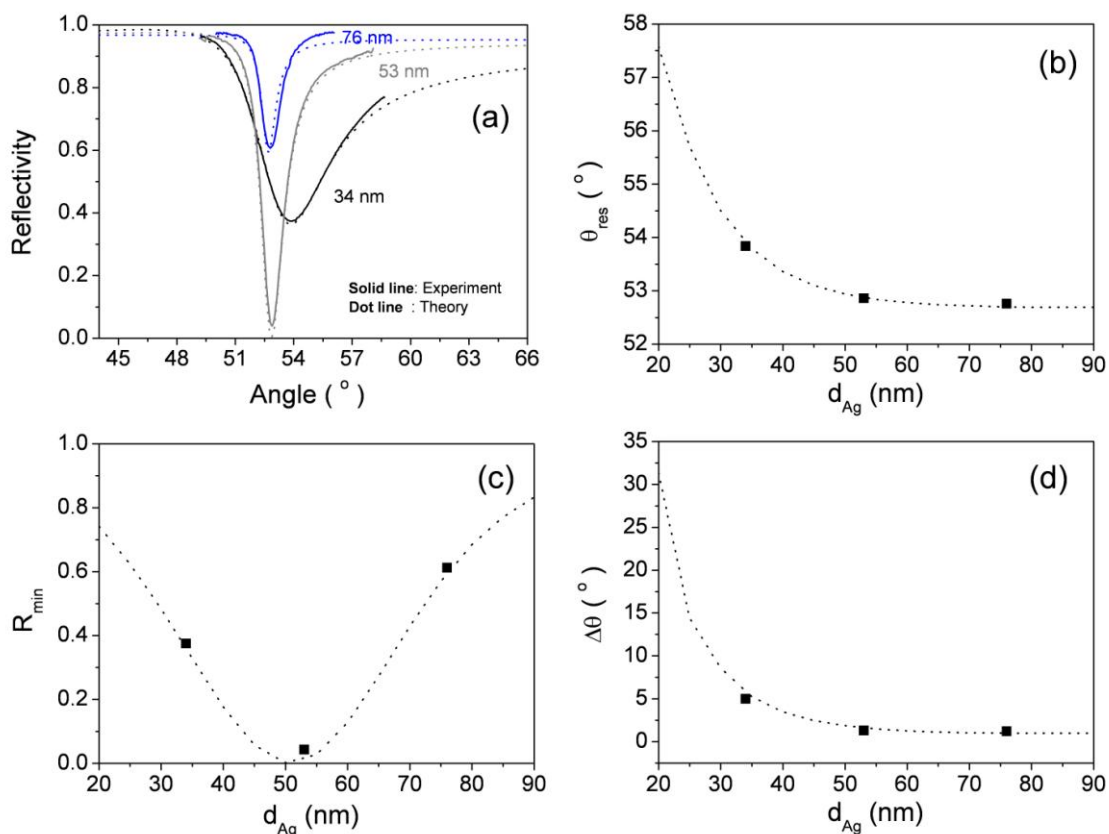


Figure 4.11 Silver thickness dependence of angular reflectivity curves from three silver in the two-layer structures comprising a Lumogen Red film of 38 nm (a) experimentally measured angular reflectivity curves (solid lines) from different silver films of 34 nm, 53 nm, and 76 nm thickness, which are fitted with theoretical curves (dotted lines). Each silver thickness is indicated as different colours of black, gray, and blue, respectively. (b) Resonance angle trend (c) Minimum angular reflectivity trend (d) Angular line width trend. The experimental data (square dots) were taken from the angular reflectivity curves in figure (a) and the dotted lines describe theoretical trends using a silver dielectric constant $\epsilon_{Ag} = -19.8 + 0.8i$.

The results in Figure 4.11 are for a fixed thickness (38 nm) of Lumogen Red layer. For two silver thicknesses, we also studied the situation when the polymer thickness d_p was varied. In these cases Lumogen Red films of 30 nm and 45 nm were controlled by the spin speed of the spin-coater. As shown in Figure 4.12, as the thickness of the polymer film increases the resonance positions move to larger angles and the angular line width becomes broader. It is noteworthy that the reflectivity at the resonance angles does not change much with polymer thickness and suggests that the matching condition (the relation between internal loss γ_i and radiation loss γ_r) is preserved irrespective of the polymer thickness. The experimental trend of resonance angle is in very good agreement with the theory as can be

seen in Figure 4.13 (a).

The reasoning behind the increase of the resonance angle with the addition of a polymer film may be appreciated by noting that the overall effective index of the structure has increased, certainly compared to not having the polymer layer; thus the resulting wavevector of the SPP supported would be expected to occur at larger value (larger angle). This sensitivity to optical environment is of course one of the well known attributes of SPPs, as discussed in §3.3.5, and seen directly from the simple SPP wavevector expression for a single interface (between two semi-finite metal and dielectric) where $k_x = k_0(\epsilon_m/(\epsilon_m + 1))$ for metal/air now becomes $k_x = k_0(\epsilon_m\epsilon_p/(\epsilon_m + \epsilon_p))$ for metal/polymer and ϵ_m and ϵ_p are dielectric constants of silver and polymer, respectively.

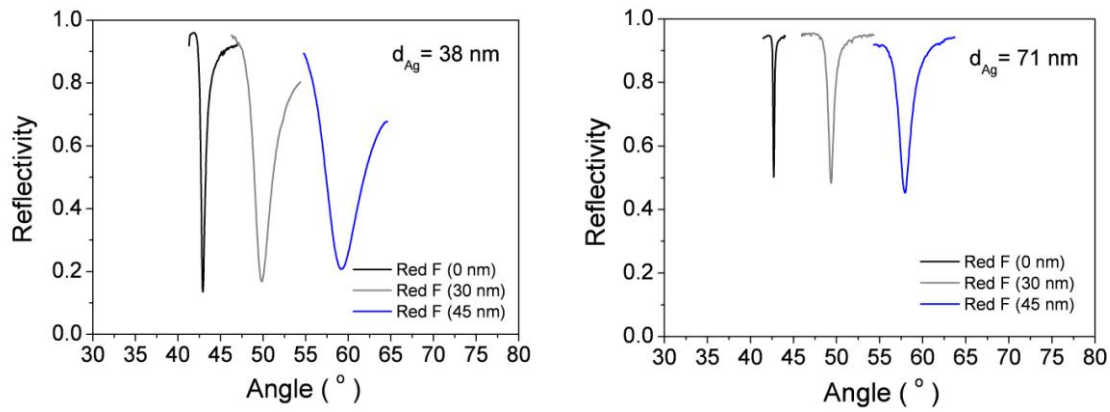


Figure 4.12 Change of angular reflectance curves from the two layer structures with 38 nm and 71 nm silver films according to the thickness variation of the Lumogen Red polymer films

The H_y field distributions shown in Figure 4.13(b) highlight the change of field patterns according to the polymer film thickness. It is seen that as the polymer thickness increases, the SPP field is more tightly confined near the silver/polymer interface, resulting in increased propagation constants (i.e. both real and imaginary parts, cf. Figure 4.9).

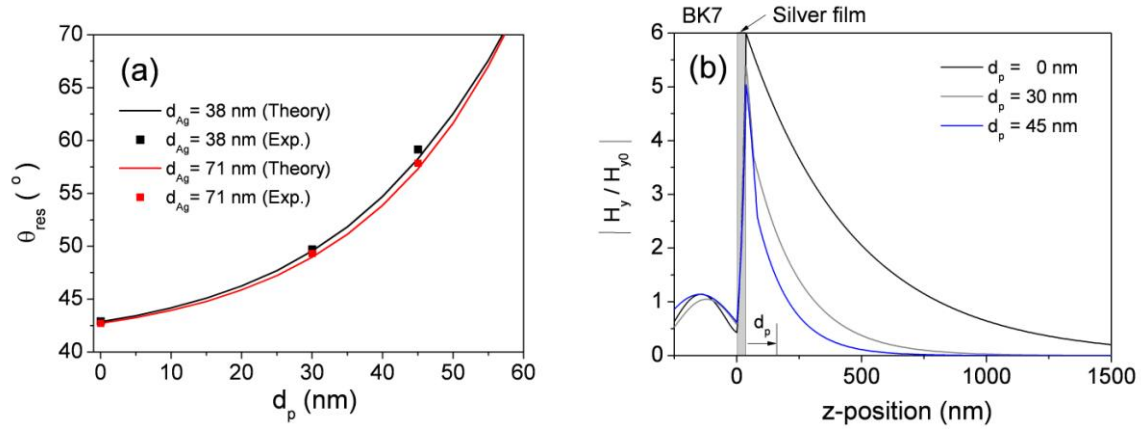


Figure 4.13 (a) Resonance angle positions for 38 nm (black colour) and 71 nm (red colour) thick silver film cases in a function of the Lumogen Red polymer thickness d_p . Dots in the graph indicate experimental data and solid lines are the TMM calculation results. (b) The calculated H_y field patterns in the two-layer structure that is BK7 prism/Ag film(38 nm)/Lumogen Red film(d_p) /Air for Lumogen Red films with 0, 30, and 45 nm. The distributions highlight the tighter confinement of the field to the interface when the polymer film is in place.

4.4.3 SPP mode versus Photonic mode

The two-layer structure we have discussed so far includes the polymer layer that has a high refractive index, considerably higher than the refractive index of the BK7 prism material. As a consequence the polymer layer can potentially support total-internal-reflection based *waveguide* modes. The ability of the structure to support additional modes will depend on the thickness of the polymer layer and the overall thickness of the structure and so our first study in this section will look at the layer dimensions.

A waveguide mode is classified by its effective index, for the present two-layer structure and a wavelength of 675 nm, propagation modes (effective indices) of either TE or TM polarization were calculated as the polymer thickness was varied (Figure 4.14). Only those modes that exhibited an effective index *lower* than the prism, and could therefore be excited in the Kretschmann geometry, were considered in the study. In Figure 4.14 we can see the SPP leaky mode (TM-polarised), excited in the thickness range below 65 nm, which we have dealt with so far. Another TM-polarised waveguide mode (TM_0) starts to appear above thicknesses of 200 nm while the equivalent TE-polarised mode (TE_0) can be excited for a thickness between 90 nm and 200 nm. The figure clearly shows that any of the photonic modes (waveguide modes) are not supported for a thickness less

than 90 nm, which can be regarded as a cut-off thickness d_c .

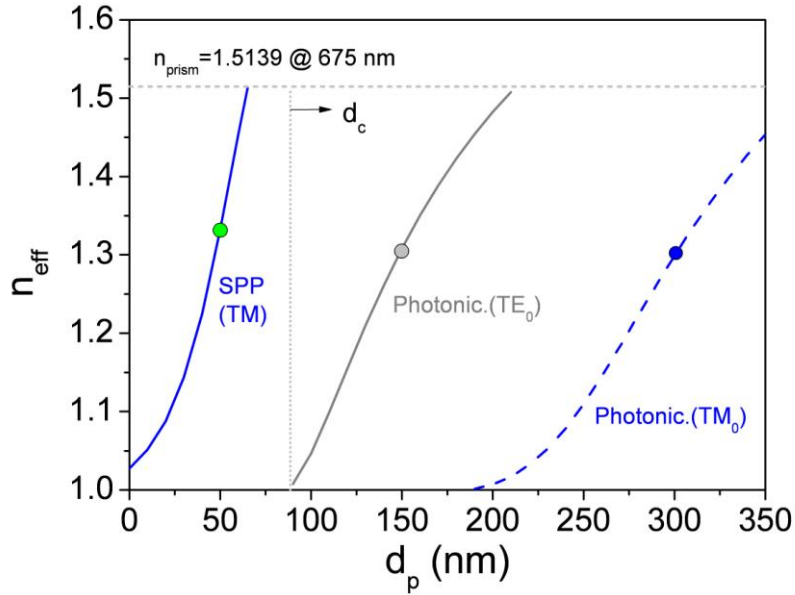


Figure 4.14 The calculated effective indices of modes supported in a prism/ silver (50 nm)/RedF film (d_p)/air layer configuration, as a function of the Lumogen Red film thickness (d_p). Three modes, at thicknesses of 50 nm, 150 nm and 300, representing TM SPP leaky mode, TE photonic mode, and TM photonic mode are marked for the later depiction of their field distributions (shown in Figure 4.15).

It is worth looking more closely at the different types of modes that may be supported in the two-layer structure, namely the TM SPP leaky mode, TE photonic mode, and TM photonic mode. To compare the field distributions of the modes, three polymer film thicknesses of 50 nm, 150 nm and 300 nm were selected (as marked in Figure 4.14). Figure 4.15 displays the calculated field distributions throughout the structure. As expected the SPP mode shows the field concentrated at the silver/polymer interface, decaying in both the silver and polymer films. In contrast, the fields of both TE or TM photonic modes are more distributed in the Lumogen Red films rather than at any interfaces. It is worth reiterating that it is through the polymer layer thickness we can excite a distinctive propagation mode. The work in later chapters is primarily concerned with studying the SPP mode and therefore, as Figure 4.14 demonstrates, we shall restrict our investigations to structures with a *thin* polymer layer of less than 50 nm.

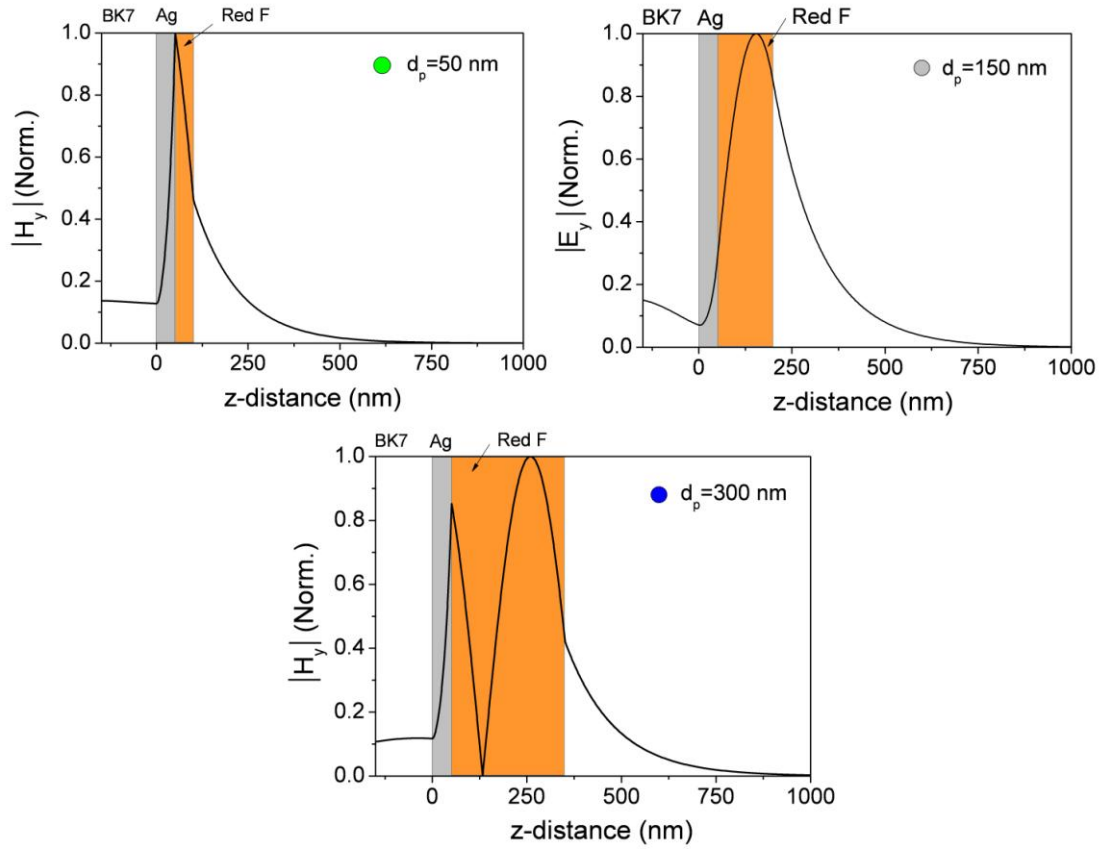


Figure 4.15 The calculated H_y field distributions (peak normalized) in a prism/silver(50nm)/ RedF film(d_p) /air layer layer configuration: (a) TM SPP mode for $d_p = 50$ nm (b) TE photonic mode for $d_p = 150$ nm (c) TM photonic mode for $d_p = 300$ nm

4.5 Film Morphology Effect on SPPs

The work to date has explained and highlighted the sensitivity of the SPP to the surrounding environment that reveals itself in the angular reflectivity curves, e.g. the dependence of metal thickness of reflectivity minimum and angular width. In this section we further demonstrate and reaffirm the high reputation in terms of sensitivity that SPP spectroscopy can bring. We focus on the SPP response for the two-layer configuration, and show how the prism-technique allows us to comment on the *morphology* of thin polymer films. This is very important, not only for the later chapters, but is a clear demonstration of an optical-based technique probing morphology; to our knowledge this is the first reports of experiments and observations of this type.

The polymer films used in the study are prepared from two different solutions, namely Chlorobenzene and Toluene, where both solvents have been widely used for fluorine-based conjugated polymers. Solution-based deposition eases fabrication process and can show film thickness controllability with less than 5 nm resolution. However, proper selection of solvents for a particular polymer material in terms of solubility and wettability on substrate is necessary to form smooth film surface. Figure 4.16 shows the microscopic views of surfaces of polymer films from Toluene (a,c) and Chlorobenzene (b,d) based solutions. Film surface conditions were tested on silver film deposited on glass substrate (Figures (a) and (b)) as well as on a glass substrate (Figures (c) and (d)). Film thicknesses were kept at around 40 nm in order to meet our requirements of only supporting the SPP mode. Irrespective of whether surfaces are glass or metal for polymer film, Chlorobenzene-based polymer films do not show any regular or irregular patterns. However from Figure 4.16(c) it is possible to make out some line patterns, of about 20 μm spacing, from the toluene-based polymer films. The line patterns were clearly revealed to be geometrical corrugation since the film surface was scanned by a stylus profiler. It is speculated that the solvent effect comes from slightly difference of boiling points and solubility according to the physical and chemical properties of both solvents (listed in Table 4.2). It is worth pointing out the line pattern from the Toluene based solution could not be detected by usual visual inspection and at first glance appeared as a good glassy film.

In view of the renowned sensitivity of SPP spectroscopy one question was whether this surface quality could be detectable using our SPP excitation in the Kretschmann geometry, potentially demonstrating a new type of assessment method in morphological studies. (The majority of studies into the morphology of polymer films are almost exclusively carried out using AFM or Raman spectroscopy, see e.g. [14,15]. To examine these points, and to demonstrate how ineffective many of the standard assessment techniques can be at probing

film morphology or roughness, we consider a number of typical optical measurements along with our SPP prism-coupling measurement. In the first instance, Figure 4.17 shows the response from polymer films on a glass substrate, measured using typical absorption and fluorescence lifetime methods. The absorption measurements (using a UV-VIS) show little significant difference between the two samples (formed from different solvents). If the line-patterning were significant we may have expected some increase in the amount of scattering from the films (indicated as Absorbance) but clearly any such scattering appears to be quite small – at least for the UV-VIS experimental arrangement.

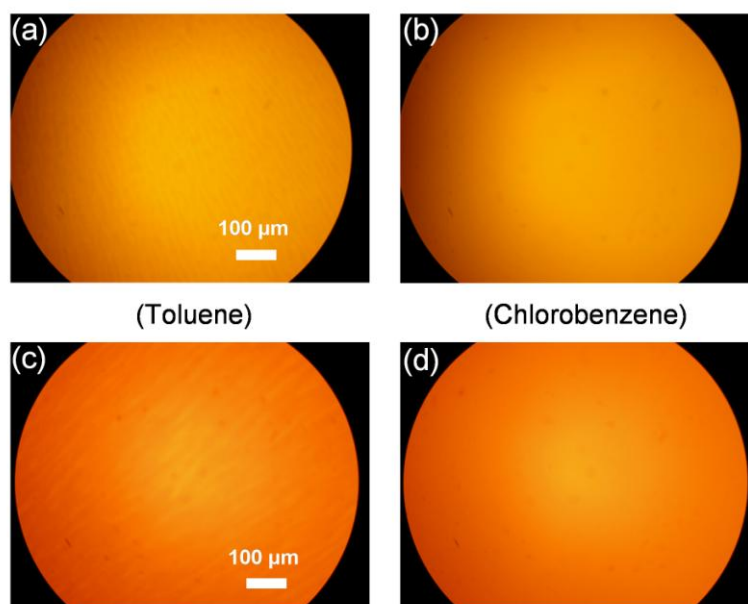


Figure 4.16 Microscopic views of film surfaces formed from Toluene (a,c) and Chlorobenzene (b, d) based solutions. (a) and (b) show polymer films on a normal glass and (c) and (d) on silver deposited on the glass.

Properties	Toluene	Chlorobenzene
Molecular formula	C_7H_8 or $C_6H_5CH_3$	C_6H_5Cl
Molar mass	92.14 g/mol	112.56 g/mol
Appearance	colorless liquid	colorless liquid
Density	0.8669 g/mL	1.11 g/cm ³ , liquid
Melting point	-93 °C	-45 °C
Boiling point	110.6 °C	131 °C
Solubility in water	0.47 g/l (20–25°C)	low
Viscosity	0.590 cP at 20°C	

Table 4.2 Physical properties of two solvents of Toluene and Chlorobenzene.

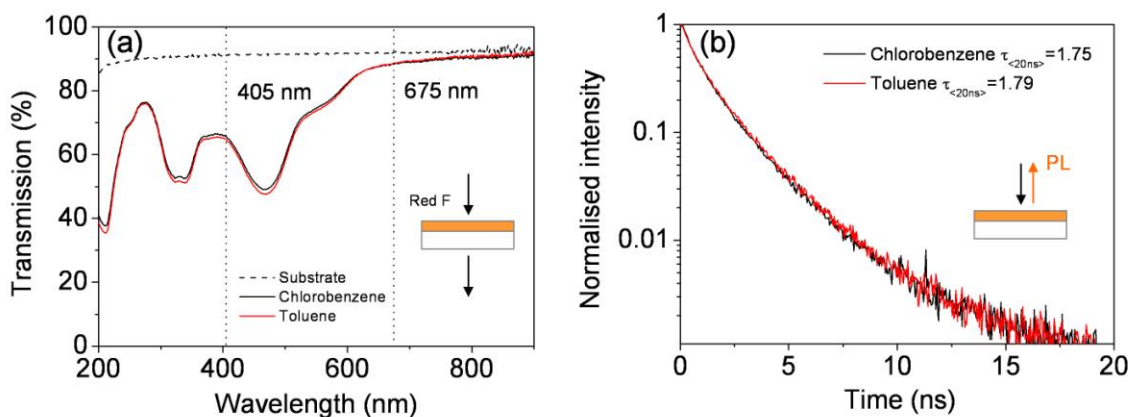


Figure 4.17 Optical properties of 40 nm thick polymer films formed by Toluene and Chlorobenzene (a) Transmission spectra using a UV-Visible spectrometer. The dotted line is a bulk glass substrate case without any films (b) Fluorescence decay curves using a streak camera system. Excitation light was 405 nm. Insets depict the film configuration, and directions of light input and detection.

In Figure 4.18 we show the angular reflectivity spectra from the prism-coupling method, recalling this is a technique deeply associated with the near field coupling to a *surface* wave. Two silver film thicknesses were used in the study, $d_{Ag}=30$ nm and $d_{Ag}=70$ nm, and both show clear differences of reflectivity dip depending on solvent used. The differences between the solvents are less visible for the $d_{Ag}=30$ nm case, recalling that as this thickness is thinner than the optimum coupling thickness coupling to the SPP is not as effective (cf. chapter 3). The situation in the case of the 70 nm film is much more dramatic (Figure 4.18(b)); the experimental curves for the Chlorobenzene case are extremely well predicted by the theoretical modeling (dotted line), while in the case for Toluene derived films the agreement is less impressive.

A point we should perhaps stress is that, regardless of the solvent used, the resonance angle for both thicknesses does not change (Figure 4.18) and suggests the effective indices of supported SPPs are the same; the key differences are instead found in the angular linewidth and reflectivity minima. Considering the angular linewidth, this is known to be a measure of the propagation loss of the SPP thus we can speculate the solvent/morphology effect shows up as a loss (scattering) mechanism of the propagating SPP modes in the structure (cf. Figure 4.10). In the $d_{Ag}=30$ nm case radiation loss γ_r is the dominant loss component, as opposed to the internal SPP propagation loss, and that is chiefly determined by the silver thickness rather than the morphology of the polymer film. Films thicker than optimum thickness (~ 50 nm) have a radiation loss of nearly zero and hence the internal

propagation loss is dominant. These results demonstrating the sensitivity of the SPP prism-coupling technique have proved to be very useful, not least for preparing the high quality polymer films on silver surfaces, but also to highlight (yet again!) the remarkable sensitivity achieved by SPP-based structures.

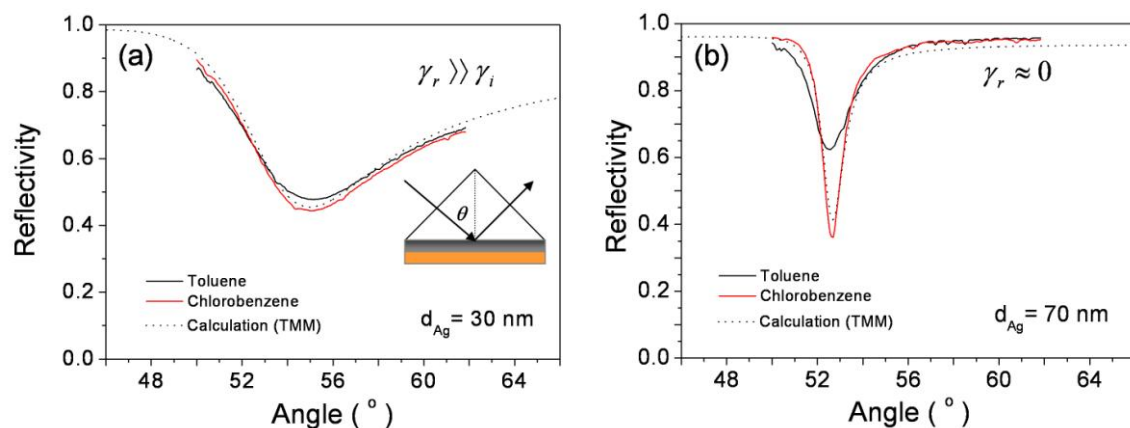


Figure 4.18 Variation of angular reflectivity curves depending on the solvents (a) $d_{Ag} = 30$ nm (b) $d_{Ag} = 70$ nm. Black and red solid lines are experimentally measured angular reflectivity curves for Toluene and Chlorobenzene, respectively. Dotted lines are modeling from the TMM approach.

4.6 Summary

One- and two-layer structures based on the Kretschmann geometry have been studied experimentally and theoretically. The results have demonstrated the effect of film variation on the order of nanometer length scale can be easily recognizable thanks to surface nature of surface plasmon polaritons supported in the multi-layer structures. With the help of hetero-material fabrication techniques we have produced precisely controlled metallo-organic multi-layer structures from which a number of the features of SPP excitation and propagation have been explored.

The overriding conclusions are that we can evaluate material properties of metals and their geometrical information such as thickness by investigating angular reflectivity curves for the multi-layer structures. Our modeling techniques and material parameters all appear to be working very well and very good agreement with a number of the SPP features are found. Two main theoretical approaches have been applied, that is modal analysis and TMM approach and we have shown how they can explain plasmonic propagation properties and what information can be extracted. The broad insight accrued from the present chapter will be fully utilized throughout the rest thesis as we turn towards

plasmonic energy transfer (chapter 5) and plasmonic gain (chapter 6).

References

- [1] D. Y. Lei, J. Li, and H. C. Ong, "Tunable surface plasmon mediated emission from semiconductors by using metal alloys," *Appl. Phys. Lett.* **91**, 021112 (2007).
- [2] T. Davis, "Surface plasmon modes in multi-layer thin-films," *Opt. Commun.* **282**, 135-140 (2008).
- [3] Z. Shi, G. Piredda, A. C. Liapis, M. a Nelson, L. Novotny, and R. W. Boyd, "Surface-plasmon polaritons on metal-dielectric nanocomposite films," *Opt. lett.* **34**, 3535-7 (2009).
- [4] R. Zia, M. D. Selker, P. B. Catrysse, and M. L. Brongersma, "Geometries and materials for subwavelength surface plasmon modes," *J. Opt. Soc. Am. A*, **21**, 2442-6 (2004).
- [5] C.-I. Lin and T. K. Gaylord, "Loss measurement of plasmonic modes in planar metal-insulator-metal waveguides by an attenuated total reflection method," *Opt. lett.* **35**, 3814-6 (2010).
- [6] W. P. Chen and J. M. Chen, "Use of surface plasma waves for determination of the thickness and optical constants of thin metallic films," *J. Opt. Soc. Am.* **71**, 189 (1981).
- [7] K. Neyts, "Microcavity effects and the outcoupling of light in displays and lighting applications based on thin emitting films," *Appl. Surf. Sci.* **244**, 517-523 (2005).
- [8] P. A. Hobson, J. A. E. Wasey, I. Sage, and W. L. Barnes, "The role of surface plasmons in organic light-emitting diodes," *IEEE J Sel. Top. Quant.* **8**, 378-386 (2002).
- [9] D. E. Chang, A. S. Sørensen, E. A. Demler, and M. D. Lukin, "A single-photon transistor using nanoscale surface plasmons," *Nature Phys.* **3**, 807-812 (2007).
- [10] M. Celebrano, R. Lettow, P. Kukura, M. Agio, A. Renn, S. Götzinger, and V. Sandoghdar, "Efficient coupling of single photons to single plasmons," *Opt. Express* **18**,

13829-35 (2010).

- [11] R. Sennett and G. D. Scott, "The structure of evaporated metal films and their optical properties," *J. Opt. Soc. Am. A* **40**, 203 (1950).
- [12] M. Vacha and S. Habuchi, "Conformation and physics of polymer chains: a single-molecule perspective," *NPG Asia Materials* **2**, 134-142 (2010).
- [13] P. Müller-Buschbaum, J. S. Gutmann, M. Wolkenhauer, J. Kraus, M. Stamm, D. Smilgies, and W. Petry, "Solvent-induced surface morphology of thin polymer films," *Macromolecules* **34**, 1369-1375 (2001).
- [14] C. L. Donley, J. Zaumseil, J. W. Andreasen, M. M. Nielsen, H. Sirringhaus, R. Friend, and Ji-Seon Kim, "Effects of packing structure on the optoelectronic and charge transport properties in poly(9,9-di-n-octylfluorene-alt-benzothiadiazole)," *J. Am. Chem. Soc.* **127**, 12890-12899 (2005).
- [15] S. E. Shaheen, C. J. Brabec, N. S. Sariciftci, F. Padinger, T. Fromherz, and J. C. Hummelen, "2.5% Efficient Organic Plastic Solar Cells," *Appl. Phys. Lett.* **78**, 841 (2001).

5 Dipole Energy Transfer to Multi-layer Structures

5.1 Introduction

Energy transfer through dipole excitation is a basic mechanism to create light-guided modes in photonic structures including conventional waveguides and plasmonic waveguides, see e.g. [1-3]. Excited dipoles with a wide momentum spectrum can transfer their energy to the various (energy) channels supported by a structure. For instance, an oscillating dipole near metal contacts excites surface plasmon polariton modes as well as electron-hole excitation. Such energy transfer channels can be controlled through the geometry of the structure, promoting or suppressing energy transfer into a particular decay channel to, for example, increase out-coupling efficiency in light-emitting devices [4-6]. This approach has been well utilized in many kinds of optoelectronic device, e.g., light-emitting diodes [7,8] and photovoltaics [9]. Understanding the role of the energy transfer in active metallic structures is of great importance not only for optimizing conventional devices, but also for the development of new nanophotonic applications such as superlenses [10,11] and nanoplasmonic lasers [12].

In the first part of this chapter we will be interested in one such channel which may be described as a surface plasmon-mediated emissive channel. The emission of light through thin metal films is of great interest from a variety of applied perspectives, including organic light-emitting diodes, solar cells and fluorescence biosensors using surface plasmon polaritons [7-9,13]. Energy from the active medium can be manipulated and routed via the energy transfer between the excitons and surface plasmon polaritons, and optical properties of the devices to fit a desired application. In this respect investigating surface plasmon coupled fluorescence (SPCE) using the Kretschmann configuration serves to understand not only the energy transfer mechanism, but also demonstrate the unique optical properties of SPPs, e.g. polarization-selected emission and highly directional emission.

In the second part of the chapter, our interest turns towards the photonic mode generation in one-dimensional polymeric waveguide structures through the stimulated emission process, namely ‘amplified spontaneous emission’ (ASE). This work will first establish the credentials of conjugated polymers as excellent waveguide materials capable of supporting optical gain. Along with the SPCE, the ASE properties available form

polymer films will be both be utilized in the following chapter when we consider plasmonic gain environments.

5.2 Surface Plasmon Coupled Emission (SPCE)

Surface plasmon mediated emission through a thin metal film has been well known as a unique plasmonic energy transfer phenomenon [14-17]. This effect originates from strong near-field interactions between the oscillating dipole and the plasmonic media. Surface plasmon coupled emission (SPCE) has been studied using the prism-based Kretschmann configuration. The SPP fields excited by the near-field interaction are decoupled to the photon continuum via a prism. SPCE has been demonstrated using various metals including aluminum, gold, silver, and platinum [18-24], in combination with several active materials, for instance, dye molecules [22-24], inorganic quantum dots [25], chemiluminescent molecules [26], biomaterials [27], and photo-switching materials [28]. Also the effect of the specific multilayer geometry has been found to be crucial in determining the efficiency of SPCE [21-23].

There has been a growing interest in the use of organic materials as active media in the context of organic photonics, due to advantages of cost effectiveness, and excellent optical properties [29-31]. By adopting a concept of combining the organic polymer and nanoplasmonic systems, the possibility of a new optical plasmonic source has been suggested [32]. In the first part of this chapter we report on a study of surface plasmon coupled emission using optically excited fluorescent organic polymer films by means of de-coupling via a prism. The polymer used is Lumogen Red conjugated copolymer (from the previous chapter), showing a broadband red emission. Taking into account this broadband emission, we study the optimization of SPCE via a comparison of experimental results and theoretical modeling for various multilayer configurations. Our results point to the possibility of using conjugated polymers as active materials in plasmonic nanodevices.

5.2.1 Energy Transfer to Surface Plasmon Polaritons

Bound electron-hole pairs (excitons) in an active medium are generated by optical or electrical pumping and their energy can be transferred to collective electron oscillations at the metal/dielectric interface through resonant coupled transitions. In the first step, we present a theoretical description of SPCE in terms of dipole energy dissipation using Ford and Weber's model [1] (Appendix A). Figure 5.1 shows the calculated dissipated power

density spectrum of a dipole parallel and perpendicular to a Lumogen Red polymer film / Ag / BK7 prism multilayer system, depicted in the inset, for a free-space emission wavelength of 675 nm, which resides within the Lumogen Red polymer film emission bandwidth. In this particular configuration, the thickness of the polymer film is 40 nm, and of the Ag film 50 nm. Such a power dissipation spectrum, plotted against the normalized in-plane wavevector with respect to *in vacuo*, k_0 , allows identification of the various energy transfer channels of the systems, including SPPs [2]

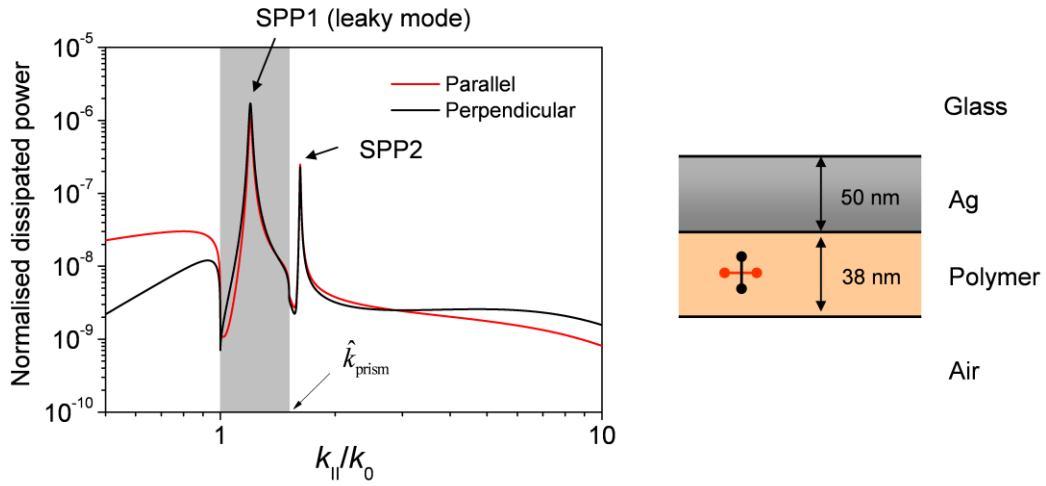


Figure 5.1 Normalized dissipated power density spectrum of a point dipole located in the middle of a Lumogen Red (38 nm) film atop a silver (50 nm) coated BK7 prism (c.f. schematic on right). The dissipated power is plotted as a function of the normalized in-plane momentum at 675 nm (c.f. Figure 5.2 for Lumogen Red emission spectrum). The black curve and red curve correspond to perpendicular and parallel dipole orientation (c.f. schematic), respectively. The peak (indicated as SPP1) in the grey colored region in momentum space corresponds to surface plasmon polaritons excited at the silver/polymer interface, which can be coupled to the prism. The higher-momentum peak (SPP2) corresponds to SPPs at the silver/prism interface, which are dissipated as heat. k_0 is light momentum in vacuum. The dissipated power density spectrum was obtained using a silver electric permittivity $\epsilon_{\text{Ag}} = -20.5 + 0.8i$ and a Lumogen Red polymer refractive index of 1.86.

Two distinct peaks in the region where the normalized in-plane momentum exceeds 1, correspond to SPP modes. Of the two SPP modes, only the SPP mode in the gray window, which is a leaky mode located at the silver/polymer interface, can be coupled through the thin metal film to a propagating field, since the momentum of the SPP is less than the momentum of photons propagating through the prism $\hat{k}_{\text{prism}} (= k_{\text{prism}}/k_0)$. This process is

known as SPCE, and results from a competition between the SPP field generation and the coupling process, with a strong dependence on geometrical parameters, such as metal film thickness [21].

5.2.2 Setup

The experimental set-up used to measure the angle-dependent emission properties from a prism-based structure is shown in Fig. 2(a). The layer structure was fabricated directly onto a BK7 prism. Each sample comprised a thin silver layer that was thermally evaporated directly onto the BK7 prism. The light-emitting polymer material was then spin-coated onto the silver layer to a thickness of nominally 38 nm for all structures studied. All fabrication stages were carried out inside a glove-box under a nitrogen atmosphere (actively purged of oxygen and water) with additional structures, on flat BK7 substrates, fabricated at the same time to confirm thicknesses. To record the angular radiation profiles from the structures, a rotating detection unit was used to collect emission from both the prism side ($0^\circ\sim 90^\circ$) and the air-side ($90^\circ\sim 180^\circ$); the prism being fixed at the axis of rotation. At the heart of the detection unit lay either a silicon photodiode or a fibre-coupled spectrometer, selected according to the nature of the measurement. A set of additional elements were also positioned in the rotation unit and comprised a polarizer and a long-pass filter to block any direct radiation from the pump beam and a 10 nm band-pass filter centered around the peak of the polymer emission. The polymer film was excited, at normal incidence from the air-side, by a solid-state laser diode operating at 532 nm. Standard lock-in techniques were used to improve the signal to noise ratio in the measurement, with the signals driving the (modulated) pump laser and those from the corresponding modulated fluorescence both fed into a lock-in amplifier.

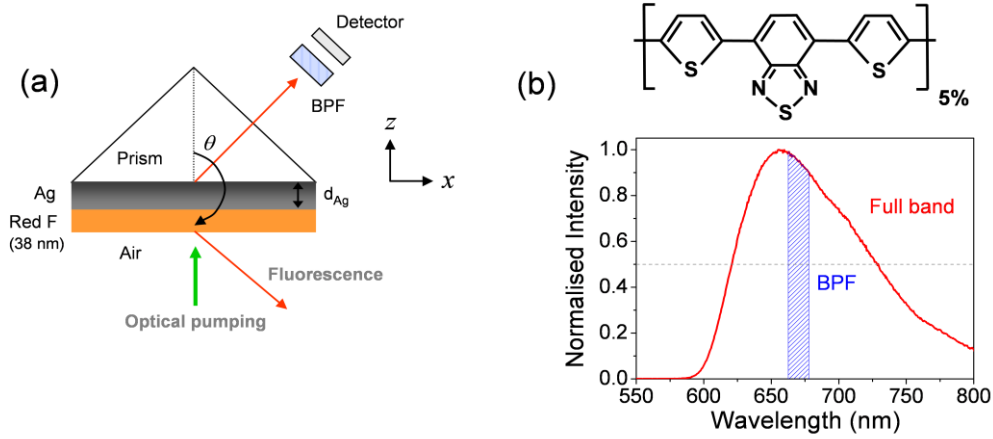


Figure 5.2 (a) Schematic of the prism structure and configuration for obtaining the angular distribution of the fluorescence from the polymer (Lumogen Red) layer. (b) Normalised fluorescence spectrum of the Lumogen Red polymer (red line) formed on a plain glass substrate. The spectral width of the bandpass filter is marked by the blue hatching and labeled BPF. The chemical structure of the thiophene-benzothiadiazole-thiophene red-emitting chromophore unit of Lumogen Red - present at a 5% fraction in the polymer - is also shown above the spectral data.

5.2.3 Modeling of Angular Emission Distribution

Numerous approaches for describing the angular distribution of emission in multi-layer structures have been proposed and employed over the years, see e.g. [33-35]. We implemented a technique, successfully used for previous SPCE investigations by Luan et al [22], based on the Lorentz reciprocity theory [33] (Appendix B). The basic approach assumes that the normalized angular emission distribution, from a dipole within a multi-layer, can be calculated from the incoming fields E_{in} , propagating from infinity and experiencing interference within the multiple layers. For each polarization, the resultant field at the dipole position, $E_{\perp,\parallel}(z_0)$, may be found and a normalized emitted power distribution may be obtained, as follows,

$$P_{\perp,\parallel}(\theta) \propto \left| \frac{E_{\perp,\parallel}(z_0)}{E_{in}} \right|^2 \quad (5.1)$$

The subscripts stand for the dipole orientation, perpendicular and parallel to the interface, respectively. Since a realistic emitter has a finite emission bandwidth the effects of spectral bandwidth on the overall emission distribution need to be considered. In view of this we

describe an overall power distribution as comprising all spectral components within a specified bandwidth, i.e.

$$P_{\Delta\lambda}(\theta) = \sum_{\Delta\lambda} \alpha(\lambda) \cdot R_{PD} \cdot P(\lambda, \theta) \quad (5.2)$$

where $P(\lambda, \theta)$ is a calculated angular emission distribution at a specific λ , $\alpha(\lambda)$ is a weighting factor reflecting a normalized fluorescence spectrum of a molecule, and R_{PD} is the responsivity of the detector that may also be wavelength dependent. Radiation patterns of a dipole are analyzed for transverse magnetic (TM) and transverse electric (TE) polarization, where TM polarized light is defined by its electric field being parallel to the propagation plane (x-z plane as depicted in Figure 5.2 (a)). In the case of a dipole oriented parallel to the interface, both TM and TE polarized radiation can be excited.

In Figure 5.3 we show the calculated angular radiation distributions for both TE- and TM-polarizations along with the calculated angular reflectivity curve for a structure comprising a 40 nm silver film and 40 nm layer of polymer material; the calculations shown here are only for a single wavelength (675 nm). These spectra exemplify the emission properties we have access to in the later experimental studies and highlight the rather unique characteristics the SPCE process yields; Strongly polarized and directed emission is clearly seen for observation from the prism side, matched in angle to the characteristic reflectivity response associated with excitation of a SPP. At each polarization, angular radiation distribution is governed by energy allocation of a dipole to SPP and outcoupling to air, determined by photon mode density in the given layer structure.

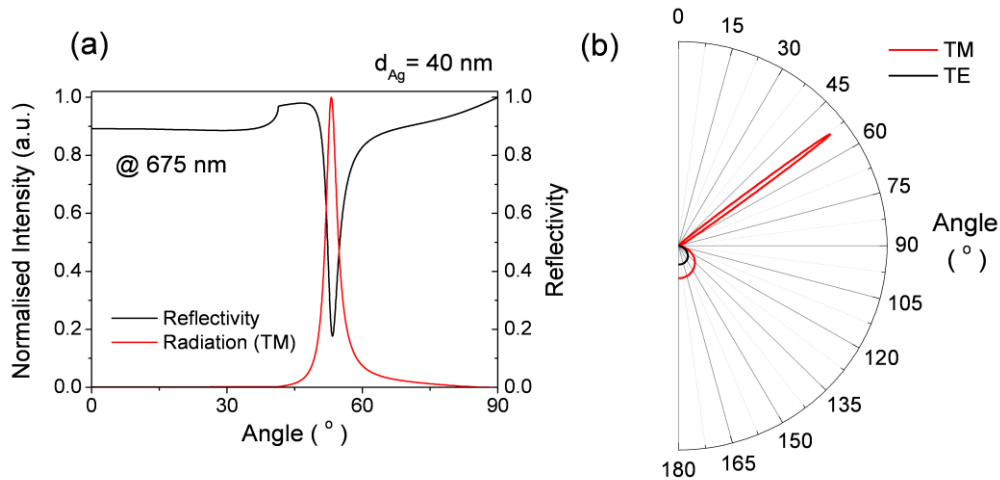


Figure 5.3 (a) Calculated TM-polarized angular reflectivity curve and the TM-polarised angular radiation patterns for a wavelength of 675 nm. The structure comprises a 40 nm thick silver film in the geometry depicted in Fig. 2. (b) The radiation profiles for both TE-

and TM-polarized emission from the structure, displayed in a polar diagram. Both the reflectivity curve and radiation curves were calculated using a silver electric permittivity $\epsilon_{Ag} = -20.5 + 0.8i$ and a Lumogen Red polymer index of 1.86.

5.2.4 Directional Emission

The expected angular radiation profile, shown in Figure 5.3, clearly illustrates the unique angular emission properties characteristic of SPCE phenomena, particularly the directed TM-polarised emission exiting the prism side of the structure. Our experimental results, collecting the radiation over the full spectral range of Lumogen Red emission with a Si-photodiode, are shown in Figure 5.4 and found to be entirely consistent with the expectations of SPCE. Specifically both Figures 4(a) and 4(b) show virtually complete suppression of any TE-polarised emission from the prism side, in contrast to the TM-polarised emission that clearly shows the increased out-coupling due to SPPs supported within each structure. From the air side (i.e. 90° to 180°) both TE- and TM-components are present and broadly follow a Lambertian (i.e. radially uniform) distribution. In Figure 5.4(d) the data for the 53 nm Ag film is displayed in a polar diagram and perhaps more visually confirms the unique angular emission profile arising from SPCE. As with earlier studies [14,18-24], the results present a clear example of SPP-mediated energy-transfer from an active source (polymer film) and effectively *through* a metal film to an overlying higher index medium. One can speculate, as others have commented [21-23], that such directed and polarized emission may find use in several applications, not least as a basic out-coupling arrangement. In view of this it is useful to question how efficient the out-coupling process is, and how it depends on (say) the metal thickness? To address this, one option is to simply find the ratio of emission component in the prism side compared to the total emission into both the prism and air (r_{prism}); this quantity has been recorded for a series of structures where the silver film thickness has been varied from 30 - 75 nm and the results are shown in Figure 5.4(c). We find for silver film thicknesses up to 45 nm, at least half the emitted radiation is coupled into the prism side, this fraction declines somewhat as the silver thickness increases above 45 nm. These observations are well described by the method outlined in the previous section and represented here by the solid curve in Figure 5.4(c). Indeed the trend of r_{prism} with silver film thickness closely follows the shape of the integrated power into the prism suggesting that the total emission, i.e. prism and air, is largely constant and the decline in power into the prism for increasing silver thickness is somewhat matched by an attendant increase of power emitted to the air side. The reduced

SPCE with silver thickness may also be understood from the observations of coupling *to* SPPs using conventional prism-coupling techniques (see e.g. [Ch1.1]) where coupling to the SPP from the prism side reduces with increasing metal thickness; in the case of SPCE we are operating in reverse i.e. coupling to the prism *from* the SPP.

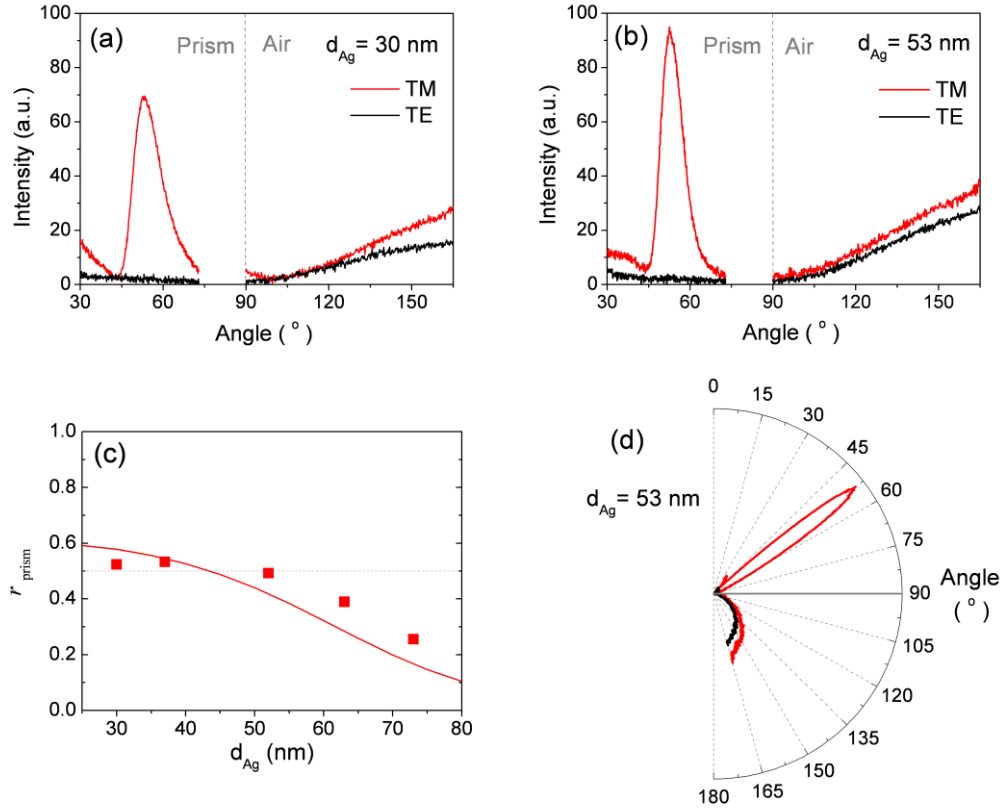


Figure 5.4 Measured angular emission profiles for both TE- and TM-polarized emission for (a) 30 nm and (b) 53 nm thick silver films; the out-coupling angle range of 30° to 90° and 90° to 165° corresponds to prism and air-side, respectively. (c) The fraction of integrated intensity emitted to the prism side r_{prism} as a function of silver thickness. Filled squares are experimental data and line is calculated. (d) The experimental angular spectra data from (b) replotted on a polar diagram.

5.2.5 Spectral Properties: SPP Dispersion

Our structures in Figure 5.2(a) are based around planar layers and as such support a continuous band of SPP modes that spans the bandwidth of the polymer emission. The results presented in Figure 5.4, carried out using a Si-photodiode, thus record an integrated SPCE process that comprises a series of different SPP contributions spectrally weighted by the underlying intensity of the polymer emission. Replacing the Si-photodiode with a fibre-fed spectrograph and charge coupled device (CCD) spectrometer, enables us to record *spectrally* resolved angular radiation and thereby reveal the underlying individual spectral contributions (Figure 5.5). In essence, using the broad emission from the polymer as a local source we may probe the SPP dispersion that is chiefly responsible for the SPCE (Figure 5.6). Data were recorded for a number of structures with different silver thicknesses. A typical set of spectra, for $d_{Ag} = 63$ nm, are displayed in Figure 5.5. The peak response observed in each spectrum indicates the optimum coupling wavelength (momentum) for SPCE at each selected collection angle. Superimposing the spectra taken for the different observation angles, the envelope of the peak responses is seen to largely follow the underlying intensity distribution from the polymer emission (cf. Figure 5.2(b)).

The connection between the spectrally resolved profiles shown in Figure 5.5 and the underlying SPP modal structure may be further appreciated through mapping to the SPP dispersion diagram for the structure. As anticipated in the discussions around Figure 5.1, while two SPPs are supported and able to couple with the emitting dipoles in the polymer layer, only one responsible for the strongly polarized and directional emission is associated with the SPCE process, i.e. the leaky-mode appearing in the shaded region in Figure 5.1. Computing the dispersion diagram for both modes, i.e. the leaky- and bound-modes, [36,37] and transferring the wavelength at which the peak response occurs for each angular spectrum to this diagram, using the corresponding wave vector $k_x = (2\pi/\lambda_{pk}) \cdot \sqrt{\epsilon_0} \sin \theta$, it becomes immediately clear that the leaky-mode is responsible for SPCE (Figure 5.6). Overlaying the results on the dispersion curves also clearly shows why the peak of the spectral response occurs at shorter wavelengths for larger observation angles (c.f. Figure 5.5). A larger wavevector component (larger angle) is required to excite the higher energy (shorter wavelength) SPPs.

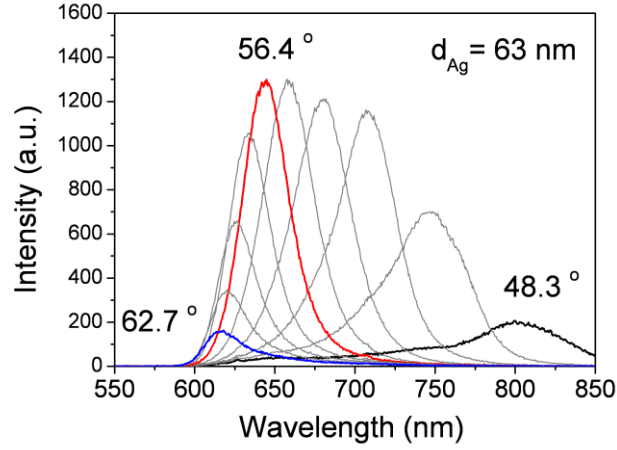


Figure 5.5 Measured emission spectra at different out-coupling angles in the range 48.3° (black solid line) to 62.7° (blue solid line) for $d_{\text{Ag}} = 63$ nm. The 56.4° spectrum is highlighted in red.

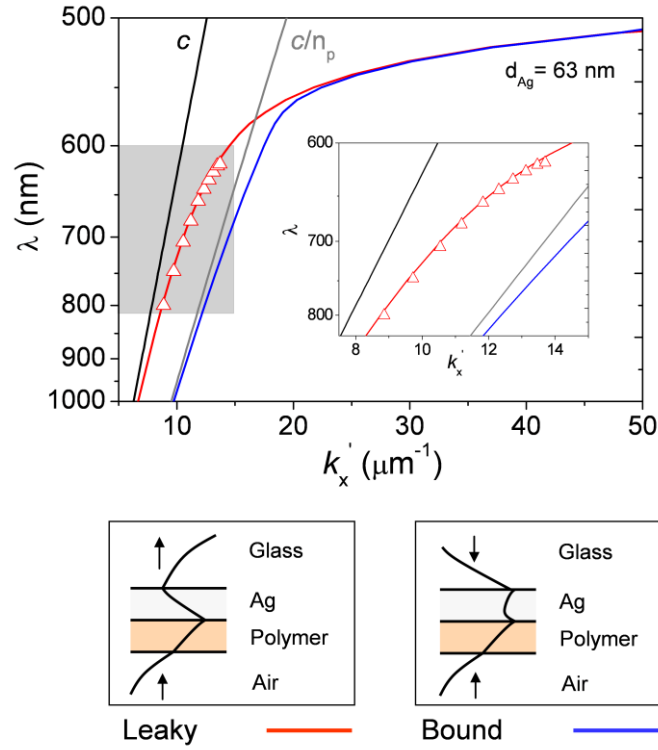


Figure 5.6 Wave vector (real part) dispersions for leaky (red line) and bound (blue) modes for $d_{\text{Ag}} = 63$ nm. Transfer matrix calculations (solid lines) are plotted together with experimental data (symbols). The light lines in vacuo (labeled c , black line) and in the prism (labeled c/n_0 , grey line) are also shown. The schematics in the lower half of the Figure show the transverse field patterns for the leaky and bound modes (the arrows indicate transverse energy flow).

5.2.6 Sensitivity to Emission Spectrum

We now examine in greater detail some of the properties of SPCE that may be useful for application. Particular attention is given to the spectral bandwidth of the local source and how this may influence the search for optimum performance using SPCE extraction. In Figure 5.7(a) we show the measured SPCE angular radiation profiles along with the reflectivity spectra recorded at 675 nm, for a structure containing a 37 nm thick silver film; the two radiation profiles shown are recorded in the absence (red trace) and presence (blue trace) of a 10 nm bandpass filter in front of the detector. As expected from the earlier results in Figures 5.5 and 5.6, there is a broader angular profile when the emission is unfiltered. This arises because more leaky-mode SPPs contribute to the SPCE signal if a larger range of wavelengths (wave vectors) is collected. In this respect filtering the output using a bandpass filter also mimics the performance that would be expected from an emissive layer with a narrower spectral content. The directional quality of the SPCE emission, i.e. the FWHM in degrees, is therefore firmly linked to the spectral content of the active layer. Another contributing factor, albeit to a lesser extent, is the thickness of the silver film. Figure 5.7(b) tracks the FWHM ($^{\circ}$) of the angular emission profile as a function of the silver film thickness. Regardless of the spectral content, structures with thinner silver films tend to exhibit broader angular emission profiles. This observation appears consistent with the trend found in conventional SPP prism-coupling studies where the resonance width of reflectivity spectra appears broader for thinner films, behaviour often rationalised in terms of a greater radiation loss, see e.g. [Ch1.1].

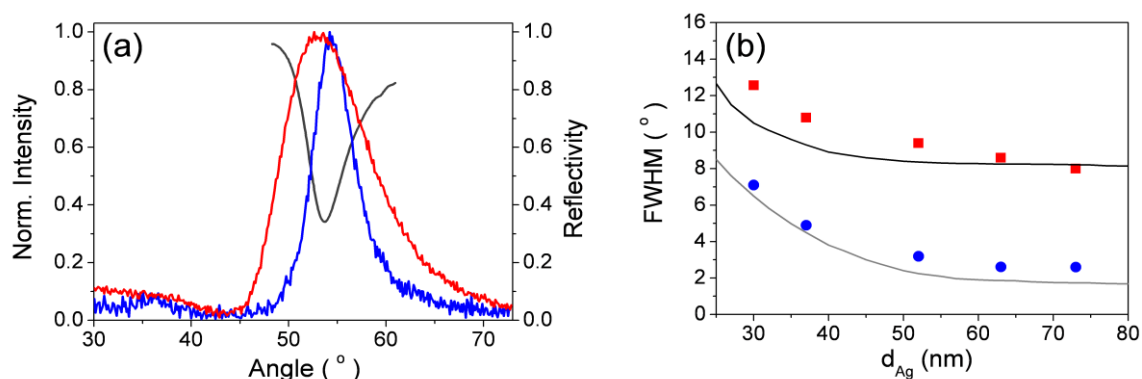


Figure 5.7 (a) Experimental angular reflectivity (black dashed line, 675 nm light) and prism side radiation profiles (red and blue lines) for a 37 nm thick silver film. The red and blue lines are angular radiation distributions for the unfiltered Lumogen Red fluorescence spectrum and for the 10 nm band-pass filtered emission as shown in Figure 5.2(b). (b) Angular full-width half-maximum values as a function of silver film thickness. The red square and blue circle data points are experimental data in the absence and presence, respectively, of the band-pass filter. The black and gray solid lines are corresponding results from modeling.

As a potentially useful out-coupling element it is instructive to examine the dependence of the SPCE peak emission intensity on silver film thickness, again particularly from the point of view of the spectral content of the polymer emission. Figure 5.8 shows this dependence, normalized to the maximum measured intensity. With the 10 nm bandpass filter in place, the SPCE has maximum intensity at around 50 nm silver thickness, a value that is close to that required to maximally couple incident radiation to SPPs in conventional prism-coupling experiments [Ch1.1]. When, however, the full (unfiltered) polymer spectral bandwidth is considered, the maximum peak intensity now appears for a slightly thinner silver thickness (~ 40 nm). In both cases, away from the optimized thickness, intensity drops, reflecting less efficient SPP coupling. This again mirrors the situation for the reflectivity minimum observed in SPP prism coupling. Modeling (solid lines in Figure 5.8) faithfully reproduces the experimental observations.

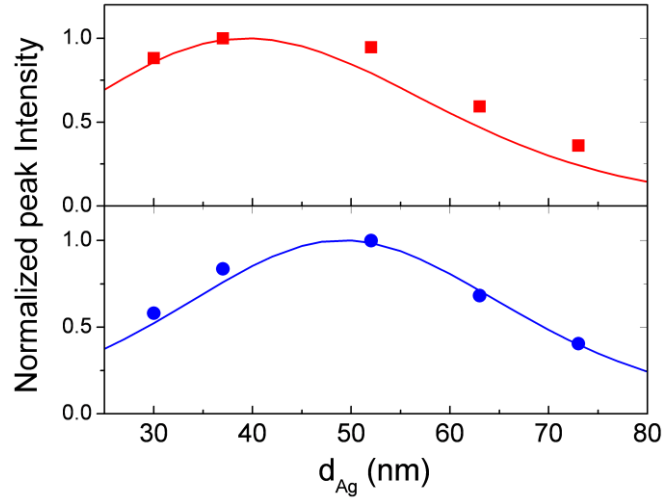


Figure 5.8 Silver film thickness dependence of the prism side emission peak intensity. The two cases shown are without (upper plot, red square data) and with (lower plot, blue circle data) 10 nm band-pass filtering. The solid lines are the calculated dependences.

5.3 Excitation of Photonic Guided Modes

Leaving behind the SPCE studies, we now turn to the characteristics of guided light from photonic modes excited in conventional waveguide structures. Planar slab waveguides can of course support the photonic modes of TE or TM polarization, even in the simplest structure where a single polymeric film (Lumogen Red conjugated polymer herein) on glass substrate can act as a guiding layer as seen in the Figure 5.9. In order to identify where dipole energy flows in such a structure and check how the energy couples to the photonic modes, the related power dissipation spectrum is presented, representing the density of photon states in a given optical structure.

A dipole oscillating at the wavelength of 675 nm is assumed to reside in the middle of the polymer film. In the Figure, the gray and yellow colour-regions represent out-coupling of photons to air and the substrate, respectively and, two sharp peaks possessing larger in-plane momentum than in the substrate indicate the photonic mode excitation of TE and TM modes. In case of parallel orientation of a dipole, TE mode is more dominant. It can also be noted that the in-momentum of the photonic modes is lower than the momentum in the bulk polymer (i.e. $1.86k_0$) indicated by the dotted line. Excited dipoles located throughout a film area emit photons spontaneously into any of the channels (i.e. air, substrate, photonic modes etc. shown) and with the help of one-dimensional guiding structure, stimulated emission along the waveguide direction can be favourably induced.

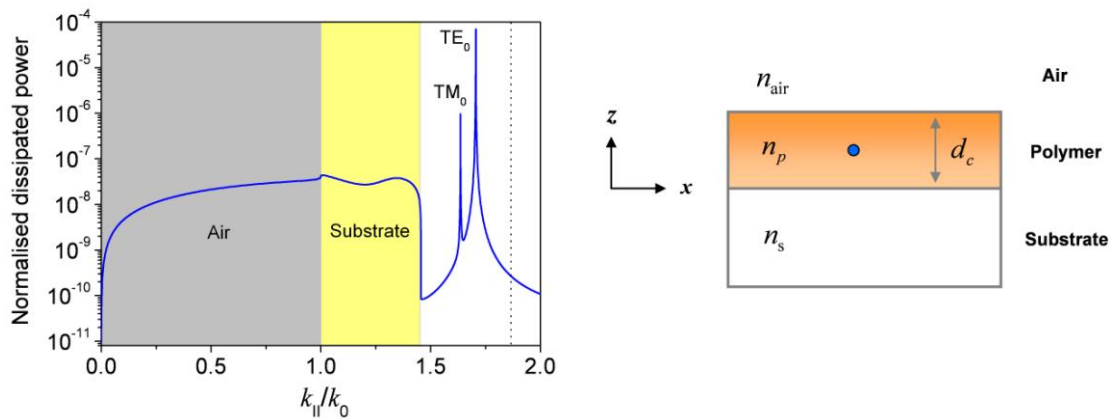


Figure 5.9 The corresponding dissipated power density spectrum of a dipole located in the middle of the Lumogen Red film (280 nm) on Spec B substrate in a function of the normalized in-plane momentum. For the calculation, a point dipole was assumed to oscillate parallel to the layer interfaces. k_0 is light momentum in vacuum. The dotted line indicates the refractive index of the core layer made of Lumogen Red co-polymer. The right plot shows the planar asymmetric waveguide structure understudy.

5.3.1 Photonic Modes in Asymmetric Slab Waveguides

As explained previously, the planar asymmetric slab waveguides can support both TE and TM polarization modes. Before examining active functions of the structures, their passive functions in terms of propagation mode behaviours will be analyzed. Figure 5.10 shows the variation in effective index of propagation modes supported in the polymer films on glass substrate (Spectrosil B) with respect to film thickness d_c . One of important characteristics that photonic modes have is the existence of cut-off thicknesses below which there are no specific guided modes. From the Figure, for thicknesses less than 70 nm, none of the modes are supported, while for films with a thickness ranging from 70 nm to 350 nm support only the fundamental TE_0 and TM_0 modes. To demonstrate amplified spontaneous emission, a structure supporting only the fundamental modes is often preferred in an attempt to maximize the dipole energy distributed into the ASE propagation mode. For this reason our experimental structures used a 280 nm thick Lumogen Red film, supporting only the fundamental modes, its position is marked in the Figure. The calculated field distributions of TE_0 and TM_0 fundamental modes for the 280 nm thick Lumogen Red film are displayed in Figure 5.11.

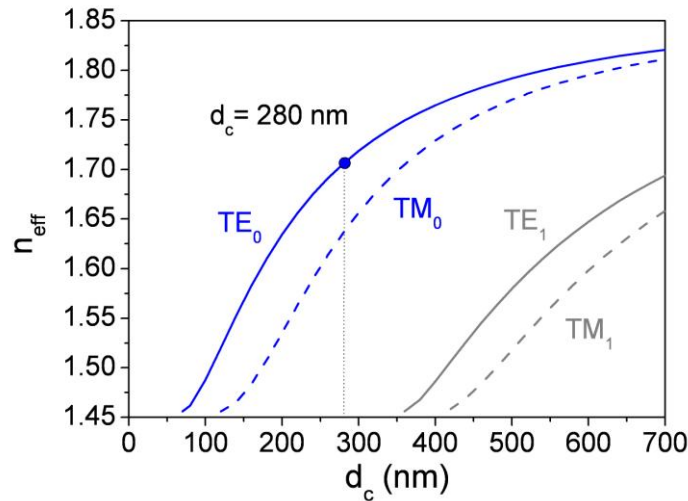


Figure 5.10 Effective index of propagation modes of TE and TM polarizations as a function of the polymer film thickness d_c , which can be excited in the asymmetric slab waveguide structure consisting of substrate (Spectrosil B glass), core layer (Lumogen Red polymer film) and cover layer (air): TE_0 and TM_0 is fundamental transverse modes, and TE_1 and TM_1 is first-order propagation modes.

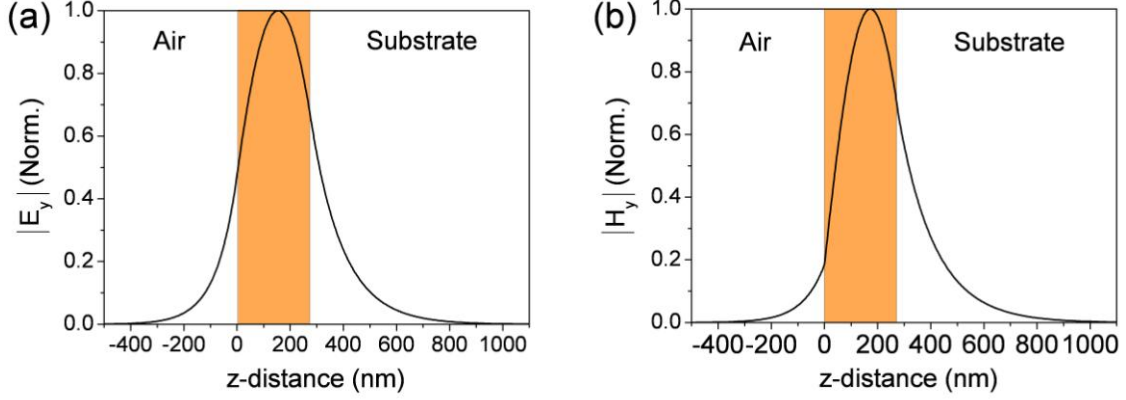


Figure 5.11 Field distributions of TE₀ and TM₀ fundamental mode in the case of polymer film with a thickness $d_c = 280\text{nm}$ at 675 nm wavelength (a) Normalized E_y field pattern of TE₀ fundamental mode (b) Normalized H_y field pattern of the TM₀ fundamental mode

The distributions shown in Figure 5.11 illustrate and are a helpful way to appreciate the factors behind maximizing optical gain in structures. To estimate optical gain in a specific guided mode we look at the power confinement factor, which indicates how much of the modal field overlaps with the active region. Here, we adopt the concept of the gain factors for TE and TM mode, which define the ratio of modal gain to material gain ($g_{\text{mod}} = \gamma g_{\text{mat}}$). Material gain is defined as optical gain in free active medium while modal gain is the propagation gain of an optical mode excited in light-guiding structures. The gain factors may be expressed by [38-40].

$$\gamma_{\text{TE}} = \frac{\int_i n_i \cdot |E_y|^2 dz}{n_{\text{eff}} \int_{-\infty}^{+\infty} |E_y|^2 dz} \quad \text{and} \quad \gamma_{\text{TM}} = \frac{n_{\text{eff}} \int_i n_i \cdot [|E_x|^2 + |E_z|^2] dz}{\int_{-\infty}^{+\infty} n_i^2 |E_z|^2 dz} \quad (5.3)$$

where n_i is the refractive index of the active layer indexed to i and n_{eff} is an effective index of the propagation mode. In a normal weak-guiding waveguide structure where the index difference of core and clad materials is rather small ($\Delta n < 10^{-2}$) and E_x field amplitude is negligible to E_z , the gain factors become approximated to the confinement factors [39] as given by

$$\Gamma_{\text{TE}} = \frac{\int_i |E_y|^2 dz}{\int_{-\infty}^{+\infty} |E_y|^2 dz} \quad \text{and} \quad \Gamma_{\text{TM}} = \frac{\int_i |E_z|^2 dz}{\int_{-\infty}^{+\infty} |E_z|^2 dz} \quad (5.4)$$

Note that under a weak guiding approximation we would have $n_p \approx n_{\text{eff}}$, $\gamma_{\text{TE,TM}} \approx \Gamma_{\text{TE,TM}}$. However, both polymeric waveguides and especially plasmonic structures tend to show

strong guiding properties. To compare the relationship between the gain factors in Eqn. (5.3) and the confinement factors in Eqn. (5.4), values for TE and TM fundamental modes are plotted in Figure 5.12. For the dominant TE mode, the gain factor is around 10% higher than the confinement factor with the gain factor for a 280 nm thick Lumogen Red films estimated to be 93%. Thus the potential gain the TE ASE mode experiences is close to material gain of the polymer material. This concept of identifying gain factors based around field distributions will be useful for the planar active plasmonic structures studied in the following chapter.

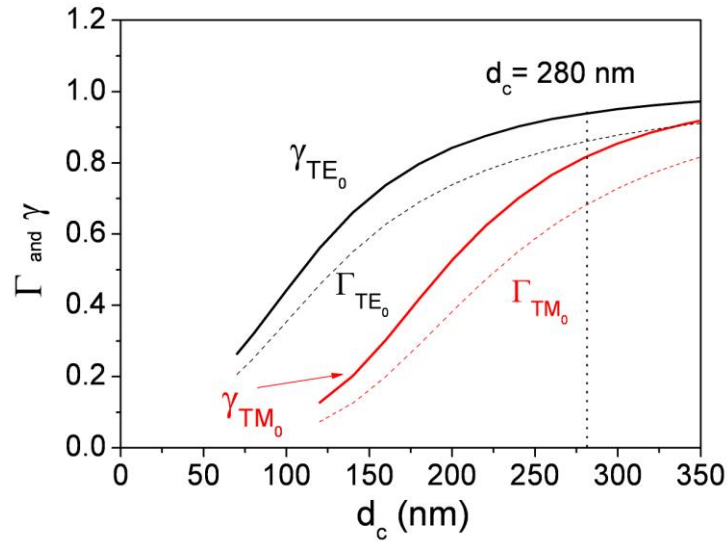


Figure 5.12 Gain factors of TE₀ and TM₀ modes as a function of the polymer film thickness d_c . For $d_c=280$ nm (the vertical dotted line), the gain factors of the TE₀ and TM₀ modes is 0.93 and 0.83, respectively. (The confinement factors for the TE₀ and TM₀ modes are 0.86 and 0.68, respectively).

5.3.2 Amplified Spontaneous Emission (ASE): Mirrorless Lasing

Amplified spontaneous emission (ASE) is a stimulated emission process in a way that spontaneous emitted photons are amplified [Ch2.21,31,41-43]. ASE can occur in waveguide structures even without any optical feedback and for that reason, it is often called ‘Mirrorless lasing’.

To study the ASE properties planar asymmetric waveguide samples were prepared comprising a Lumogen Red conjugated film formed on Spec B substrate. Despite the absence of any optical feedback, the asymmetric waveguides still act as an excellent spatial filter that is enough to lead to stimulated emission and, as we have shown, they also have relatively high optical gain/confinement factors. Figure 5.13 depicts the basic ASE measurement scheme. A pump beam passes through geometrical optics to spatially define an active gain-guided region with an area of $L \times W$ on the film surface. ASE light generated by the pump beam is collected at the edge of the film using a microscope objective lens then passed via a fibre to a CCD spectrometer. For that measurement, filtering photon polarization was not necessary. The reason is that conjugated polymers formed by spin-coating are known to be oriented mostly parallel to the substrate, thereby resulting in horizontal dipole orientation [Ch4.14] and in that condition mainly TE mode is a dominant waveguide mode as shown in Figure 5.9. And as an experimental factor, polarization of a pump beam does not affect fluorescence intensity because molecule chains are isotropically distributed on a surface. The resulting spectrum depends on a number of conditions such as stripe length or pump energy density, which may be analyzed using a ‘travelling-wave’ governing equation.

In the small signal regime, i.e. where the ASE signal output I_{ASE} is much smaller than saturation intensity I_s , the governing equation [44] may be expressed by

$$I_{ASE}(L) = \frac{\Omega}{g} (e^{gL} - 1) \quad (5.5)$$

where L is the stripe length, Ω is the spontaneous emission (SE) parameter that relies on mainly the population inversion density, g is the net modal gain, which is the gain coefficient γ minus the absorption coefficient α . Using experimental data and a fitting procedure equation (5.5) extracts the net modal gain from the sample. When the pump length is short or pump energy is fairly low, fluorescence dominates over ASE, i.e. $gL \ll 1$, and equation (5.5) may be approximated by

$$I_F(L) \approx \Omega L \quad (5.6)$$

Here, in the spontaneous emission dominance region, output intensity increases linearly with stripe length. At the threshold condition of L_{th} , the ASE output intensity becomes twice the fluorescence intensity since the photon flux of the fluorescence and ASE are equal allowing us to write [44],

$$I_{ASE}(L_{th}) = 2I_F(L_{th}) \quad (5.7)$$

Hence using equations (5.5-5.7) the net modal gain from planar structures can be extracted.

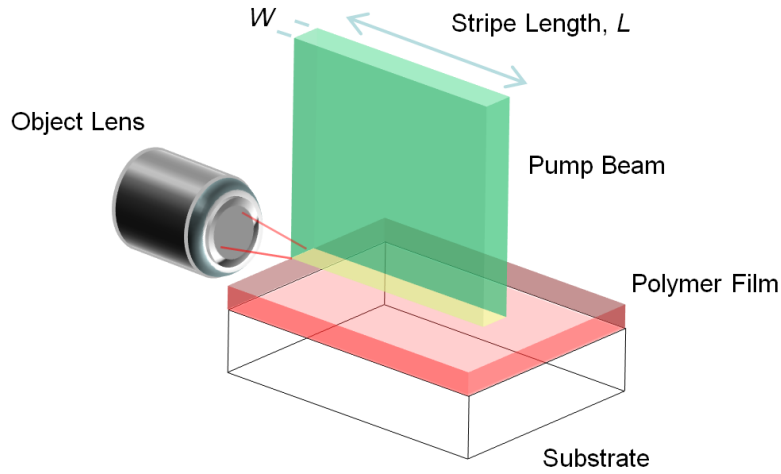


Figure 5.13 A Schematic showing the amplified spontaneous emission (ASE) measurement method for planar asymmetric slab waveguide structures. The stripe length L and pump energy density vary to investigate gain properties.

In the following section two common experimental approaches have been applied to study the ASE properties of Lumogen Red films: Variable pump intensity (VPI) method and Variable stripe length (VSL) method. Among the many parameters available it is primarily the pump intensity and pump stripe length that determine the ASE output. We use both these variables and apply both methods, as a self-consistent check, to identify and characterize ASE phenomena.

5.3.3 Variable Pump Intensity (VPI) Method

The variable pump intensity (VPI) measurement method examines ASE spectra I_{ASE} as a function of E_{pump} in a given pump beam stripe length. The 532 nm pump beam is from a pulsed source with a 10 ns duration and 20 Hz repetition rate. The beam stripe width was

fixed at 84 μm and the stripe length varied from 1 mm to 3 mm. Pump energy density dependence from the peak of the ASE spectrum were collected for stripe lengths of 1.0mm, 1.5mm, 2.0mm, 2.5mm, and 3.0mm and shown in Figure 5.14 (a). All the stripe lengths considered showed spectral output featuring ASE; for example the 3 mm stripe, the threshold energy density E_{th} at which ASE begin to arise can be easily identified from the rapid change in slope giving E_{th} around 130 $\mu\text{J}/\text{cm}^2$.

For energy densities less than E_{th} it is the fluorescence that dominates while above E_{th} two distinctive features of ASE behavior are seen, i.e. superlinear behavior of the peak intensity (Figure 5.14(a)) and spectral narrowing (Figure 5.14(b)). Output spectra obtained from four energy densities are shown in Figure 5.14(b). In Figure 5.15 we focus on the ASE evolution for 3 mm case in terms of the spectrum FWHM changes and the peak intensity. It is noticeable that FWHMs collapsed from 75 nm down to 14 nm around E_{th} .

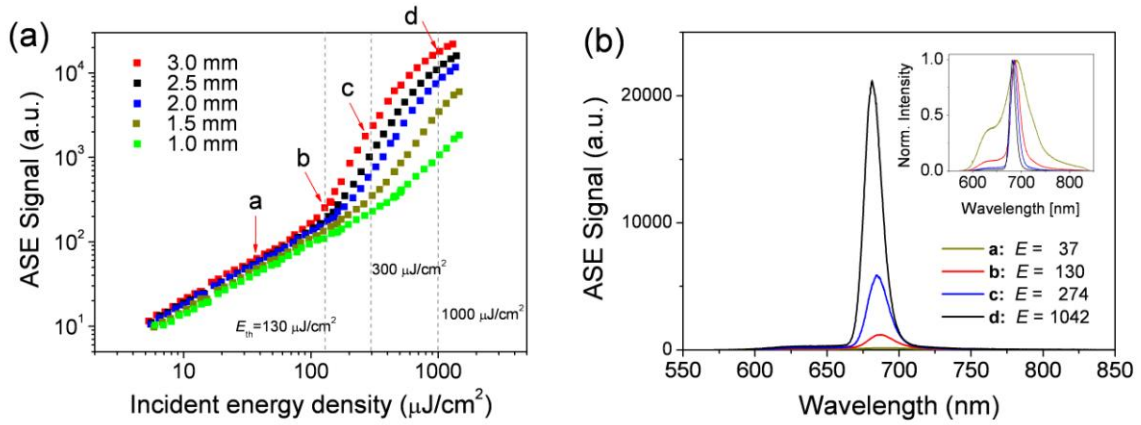


Figure 5.14 (a) ASE signal intensity as a function of pump incident energy density for the five stripe length cases of 1.0 mm, 1.5 mm, 2.0 mm, 2.5 mm, and 3.0 mm (b) ASE spectra at four incident energy densities (a, b, c and d) of the unit of $\mu\text{J}/\text{cm}^2$ from the 3 mm stripe length in Figure 5.7(a). Inset: Normalized spectra of the corresponding ASE signals are shown for visual clarity of the collapse of the FWHM.

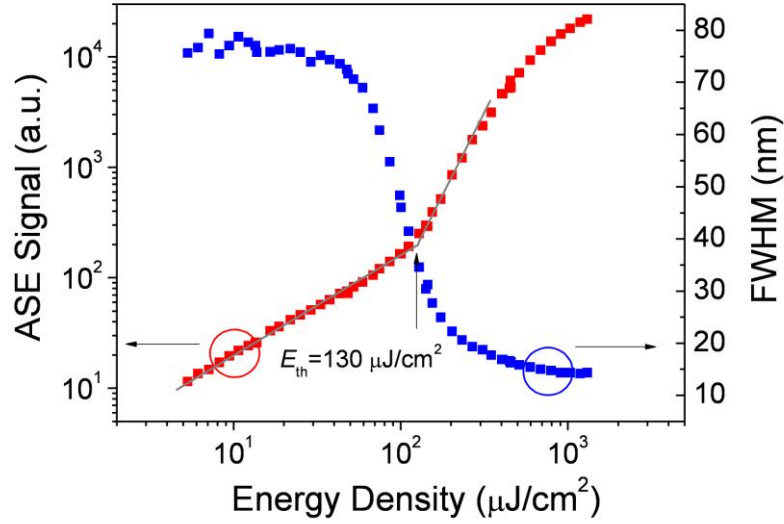


Figure 5.15 ASE signal intensity as a function of pump incident energy density and the corresponding full-width half-maximum (FWHM) of the spectra. Both measures can be used to identify the ASE threshold which is marked by $E_{th} = 130 \mu\text{J}/\text{cm}^2$.

In order to extract gain values from the ASE signal data in Figure 5.14(a), a set of data points are selected at particular pump energy densities and then the ASE signal data are re-plotted against the stripe length as shown in Figure 5.16(a). Two shaded areas, A and B for $E_{\text{pump}} = 300 \mu\text{J}/\text{cm}^2$ and $E_{\text{pump}} = 1000 \mu\text{J}/\text{cm}^2$ in Figure 5.16(a) are in the small-signal regime identified in VSL data analysis. Equation (5.5) governing the small-signal region was applied to fit the data in the shaded area and then gain values were extracted. At $E_{\text{pump}} = 1000 \mu\text{J}/\text{cm}^2$, with the two data point fitting giving around 22.4 cm^{-1} while the three data point fitting producing 17.1 cm^{-1} . Thus the net gain can be estimated to lie between 17.1 cm^{-1} and 22.4 cm^{-1} . Following a similar procedure, the net gain value for $E_{\text{pump}} = 300 \mu\text{J}/\text{cm}^2$ case is found to be 12.4 cm^{-1} , which as expected is smaller than that found for $E_{\text{pump}} = 1000 \mu\text{J}/\text{cm}^2$. While the gain values seem reasonable [31], the main advantage of the VPI method has been the clear evaluation of threshold energy density and the spectral behaviour. In the following section we will apply the VSL method that is shown to be more reliable method from which to extract the net gain values.

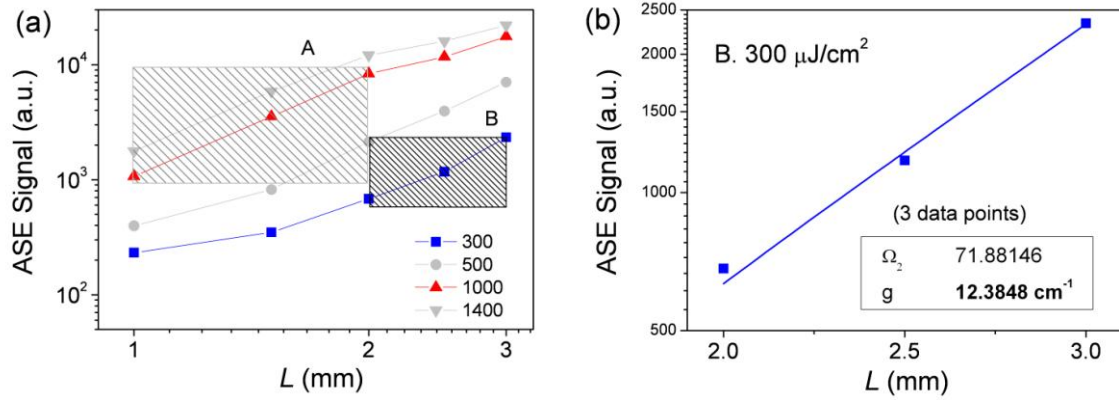


Figure 5.16 (a) ASE signal intensity dependence on the stripe length at four particular incident energy densities of the unit of $\mu\text{J}/\text{cm}^2$. Two shaded areas, A and B for $E_{\text{pump}} = 300 \mu\text{J}/\text{cm}^2$ and $E_{\text{pump}} = 1000 \mu\text{J}/\text{cm}^2$ cases are considered as the small signal length region (b) The selected ASE signal data for $E_{\text{pump}} = 300 \mu\text{J}/\text{cm}^2$ in the shaded area B from Figure 5.16(a) and the corresponding fitted line of equation (5.5).

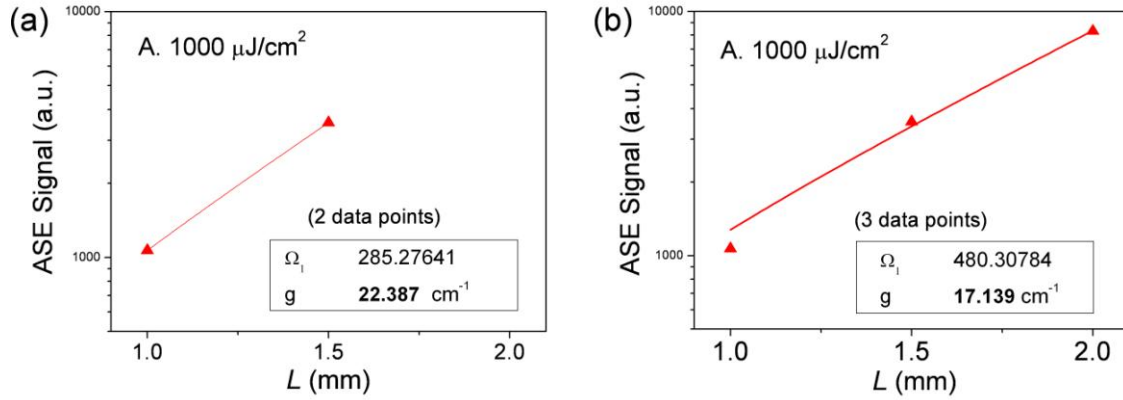


Figure 5.17 Extraction of photonic modal gain (a) The selected ASE signal data (two data points) for $E_{\text{pump}} = 1000 \mu\text{J}/\text{cm}^2$ in the shaded area A from Figure 5.16(a) and the corresponding fitted line of equation (5.5) (b) the selected ASE signal data (three data points) in the shaded area A for $E_{\text{pump}} = 1000 \mu\text{J}/\text{cm}^2$ from Figure 5.7(a) and the corresponding fitting line of equation (5.5).

5.3.4 Variable Stripe Length (VSL) Method

The variable stripe length (VSL) method has been used by many researchers to evaluate a number of active polymeric materials [31,44]. The VSL method produces ASE spectra I_{ASE} as a function of L for a given pump beam energy density (fluence). After collecting data using the VSL method, two analysis steps are executed to extract gain values. Linear fitting

of equation (5.6) into an initial length range of the full data set representing fluorescence dominance regime is performed in order to determine Ω values first, consequently giving rise to a threshold length L_{th} from the criterion of equation (5.7), and then equation (5.5) using the obtained Ω value is fitted into data at longer stripe lengths than L_{th} , which finally produces an optical gain value. Here, the ASE characteristics at two pump energy densities of $E_{pump} = 300 \mu\text{J}/\text{cm}^2$ and $1000 \mu\text{J}/\text{cm}^2$ were examined. Data fitting was carried out on consecutive data sets that included at least five data points among the small-signal length regime from 0.9 mm to 2.1 mm. The reason taking this strategy is to validate the fitting process to get more accurate gain values.

Table 5.1 lists the nine selected data sets used for $E_{pump} = 1000 \mu\text{J}/\text{cm}^2$ case with the peak intensity data is shown in Figure 5.18(a). The blue straight line drawn in Figure 5.18(a) is the linear plot whose gradient corresponds to Ω from fitting of equation (5.6) for the data set of 0.2~0.5 mm (3 data points) in the short stripe length range. In Figure 5.11(b), the extracted net gain $g(\Omega)$ and R-squared values for each data set are plotted. The shaded data set region in these Figures indicate when R-squared values are close to 1, indicating more reliable extracted gain values. The net gain value found using the pre-obtained $\Omega_1 (=15053)$ was $21.7 \pm 0.2 \text{ cm}^{-1}$.

Set	Length Range	Data points	$g [\text{cm}^{-1}]$	R^2
1	0.9~1.3 mm	5	20.90	0.920
2	1.0~1.4 mm	5	21.60	0.960
3	1.1~1.5 mm	5	21.90	0.986
4	1.2~1.6 mm	5	21.90	0.996
5	1.3~1.7 mm	5	21.80	0.994
6	1.4~1.8 mm	5	21.50	0.960
7	1.5~1.9 mm	5	21.00	0.900
8	1.6~2.0 mm	5	20.60	0.810
9	1.7~2.1 mm	5	20.00	0.640

Table 5.1 Selected data sets and calculated net gain values and R-squared values by using the fixed $\Omega_1 (=15053)$ value for $E_{pump} = 1000 \mu\text{J}/\text{cm}^2$ case.

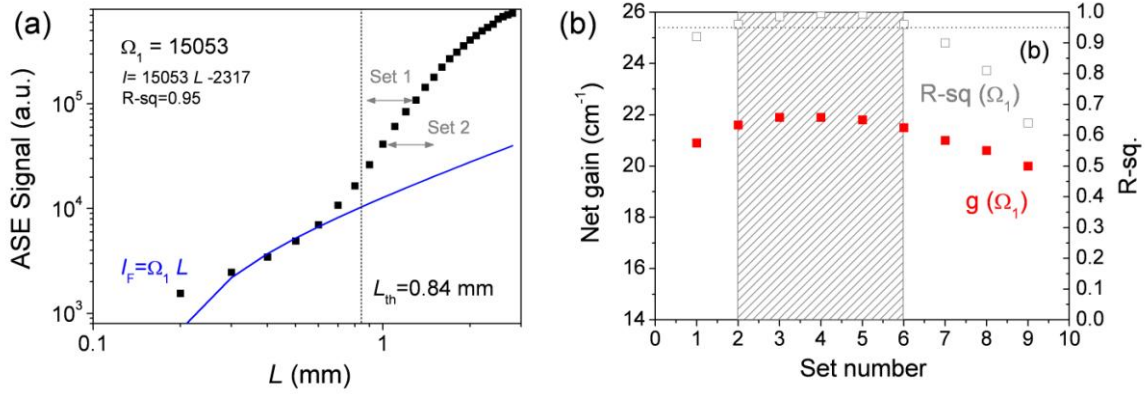


Figure 5.18 (a) Measured ASE signals in a function of the stripe length L at $E_{\text{pump}} = 1000 \mu\text{J}/\text{cm}^2$. Blue line: The linear fitting line for the data set of 0.2~0.5 mm (3 data points) to determine Ω_1 value. (b) Extracted gain values and R-squared values produced by fitting equation (5.4) into the selected data sets for the determined Ω_1 value. The shaded region from set 2 to 6 has R-sq values over 0.95.

A similar procedure was also attempted for ASE signal data corresponding to $E_{\text{pump}} = 300 \mu\text{J}/\text{cm}^2$ (Figure 5.12) and an extracted net gain value of $12.3 \pm 0.1 \text{ cm}^{-1}$ was found. The ratio of output intensities in the fluorescence regime at the two energy densities can be approximately expressed as the ratio of Ω values. The measured ratio was about $2.8 (= I_{1000}/I_{300} = \Omega_1/\Omega_2)$. The obtained ratios from the VPI method were 3.9 and 6.7 for two length and three length data point cases, respectively. Thus, it can be speculated that the two data point fitting case is more appropriate selection of a length range to estimate gain values. This cross-checking procedure adds further confidence to the reliability of the overall analysis.

Set	Length Range	Data points	$g [\text{cm}^{-1}]$	R^2
1	1.5~1.9 mm	5	11.6	0.948
2	1.6~2.0 mm	5	11.9	0.956
3	1.7~2.1 mm	5	12.2	0.952
4	1.8~2.2 mm	5	12.3	0.967
5	1.9~2.3 mm	5	12.4	0.978
6	2.0~2.4 mm	5	12.4	0.980
7	2.1~2.5 mm	5	12.4	0.984
8	2.2~2.6 mm	5	12.3	0.992
9	1.6~2.7 mm	12	12.2	0.992

Table 5.2 Selected data sets from the measured and corresponding net gain values and R-squared values by using fixed $\Omega_2=5356$ values for $E_{\text{pump}}=300 \mu\text{J}/\text{cm}^2$ case.

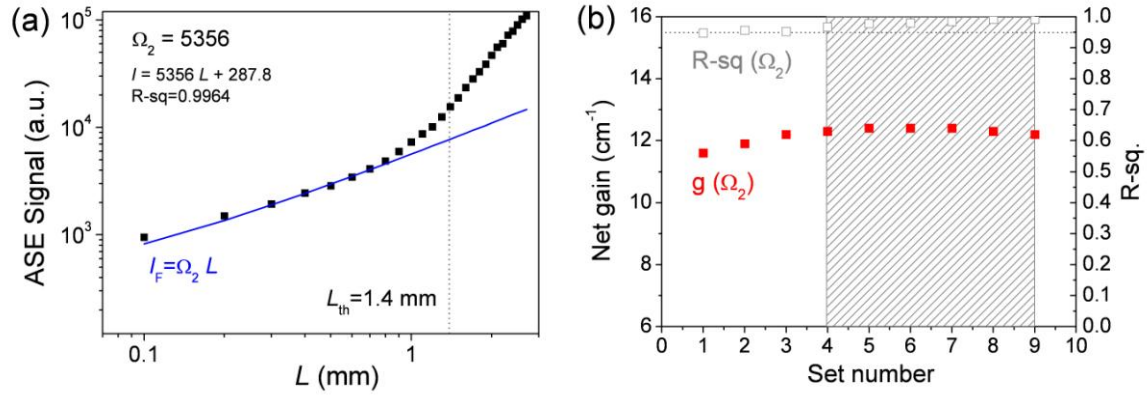


Figure 5.19 (a) Measured ASE signals in a function of the stripe length L at $E_{\text{pump}}=300 \mu\text{J}/\text{cm}^2$. Blue line: The linear fitting line for the data set of 0.2~0.5mm (3 data points) to determine Ω_2 value. (b) Extracted gain values and R-squared values for the determined Ω_2 value. The shaded region from set 4 to 9 has R-sq values over 0.95.

To summarize the gain measurements, the ASE characteristics from Lumogen Red films on Spec B substrate have been investigated using both the variable stripe length (VSL) method and the variable pump intensity (VPI) method. In general the VSL method has provided far more reliable method to extract the gain, although the VPI method is very useful approach to help extract the threshold energy density. The cross-examination of data from both measurement methods has led to a reasonable accurate assessment of net gain. Table 5.3 summarizes the obtained net gain values at $300 \mu\text{J}/\text{cm}^2$ and $1000 \mu\text{J}/\text{cm}^2$ from both methods. Our values are found to be in very good agreement with ealier studies on the material Ruidong's work [31]. That the Lumogen Red polymer exhibitis optical net gain around 675 nm will be important for the studies in the following chapter, where the interest will turn towards measuring gain in plasmonic systems.

Measurement method	$E_{\text{pump}} = 300 \mu\text{J} / \text{cm}^2$	$E_{\text{pump}} = 1000 \mu\text{J} / \text{cm}^2$
VSL method	$12.3 \pm 0.1 \text{ cm}^{-1}$	$21.7 \pm 0.2 \text{ cm}^{-1}$
VPI method	$12.4 \pm 0.1 \text{ cm}^{-1}$	$17.1 \sim 22.4 \text{ cm}^{-1}$

Table 5.3 Obtained net gain at $300 \mu\text{J}/\text{cm}^2$ and $1000 \mu\text{J}/\text{cm}^2$ pump energy condition from both variable stripe length (VSL) method and variable pump intensity (VPI) method

5.4 Summary

Energy transfer from an excited dipole is a prerequisite process to enable light amplification in nanoscale structures. This chapter has been concerned with verifying and investigating some of the underlying energy transfer properties using the Lumogen Red polymer, although the main conclusions should be applicable to any active material. We have investigated two representative planar structures that contain the same gain material, Lumogen Red: conventional planar photonic waveguide structures and plasmonic multi-layer structures.

In the first part of the chapter, the SPCE process was studied using thin conjugated polymer films as emission layers deposited atop silver coated glass prisms. Our clear demonstration of SPCE for these layers allowed us to explore the sensitivity of the SPCE process to the parameters of the structure (silver film thickness) and to the bandwidth of the emission layer (10 nm bandpass filtering versus full polymer bandwidth). This plasmonic mediated light extraction scheme was found to efficiently deal with the broadband emission from the underlying source. This is significant and points towards a method for improving extraction efficiency *without* the need for potentially complex resonant structures such as periodic corrugation or resonant cavities. In addition to this, the SPCE investigations have provided a good platform to better understand SPP-mediated energy-transfer mechanisms and help identify optimal geometries for a range of out-coupling and fluorescence sensing applications.

In the second part of the chapter our interest turned towards the stimulated emission properties from the Lumogen Red films. The amplified spontaneous emission (ASE) experiment was based on the planar asymmetric waveguide and demonstrated that Lumogen Red conjugated polymer is an excellent optical gain material. The experiment, which utilized conventional photonic modes (TE and TM) has provided us with optical gain values for the material, and will form the basis for the helping estimate the potential gain that the material can deliver for the new plasmonic system we will discuss in the next chapter.

References

- [1] G. Ford and W. Weber, "Electromagnetic interactions of molecules with metal surfaces," Phys. Rep. **113**, 195–287 (1984).

- [2] W.L. Barnes, "Fluorescence near interfaces: the role of photonic mode density," *J. Mod. Opt.* **45**, 661-699 (1998).
- [3] V. Giannini, A.I. Fernández-Domínguez, Y. Sonnefraud, T. Roschuk, R. Fernández-García, and S.A. Maier, "Controlling light localization and light-matter interactions with nanoplasmonics," *Small* **6**, 2498-2507 (2010).
- [4] A. Hryciw, Y.C. Jun, and M.L. Brongersma, "Plasmon-enhanced emission from optically-doped MOS light sources," *Opt. Express* **17**, 185-192 (2009).
- [5] J.F. Revelli, "Excitation of waveguide modes in organic light-emitting diode structures by classical dipole oscillators," *Appl. Opt.* **45**, 7151-7165 (2006).
- [6] T. Neal, K. Okamoto, and A. Scherer, "Surface plasmon enhanced emission from dye doped polymer layers," *Opt. Express* **13**, 5522-5527 (2005).
- [7] P. Hobson, S. Wedge, J. E. Wasey, I. Sage, and W.L. Barnes, "Surface plasmon mediated emission from organic light-emitting diodes," *Adv. Mater.* **14**, 1393-1396 (2002).
- [8] S. Wedge, J. E. Wasey, W.L. Barnes, and I. Sage, "Coupled surface plasmon-polariton mediated photoluminescence from a top-emitting organic light-emitting structure," *Appl. Phys. Lett.* **85**, 182 (2004).
- [9] T.D. Heidel, J.K. Mapel, M. Singh, K. Celebi, and M.A. Baldo, "Surface plasmon polariton mediated energy transfer in organic photovoltaic devices," *Appl. Phys. Lett.* **91**, 093506 (2007).
- [10] N. Fang, H. Lee, C. Sun, and X. Zhang, "Sub-diffraction-limited optical imaging with a silver superlens," *Science* **308**, 534-537 (2005).
- [11] S. Shi, Z. Zhang, M. He, X. Li, J. Yang, and J. Du, "Analysis of surface-plasmon-polariton-assisted interference imaging by using silver film with rough surface," *Opt. Express* **18**, 10685-10693 (2010).
- [12] R.F. Oulton, V.J. Sorger, T. Zentgraf, R.-M. Ma, C. Gladden, L. Dai, G. Bartal, and X. Zhang, "Plasmon lasers at deep subwavelength scale," *Nature* **461**, 629-632 (2009).

- [13] K. Toma, J. Dostalek, "Long range surface plasmon-coupled fluorescence emission for biosensor applications," *Opt. Express* **19**, 11090 (2011).
- [14] P. Andrew and W.L. Barnes, "Energy transfer across a metal film mediated by surface plasmon polaritons," *Science* **306**, 1002-1005 (2004).
- [15] F. Reil, U. Hohenester, J.R. Krenn, and A. Leitner, "Förster-type resonant energy transfer influenced by metal nanoparticles," *Nano Lett.* **8**, 4128-4133 (2008).
- [16] W. Wei, S. Li, L. Qin, C. Xue, J.E. Millstone, X. Xu, G.C. Schatz, and C. Mirkin, "Surface plasmon-mediated energy transfer in heterogap Au-Ag nanowires," *Nano Lett.* **8**, 3446-3449 (2008).
- [17] V.K. Komarala, A. L. Bradley, Y.P. Rakovich, S.J. Byrne, Y.K. Gun'ko, and A.L. Rogach, "Surface plasmon enhanced Förster resonance energy transfer between CdTe quantum dots," *Appl. Phys. Lett.* **93**, 123102 (2008).
- [18] I. Gryczynski, J. Malicka, Z. Gryczynski, K. Nowaczyk, and J.R. Lakowicz, "Ultraviolet surface plasmon-coupled emission using thin aluminum films," *Anal. Chem.* **76**, 4076-4081 (2004).
- [19] M.J.R. Previte, Y. Zhang, K. Aslan, and C.D. Geddes, "Surface plasmon coupled fluorescence from copper substrates," *Appl. Phys. Lett.* **91**, 151902 (2007).
- [20] K. Ray, M. H. Chowdhury, and J. R. Lakowicz, "Observation of surface plasmon coupled emission using thin platinum films," *Chem. Phys. Lett.* **465**, 92-95 (2008).
- [21] G. Winter and W.L. Barnes, "Emission of light through thin silver films via near-field coupling to surface plasmon polaritons," *Appl. Phys. Lett.* **88**, 051109 (2006).
- [22] L. Luan, P.R. Sievert, W. Mu, Z. Hong, and J.B. Ketterson, "Highly directional fluorescence emission from dye molecules embedded in a dielectric layer adjacent to a silver film," *New J. Phys.* **10**, 073012 (2008).
- [23] S. Hayashi, Y. Yamada, A. Maekawa, and M. Fujii, "Surface plasmon-mediated light emission from dye layer in reverse attenuated total reflection geometry," *Jpn. J. Appl. Phys.* **47**, 1152-1157 (2008).

- [24] K. Kato, M. Imaia, Y. Ohdaira, K. Shinbo, and F. Kaneko, "Surface plasmon emission light from Ag/MgF₂/Organic Dye/MgF₂/Ag films," *Mol. Cryst. Liq. Cryst.* **472**, 51-59 (2007).
- [25] I. Gryczynski, J. Malicka, W. Jiang, H. Fischer, W.C.W. Chan, Z. Gryczynski, W. Grudzinski, and J.R. Lakowicz, "Surface-plasmon-coupled emission of quantum dots," *J. Phys.Chem.B* **109**, 1088-1093 (2005).
- [26] M.H. Chowdhury, S.N. Malyn, K. Aslan, J.R. Lakowicz, and C.D. Geddes, "First observation of surface plasmon-coupled chemiluminescence (SPCC)," *Chem. Phys. Lett.* **435**, 114-118 (2007).
- [27] Y. Kostov, D.S. Smith, L. Tolosa, G. Rao, I. Gryczynski, Z. Gryczynski, J. Malicka, and J.R. Lakowicz, "Directional surface plasmon-coupled emission from a 3 nm green fluorescent protein monolayer," *Biotechnol. Prog.* **21**, 1731-1735 (2005).
- [28] K. Kato, "Attenuated total reflection and emission due to surface plasmon excitation of layer-by-layer ultrathin films containing azo-dye," *Thin Solid Films* **438-439**, 101-107 (2003).
- [29] J. Clark and G. Lanzani, "Organic photonics for communications," *Nature Photon.* **4**, 438-446 (2010).
- [30] B.K. Yap, R. Xia, M. Campoy-Quiles, P.N. Stavrinou, and D.D.C. Bradley, "Simultaneous optimization of charge-carrier mobility and optical gain in semiconducting polymer films," *Nature Mater.* **7**, 376-380 (2008).
- [31] R. Xia, G. Heliotis, Y. Hou, and D.D.C. Bradley, "Fluorene-based conjugated polymer optical gain media," *Org. Electron.* **4**, 165-177 (2003).
- [32] D.M. Koller, A. Hohenau, H. Ditlbacher, N. Galler, F. Reil, F.R. Aussenegg, A. Leitner, E.J.W. List, and J.R. Krenn, "Organic plasmon-emitting diode," *Nature Photon.* **2**, 684-687 (2008).
- [33] M. Nieto-Vesperinas and E. Wolf, "Generalized stokes reciprocity relations for scattering from dielectric objects of arbitrary shape," *J. Opt. Soc. Am. A* **3**, 2038-2046

(1986).

[34] J. Courtois, J. Courty, and J. Mertz, "Internal dynamics of multilevel atoms near a vacuum-dielectric interface," *Phys. Rev. A* **53**, 1862-1878 (1996).

[35] K. Celebi, T.D. Heidel, and M.A. Baldo, "Simplified calculation of dipole energy transport in a multilayer stack using dyadic Green's functions," *Opt. Express* **15**, 1762-1772 (2007).

[36] J. Burke, G. Stegeman, and T. Tamir, "Surface-polariton-like waves guided by thin, lossy metal films," *Phys. Rev. B* **33**, 5186–5201 (1986).

[37] C. Chen, P. Berini, D. Feng, S. Tanev, and V. Tzolov, "Efficient and accurate numerical analysis of multilayer planar optical waveguides in lossy anisotropic media," *Opt. Express* **7**, 260-272 (2000).

[38] J. Haes, B. Demeulenaere, and R. Baets, "Difference between TE and TM modal gain in amplifying waveguides: analysis and assessment of two perturbation approaches," *Opt. Quant. Electron.* **29**, 263-273 (1997).

[39] T. Visser, H. Blok, B. Demeulenaere, and D. Lenstra, "Confinement factors and gain in optical amplifiers," *IEEE J. Quantum Elect.* **33**, 1763–1766 (2002).

[40] Y. Z. Huang, "Comparison of modal gain and material gain for strong guiding slab waveguides," in *Optoelectronics, IEE Proceedings* **148**, 131–133 (2002).

[41] H. Nakanotani, S. Akiyama, D. Ohnishi, M. Moriwake, M. Yahiro, T. Yoshihara, S. Tobita, and C. Adachi, "Extremely low-threshold amplified spontaneous emission of 9, 9'-spirobifluorene derivatives and electroluminescence from field-effect transistor structure," *Adv. Funct. Mater.* **17**, 2328–2335 (2007).

[42] S. Brovelli, T. Virgili, M. M. Mroz, G. Sforazzini, A. Paleari, H. L. Anderson, G. Lanzani, and F. Cacialli, "Ultra-broad optical amplification and two-colour Amplified Spontaneous Emission in Binary Blends of Insulated Molecular Wires.," *Adv. Mater.* (Deerfield Beach, Fla.) **87545**, 1-5 (2010).

[43] E. M. Calzado, P. G. Boj, and M. A. Díaz-García, "Amplified spontaneous

emission properties of semiconducting organic materials.," International journal of molecular sciences **11**, 2546-65 (2010).

[44] L. Cerdán, A. Costela, and I. Garcia-Moreno, "On the characteristic lengths in the variable stripe length method for optical gain measurements," J. Opt. Soc. Am. B **27**, 1874–1877 (2010).

6 Plasmonic Gain

6.1 Introduction: Amplification of Surface Plasmon Polaritons

Rather short propagation length of surface plasmon polariton modes is one of the main drawbacks, prohibiting nano-scale functional devices being developed into feasible applications as described in earlier chapters. It brings strong demands to develop new concepts for possessing long enough propagation lengths to deliver optical information over a long distance. Compensating SPP propagation loss is one of great challenges not only to realize nano-optic devices, but also to understand related physics on the nanoscale, requiring the introduction of new plasmonic architectures. There may be two approaches for increasing the propagation length of SPPs: one method is to create coupled plasmonic structures such metal/dielectric/metal (MIM) [1,2] or dielectric/metal/dielectric (IMI) [3], which can support coupled modes from multiple metal/dielectric interfaces, so that their electric fields can be distributed mostly in dielectric layers rather than in metal layers, resulting in reduced propagation loss. Using such structures, we also can modify the light-matter interaction properties that SPPs give rise to, in addition to the increased propagation length. The other is to incorporate active materials providing optical gain in a plasmonic waveguide in order to amplify the plasmonic signal. Furthermore, we can come up with approaches combining both methods.

David Bergman and Mark Stockman [Ch1.85] provided a theoretical background to demonstrate the possibility of surface plasmon amplification of stimulated emission of radiation, abbreviated to ‘SPASER’. Recently, the amplification of SPP signals has been demonstrated experimentally in various platform; the attenuated total internal reflection [4,5], stripe plasmonic channel waveguides [6-8], and the lasing concept via nano-cavity has been suggested using organic dye [9,10], semiconductor nanostructures [11]. However, amplification of propagating SPP using *thin* active polymer films has never been demonstrated experimentally. Plasmonic excitation by excitonic dipoles discussed in chapter 5 do not necessarily require bulky gain medium because only dipoles located at up to around 100 nm from a metallic interface can deliver their energy into surface plasmon propagation [Ch5.1]. In practical viewpoint, geometrically thinner active elements are more advantageous for various device applications. The works shown in previous chapters (particularly Ch. 4 and Ch 5) are preliminary studies for supporting that plasmonic gain via optically excited dipoles may be possible.

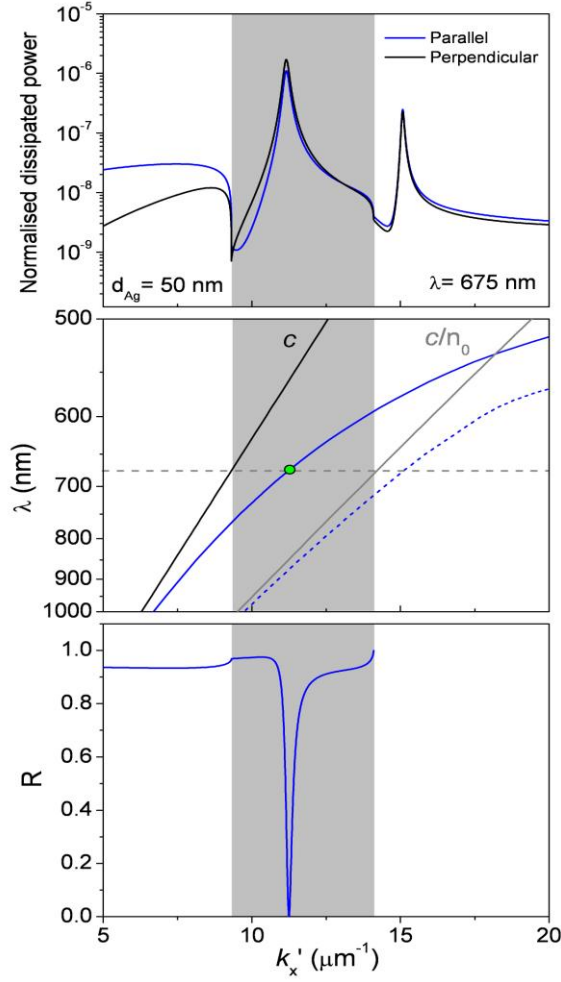


Figure 6.1 Three aspects of SPP modes that arise in the active ‘two-layer’ configuration with $d_{Ag}=50$ nm and $d_p=38$ nm. The upper figure is the power dissipation spectra for parallel and perpendicular dipole orientation in the in-plane momentum range from $k_x' = 5$ to $20 \mu\text{m}^{-1}$ (c.f. figure 5.1) at 675 nm. The figure at the middle shows the dispersion relation of the leaky SPP mode. The in-plane momentum at 675 nm in the dispersion curve is pointed out as a green circle. The corresponding configuration shows the reflectivity curve with respect to the in-plane momentum, $k_x'=(2\pi/\lambda_s)\cdot n_0\sin\theta$, where θ is the incidence angle and $n_0(=1.5139)$ is refractive index of the prism (the lower figure). In the grey widow, the peak position of the power dissipation spectra and the minimum reflectivity position are identical to the green circle position.

In figure 6.1 theoretical calculations of power dissipation spectra, SPP dispersion and angular reflectivity in the two-layer configuration are displayed with respect to in-plane momentum vector in order to give an insightful view of SPPs that arise in the structures as far as in-plane momentum matching is concerned. The common grey window from $k_x' = 5$ to $20 \mu\text{m}^{-1}$ of the three graphs at 675 nm is the momentum window where there is the SPP

mode concerned, which appears as a reflectivity form via prism coupling (the graph at the bottom). The graph at the top shows the possible excited SPP modes (two sharp peaks) via dipole oscillation, one of which within the window may be able to create stimulated emission of the SPP mode (see section 5.2). It is found that the in-plane momentum of the SPP mode via both the prism coupling and the dipole coupling is identical each other to the calculated momentum from the dispersion relation at the wavelength (as pointed as a green circle in the middle graph), suggesting that the combination of the both approaches may enable SPP amplification.

This chapter will explain the basic mechanism of plasmonic gain and how it appears in the reflectivity curves. We then go on to show experimental demonstration of SPP amplification via the ATR method using the two-layer structure incorporating *thin* polymer film, which is the same structure used in Chapter 5. The verification of the modified double modulation technique for detecting gain signals are presented and theoretical estimation of plasmonic modal gain in the layer configuration is suggested. This work will facilitate developing efficient light-plasmon interaction, which could lead to nano-lasers and nanoscale modulators.

6.2 Experimental Realization

6.2.1 Gain Effects in the ATR configuration

The change in angular reflectivity by optical gain effects in the Kretschmann configuration based on the metallo-organic multi-layers (the two-layer structures) will be described in this section. We found that the leaky modes of SPPs emerged in the layer configuration show different loss behavior in angular reflectivity according to the metal film thickness (see section 4.3). Consequently the gain effects on the modes are expected to be strongly dependent on the metal film thickness. In this respect, first, we intend to explain the plasmonic gain effect on the Kretschmann-Reather configuration in terms of the two loss components, both internal loss γ_i and radiation loss γ_r that were catergorised from the calculated imaginary part of a propagation vector k_x'' as discussed in Section 3.3.3. This could lead to a better understanding of plasmonic modal gain behind angular reflectivity changes that experimentally arise because the prism-coupling method is an indirect way to probe the optical characteristics of the SPP near fields. We present how both internal loss γ_i and radiation loss γ_r change when silver thickness varies and both the

loss factors link to angular reflectivity behaviors. We divide metal thickness into two regions with respect to the silver thickness away from optimum thickness T_0 (~50 nm) giving zero minimum reflectivity, $T < T_0$ and $T > T_0$ because each region has distinctively different behaviour of angular reflectivity change. Here we define the differential angular reflectivity as reflectivity changes between with gain and without gain.

$$\Delta R = R_g - R_0 \quad (6.1)$$

where R_g is a reflectivity curve in the presence of gain and R_0 is a normal reflectivity curve in the absence of gain. This value is what we measure experimentally. It is assumed that when there is optical gain in the active layer, a negative, imaginary value of the electric permittivity of the layer, $\Delta\epsilon_p''$ may be created. The calculation of ΔR curves is performed by inserting $\Delta\epsilon_p''$ values into the TMM calculation.

To understand why the two thickness regions show different behavior under optical gain, the change of the modal loss components from k_x'' should be analyzed. Figure 6.2 (a) describes the change of total modal loss $\gamma_i + \gamma_r$, which corresponds to the imaginary part of complex propagation vector, k'' and radiation loss γ_r with respect to the thickness of Ag films. The white straight line corresponds to internal loss γ_i . If there is optical gain, the total loss γ decreases (the dotted line). To visually confirm the gain effect, a relatively large gain of 10^4 cm^{-1} was applied to the k_x'' calculation, however, the overall trends do not change for much smaller values ($< 10^2 \text{ cm}^{-1}$) that in general fluorescent conjugated polymers possess. It is found that an amount of decreased loss is uniform irrespective of the silver film thickness (the dotted line), that basically means that any silver thicknesses can experience a same amount of loss compensation, reflecting the decrease of angular linewidth $\Delta\theta$ over all the thickness range, however only the internal loss is affected by gain and the radiation loss is determined only by the geometry, mainly the metal thickness.

Here, we introduce a factor $\hat{\gamma} = (\gamma_r - \gamma_i) / \gamma_i^{d \rightarrow \infty}$ to explain the gain effect on ΔR as presented in figure 6.2(b). As discussed previously, the optimum coupling thickness have equal values of γ_r and γ_i , i.e. $\hat{\gamma} = 0$, see . For the thinner metal films ($T < T_0$, blue circle region) having $\hat{\gamma} > 0$ where the radiation loss is dominant, $\hat{\gamma}$ increases, moving away from the optimum condition and accordingly R increases around resonance angles ($\Delta R_{\min} > 0$) as gain is present, while the thicker films ($T > T_0$, red circle region) where $\hat{\gamma} < 0$ present $\Delta R_{\min} < 0$ because $\hat{\gamma}$ approaches to the optimum coupling condition ($R=0$). The calculated angular reflectivity curves of two regions are clearly exemplified for 34 nm (blue line) and 76 nm (red line) thick film cases (figure 6.2(c)). The common effect for both cases is decreased $\Delta\theta$, implying decreased propagation loss k_x'' . However, ΔR curves show different behaviour. As the thinner thickness present increased ΔR ($\Delta R > 0$), while the thicker thickness shows decreased ΔR ($\Delta R < 0$). It should be reiterated that the two

thickness regions obtain the same amount of gain despite the different differential angular reflectivity curves. In summary, thinner and thicker metal films than optimum thickness (about nominal 50 nm) exhibit different sign of maximum changes in angular reflectivity while commonly experiencing narrowing of angular reflectivity curves, directly implying reduced propagation loss due to an obtained gain.

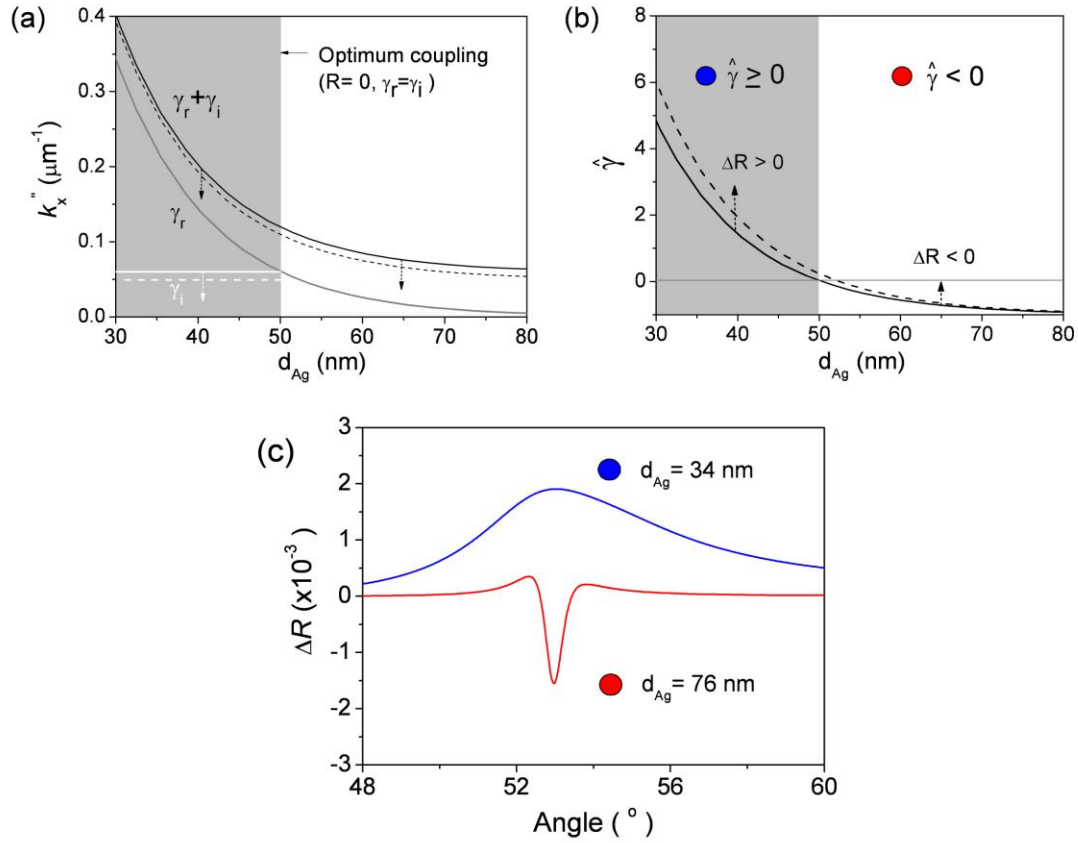


Figure 6.2 (a) The trend of internal loss γ_i and radiation loss γ_r with respect to the thickness of Ag films. The dotted line indicates decreased total loss k_x'' ($=\gamma_i+\gamma_r$) due to optical gain (a gain value of 10^4 cm^{-1} is applied to the calculation for visually clarifying the gain effect). The grey window region is $d_{\text{Ag}} < T_0$. (b) The parameter $\hat{\gamma} = (\gamma_r - \gamma_i) / \gamma_i^{d \rightarrow \infty}$ related to the difference of both the loss factors with respect to the thickness of Ag films. The blue circle region ($d_{\text{Ag}} < T_0$) is $\hat{\gamma} \geq 0$ and the red circle region is $\hat{\gamma} < 0$. (c) Calculated differential angular reflectivity curves for $d_{\text{Ag}} = 34$ nm (blue line) in the blue circle region and 76 nm (red line) in the red circle region using $\Delta\epsilon_p'' = -1 \times 10^{-4}$.

6.2.2 Optical Pumping Conditions

The experimental realization of plasmonic gain in the two layer structure will be discussed in this section. Our experimental conditions and an expected gain value are compared with other groups' works in Table 6.1. Seidel [4] and Noginov [5] used the dye molecules as a gain medium with semi-infinite thickness, but we will use thin Lumogen Red conjugated polymer films as the gain medium, which has about 40 nm thickness. This geometrical condition is more applicable to practical devices such as organic light-emitting diodes with tens of nm thick active layer [Ch2.12,Ch2.17] and the value of imaginary part of electric permittivity $\Delta\epsilon_p''$ of the Lumogen Red polymer due to gain is inferred from the measured maximum value of reflectivity changes. Optical gain of bulk medium under a given pump energy termed 'material gain' can be calculated by the following equation based on the classical approach [13].

$$g_m = k_0 \frac{\Delta\epsilon_p''}{n_p} \quad (6.2)$$

where k_0 is light momentum in vacuum and n_p is the index of refraction of the polymer material. From the quantum mechanical viewpoint, material optical gain at a transition frequency may be described by

$$g_m = N_e \cdot \sigma_e \quad (6.3)$$

where N_e is the number density of excited molecules and σ_e is the emission cross section at an emission frequency.

Since steady state condition at an energy level system for conjugated molecules is considered (the pump pulse width is approximately five times longer than the fluorescence decay time), the population of excited molecules can be expressed by the ratio of the pump rate and the spontaneous transition rate considering quantum efficiency of an active medium, η [14].

$$N_e = N \cdot \frac{\eta \cdot \gamma_p}{\eta \cdot \gamma_p + \gamma_s} \quad (6.4)$$

The spontaneous transition rate γ_s is inversely proportional to fluorescence decay time τ that may be measured via streak camera method. The pump transition rate in molecules under the pump energy is given by

$$\gamma_p = \sigma_a \cdot \frac{I}{h\nu_p} = \frac{\varepsilon_0 n_p \sigma_a \lambda_p |E|^2}{2h} \quad (6.5)$$

$$= \frac{n_p \sigma_a P_p}{n_{air} h \nu_p \cdot A_p}$$

where I is the optical pump intensity, $h\nu_p$ is the photon energy, $P_p(=E_p/\tau_{pulse})$ is pump peak power, A_p is the pump beam area and σ_a is the absorption cross section at the pump frequency. As experimental conditions listed in table 6.1, 40 nm thick Lumogen Red polymer has the fluorescence decay time of about 1.8 ns that corresponds to the spontaneous transition rate of $5.56 \times 10^8 \text{ s}^{-1}$. From input pump beam size A_p of 0.25 cm x 0.038 cm (the stripe beam shape for the reason that the probe beam on the prism surface slightly shifts as the incidence angle varies). $\sigma_e = 7.73 \times 10^{-16} \text{ cm}^2$ [Ch5.30], the obtainable maximum material gain may be estimated to be about 50 cm^{-1} . For the input conditions mentioned previously, the population density is estimated to be $N_e = N \cdot 0.1$.

	J. Seidel [4]	M. A. Noginov [5]	This work
Pump Source	CW dye laser	Nd:YAG laser	Nd:YAG laser
Pump λ_p	632.8 nm	594 nm	532 nm
Emission λ_e	580 nm	532 nm	675 nm
Energy per pulse	(Power=10mW)	18 mJ	1 mJ/cm ²
τ (duration)	continuous wave	10 ns	10 ns
Peak pump density P/S	$\sim 12 \text{ W/cm}^2$	$\sim 1.7 \times 10^7 \text{ W/cm}^2$	$\sim 2 \times 10^4 \text{ W/cm}^2$
n_g (active medium)	1.3 (Dye solutions)	1.5 (R6G+PMMA)	1.8618 (Lumogen Red)
n_p (prism)	1.5152 (BK7)	1.784	1.5139 (BK7)
Concentr. of molecules N	$7 \times 10^{17} \text{ cm}^{-3}$	$1.2 \times 10^{22} \text{ cm}^{-3}$	$N_e \sim 10^{17} \text{ cm}^{-3}$
Emiss. cross sec. σ_e	$3 \times 10^{-16} \text{ cm}^2$	$2.7 \times 10^{-16} \text{ cm}^2$	$7.73 \times 10^{-16} \text{ cm}^2$
Absorp. cross sec. σ_a	$3 \times 10^{-16} \text{ cm}^2$	$2.7 \times 10^{-16} \text{ cm}^2$	$\sim 10^{-16} \text{ cm}^2$
n (emiss.life time)	3 ns	3 ns	2.5 ns
N_e (density of higher states)	$3 \times 10^{-3} N$	$> 0.95 N$	$0.1 N$
ε'' (gain medium)	-9×10^{-6}	-6×10^{-3}	< -0.001
ΔR (max. differential R)	5×10^{-5}	0.1	$< 1 \times 10^{-2}$
Material gain	0.8 cm^{-1}	420 cm^{-1}	50 cm^{-1}

1. Data for Lumogen Red polymer were given in [Ch2.25,5.30]

2. All equations in the Table 2 were taken in [4]

Table 6.1 Comparison of experimental conditions with Seidel's and Noginov's works

6.3 Setup

In our experiments the expected signal change of reflectivity due to gain is of the order of 10^{-3} or less than that. To detect such a small signal variation, we need to increase detection sensitivity and to discriminate SPP amplification against spontaneous emission by using appropriate measurement techniques such as dual-cascaded lock-in amplifier methodology that has often been exploited in a number of spectroscopic fields [15-17]. Lock-in amplifiers are generally used to attain a high detection sensitivity by selecting a Fourier frequency component of modulated signals [18]. Thus, modulating light signals at particular frequencies (in this instance, both pump and probe beam) is essential for implementing the lock-in detection.

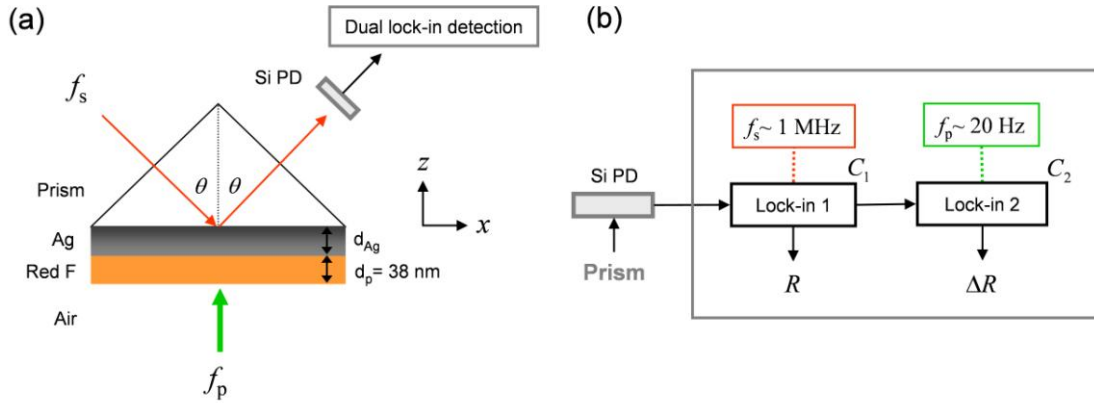


Figure 6.3 Schematic of pump-probe measurement system for plasmonic gain (a) The pump-probe experimental setup in the Kretschmann-Raether configuration in conjunction with the double-cascaded lock-in amplifiers. Probe light of 675 nm wavelength is modulated at $f_s = 1 \text{ MHz}$, while pulsed pump light of 532 nm wavelength have a repetition rate of $f_p = 20 \text{ Hz}$. (b) Double cascaded lock-in detection system. The system comprises the lock-in amplifier 1 locking signals at f_s and the lock-in amplifier 2 at f_p , producing signals related to reflectivity R and differential reflectivity ΔR , respectively. The calibration factors C_1 and C_2 that result from short pump pulses will be explained at following sections in more detail.

Figure 6.3 depicts the schematic of our detection setup. The double modulation detection part containing two cascaded lock-in amplifiers working at different detection frequencies, which will be explained in the next section, is added to the prism coupling system. The probe beam at 675 nm that excites SPPs on the nano layer structures discussed so far was modulated by an electro-optic modulator at about 1 MHz, while the pump beam

from a diode-pumped Nd:YAG laser at 532 nm is the pulsed output at 20 Hz repetition rate with about 10 ns time duration. While the prism sample rotates under the exposure of the pump beam normal to the active film, a silicon photodetector records intensity variation of the probe beam.

6.3.1 Double Modulation Technique

This section explains the double modulation technique for signal detection and its feasibility in more detail. Our pump-probe experiment uses cascaded lock-in amplifiers for two reasons. First fluorescence light contains light of the same wavelength as the probe beam. So we have to discriminate the amplified probe signals against fluorescence background. The second reason is to single out the weak signals and to improve the signal to noise ratio (SNR). Both pump and probe beam are modulated at different frequencies and each corresponding reference modulation signal is fed into each corresponding lock-in amplifier.

Here, the signal process of dual-cascaded lock-in amplifiers for pump-probe experiment is explained in the Fourier domain as seen in Fig 6.4. It is assumed that a pump beam is modulated at a frequency f_p and a probe beam is at a frequency f_s . The probe beam experiences additional amplitude modulation at a beat frequency between the probe and pump modulation frequencies, induced by stimulated emission.

The basic functions of a lock-in amplifier comprise a signal multiplier and a low-pass filter with time constant T_c that plays an important role in performing the double modulation scheme. The pump beam induces a modulation of the probe beam at $f_p + f_s$ and $f_p - f_s$ (beat frequencies) (c.f. Fig 6.4(a)). In the lock-in amplifier 1, signals related to reflectivity R are filtered out while the beat signal pass over to the lock-in amplifier 2 by opening a passband of the low-pass filter in lock-in amplifier 1, finally detected at the lock-in amplifier 2, which directly corresponds to ΔR due to gain (see eqn (6.6)). The time constant T_c ($1/f_p < T_{c1} < 1/f_s$) is set to be small enough for the beat signal to be able to pass (not averaged out), e.g. $T_c = 1$ ms gives 250 Hz passband (RC slope: 6 dB/oct).

C is a total calibration factor, the multiplication of C_1 and C_2 that arise due to the short duty cycle of signals at the lock-in amplifier 1 and 2, respectively, which will be described in Section 6.3.3. The mathematical description of the total signal processes were presented in detail in Appendix C.

$$\begin{aligned} V_{lock1} &\propto R \\ V_{lock2} &\propto 1/C \cdot \Delta R \end{aligned} \tag{6.6}$$

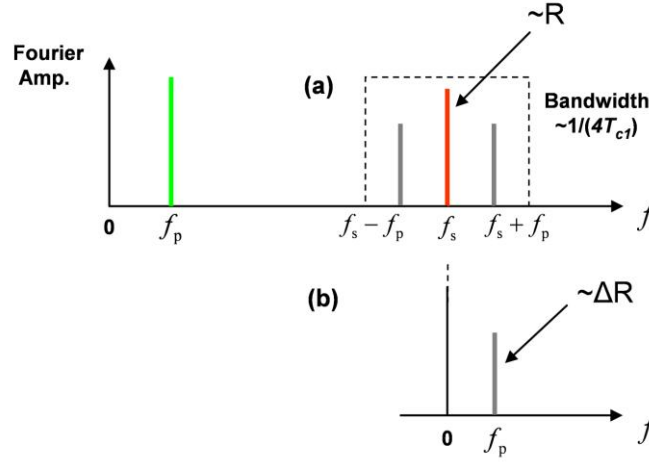


Figure 6.4 (a) Role of the lock-in amplifier 1: signals related to reflectivity R are filtered out, while the beat signals associated with both the pump and probe modulation pass through opened frequency window determined by a time constant setting T_c (b) Role of the lock-in amplifier 2: signals related to reflectivity ΔR are filtered out. Adopted from Ref. [17]

6.3.2 Photodetector Setting

In the double modulation detection, signals that get involved in amplification of surface plasmon propagation are modulated at certain frequencies. Detectors must handle those signal components with different modulation frequencies. Here, we describe photodetector setting in terms of a terminating resistor for supporting pump conditions with short duty time (short duration time compared to pulse repetition period). 50% duty cycle of modulated signal is ideal for signal detection in lock-in amplifiers. In our experiment, however, pulsed pump light with short duration time is used for efficient pumping as well as lessening photobleaching of conjugated polymers, correspondingly output signals have short duty time. Lock-in amplifiers can detect a weak signal even with strong noise background thank to the phase-sensitive technique. Also the instruments make it possible to even detect single photons (a delta function in time) by setting proper terminating resistors of photodetectors [19].

Output signals from the Si photodiode (Thorlabs, DET 36A) with different output resistor setting were examined as depicted in figure 6.5(a). The 532 nm pulsed light with

20 Hz repetition rate was injected into the detector and Fourier amplitudes of the output signals were detected in the lock-in amplifier and the falling time of the signals were measured using an oscilloscope. The relation between the resistor R_{Load} and signal falling time that determines corresponding signal bandwidth f_{BW} is expressed by [20]

$$t \propto 1/f_{BW} \propto R_{Load} \quad (6.7)$$

The output from the lock-in amplifier increases as R_{Load} increases, which is due to increased pulse length, but the peak amplitude of signals were not affected much as can be seen in figure 6.5(b). For the lock-in detection, hence, R_{Load} was set to maximum resistance, 50 k Ω .

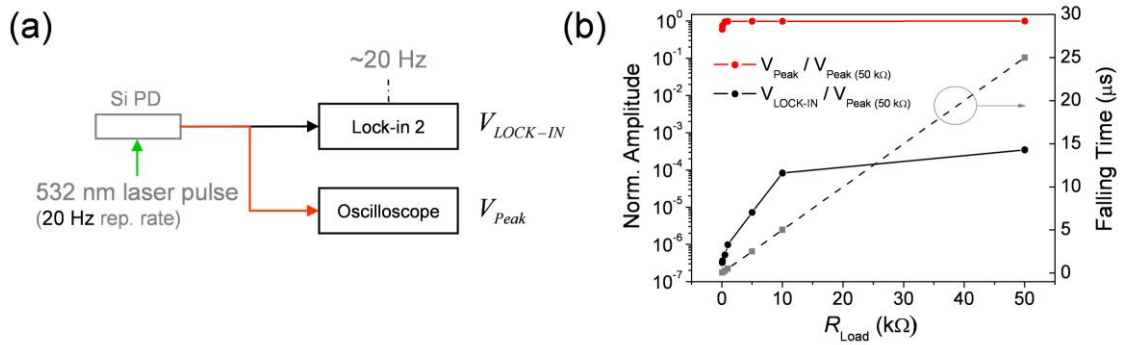


Figure 6.5 (a) Sketch of the experiment to evaluate the change of output signal from the Si photodiode with different output resistor setting (b) Normalized output amplitude variation obtained from the oscilloscope (red dots) and the lock-in amplifier (black dots) with respect to the output resistor, and the change of the falling times of the output pulse signals measured using the oscilloscope (grey dotted line)

6.3.3 Calibration Factors

The signal amplitude of an input signal, which depends on the duty cycle of the signals can be underestimated in the lock-in detection process due to decreased Fourier amplitude. We explain two calibration factors C_1 and C_2 that must be taken into consideration for precisely quantifying signal amplitude, which arise in the signal process of lock-amplifier 1 and 2, respectively.

Calibration Factors C_1

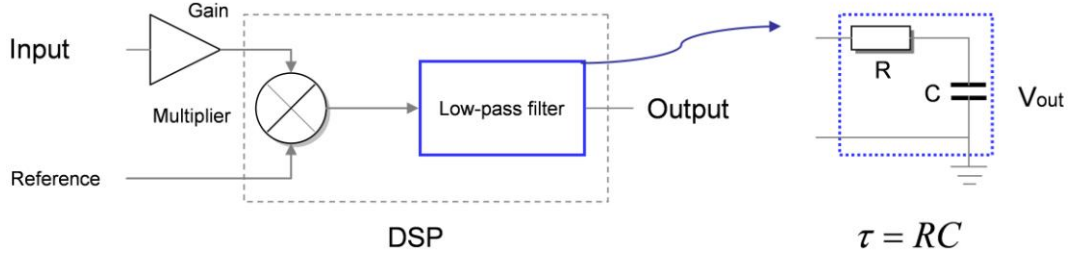


Figure 6.6 Schematic of basic functions of a lock-in amplifier [21] and depiction of a low-pass filter in the lock-in amplifier, which is an equivalent of analog resistor-capacitor filters with a time constant $\tau(=RC)$.

Signal multiplier and low-pass filter are essential components in lock-in amplifiers. Low-pass filters in digital lock-in amplifiers are digital counterpart of analog RC (Resistor-Capacitor) electrical filters with a time constant $\tau(=RC)$, that is, integration time (figure 6.6). Temporal shape and amplitude of input pulse signals are determined by the time constant. When the input pulse width is shorter than the time constant, resultant output pulses have the pulse width comparable to the selected time constant and a decreased amplitude because the pulses spread in time as depicted in figure 6.7. The ratio of output amplitude to input amplitude may be given by the following equation, which becomes the calibration factor C_1 [22].

$$V_1 / V_0 = 1 - e^{-T/\tau} = C_1 \quad (6.8)$$

As mentioned at the previous section, what we need to know is the input original amplitude. Therefore, from input pulse width, single amplitude can be obtained by taking a calibration factor C_1 that is inversely proportional to the ratio.

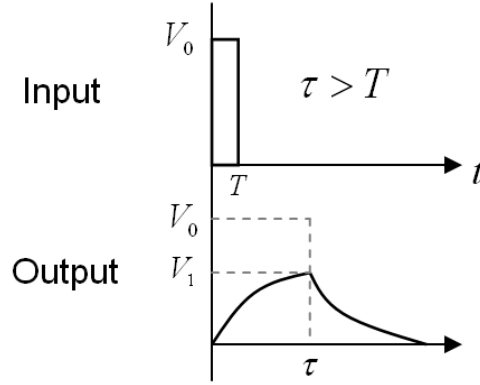


Figure 6.7 Description of pulse signal behaviour after passing through a low pass filter (RC filter): the case of input signal pulse whose time width T is shorter than the integration time τ of the low pass filter

Figure 6.8 shows output signals from the lock-in amplifier 1 where various time constants are set. Input pulse width was $25 \mu\text{s}$. As expected from equation 6.7, longer time constant setting produces longer output pulses with decreased amplitudes. At a long time constant such as 1 ms , the input pulses were almost averaged out to zero. For the feasible detection application, shortest time constant setting, which is no filter setting at the SR844 RF lock-in amplifier gives a smallest time constant [23], is more favorable because shortest time constant setting can have broadest frequency pass-window around the locking frequency. Therefore, we obtain $C_1 \approx 1/(1 - e^{-25\mu\text{s}/40\mu\text{s}}) \approx 2.15$ for the setting condition.

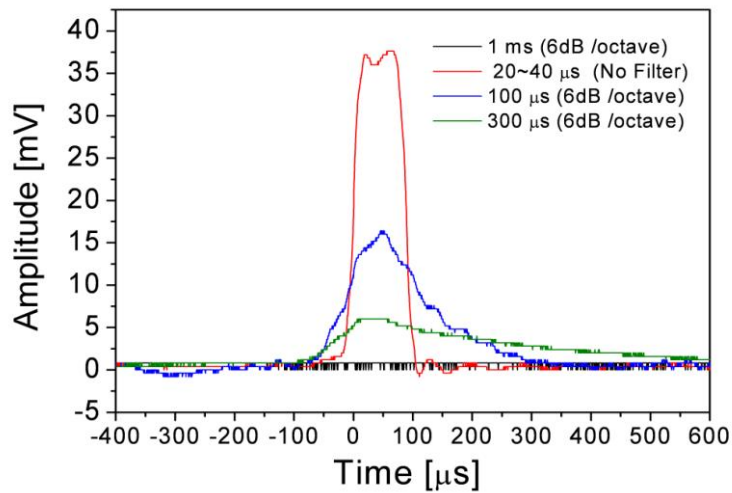


Figure 6.8 Measured output pulse signals from the RF lock-in amplifier (Stanford Research: SR 844) via the fast oscilloscope against the time constant setting in the lock-in amplifier

Calibration Factors C_2

The calibration factor C_2 is considered to occur in the signal process of the lock-in amplifier 2. As the duty cycle decreases while the signal amplitude is maintained, the output signal from the lock-in amplifier decreases accordingly due to decreased amplitude of first-order Fourier component of original signal. To quantify the C_2 according to the duty time, the output performance of the lock-in amplifier was tested by selecting the duty time via a pulse generator, shown in Figure 6.9. A ratio of output amplitude for a certain duty time to the output amplitude for full 50% duty cycle time, r_d (r_d is 1 for the full duty time of 25 ms at 20 Hz modulation frequency) was measured with respect to the duty time, from which $C_2(=1/r_d)$ is obtained. The measurement data from the lock-in amplifier perfectly agree with the Fast Fourier transform (FFT) modeling, which indicates that C_2 can be precisely predicted at a given duty cycle of any modulation frequency. In our case, input pulses with about 90 μ s duration time at 20 Hz repetition rate produce $C_2 \sim 178$.

Many pump-probe spectroscopic experiments using a short pulse pump laser have employed a tactic to improve signal-to-noise ratio, which is a modification of patterns of pump pulses [15]. The method is to use multiple pulses rather than a single pulse in a given repetition time, mimicking continuous beam modulation (quasi-continuous wave (CW)). For instance, if pulse light with 1 kHz repetition rate is additionally modulated at 20 Hz by means of a mechanical chopper, 25 pulses become equally distributed in time in the full duty time of 25 ms for the 20 Hz. Hence this scheme helps relieve detection difficulty by pulling up r_d (C_2 becomes around 10) as predicted in figure 6.9 (black dashed line), but we used this scheme only for proving the overall trends of ΔR curves for the reason that high energy multiple pulses accelerate photodegradation of a polymer film.

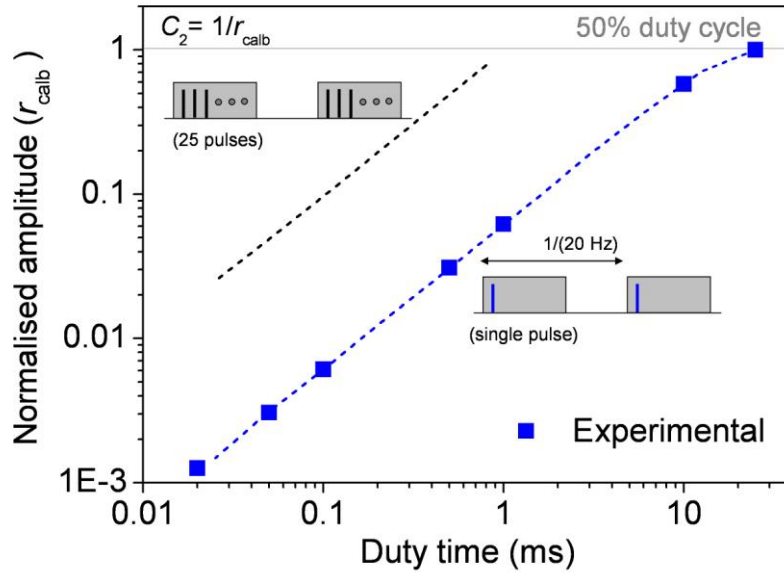


Figure 6.9 Measured normalized output amplitudes (blue dots) of input pulse signals modulating at 20 Hz at the lock-in amplifier 2 (Stanford Research: SR 830) against varying pulse duty time (50% full duty time: 25 ms) along with the Fast Fourier transform (FFT) modeling (blue dashed line). Black dashed line corresponds to the modeling of the quasi-CW case with 25 pulses in the full duty time.

6.3.4 Verification of the Detection Scheme

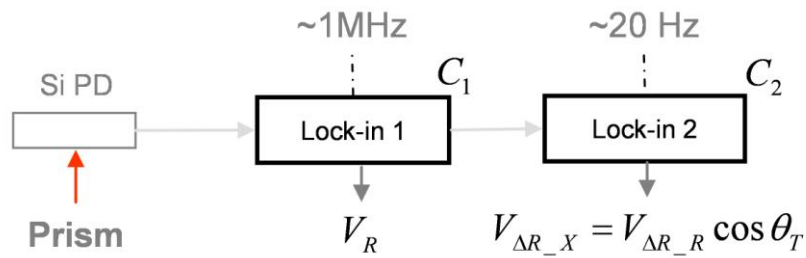


Figure 6.10 Schematic of signal outputs and calibration factors (C_1 and C_2) from the series of lock-in amplifiers locked at 1 MHz and 20 Hz. The output signal from the lock-in amplifier 1 corresponds to reflectivity and one from the lock-in amplifier 2 corresponds to differential reflectivity

The differential reflectivity from the double lock-in system (Figure 6.10) is expressed by

$$\Delta R = (V_{\Delta R_X} / V_{R0} / g_1) \cdot C_1 \cdot C_2 \quad (6.9)$$

,which includes a gain factor, g_1 in the lock-in amplifier 1, and the two calibration factors, C_1 and C_2 , $V_{\Delta R_X}$ is an in-phase term considering output phase term θ_T . To verify that this measurement scheme works, the signal $V_{\Delta R_X}$ were measured in time scale according to the presence of pump and probe beam on the prism surface (Figure 6.11). When only both the pump and the probe beam were present together, the output signal existed, confirming that the signal results from the interaction between the pump and the probe beam. In addition, the signals were produced when both the beams were spatially overlapped on the prism surface. If both beam does not overlap each other, no signals come out because the probe beam experiences no change.

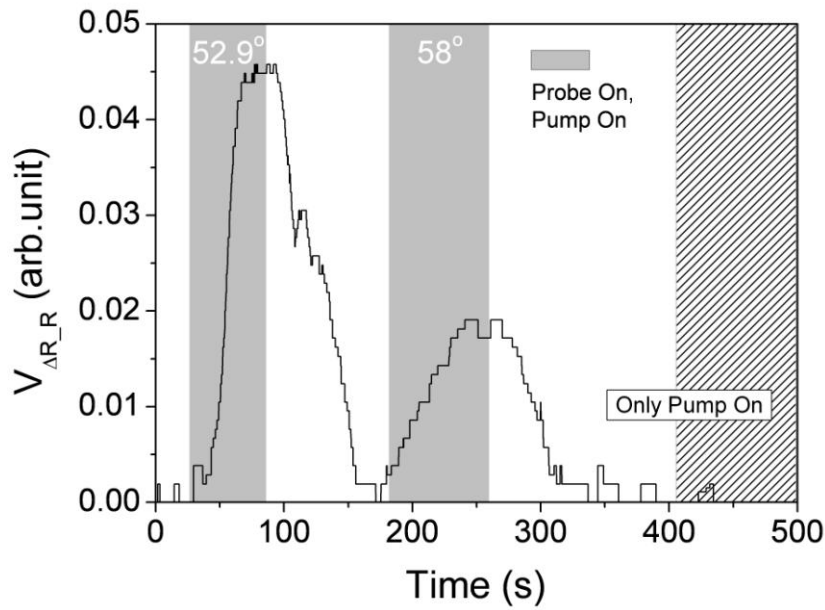


Figure 6.11 Presence of signals from first lock-in amplifier 2 locking at low frequency ω_s , from a prism sample with 30 nm thick silver and 38 nm thick Lumogen Red polymer film with optical gain according to presence of pump and probe beam on the prism surface. Time constant was set to 3 s (18 dB/oct)

6.4 Results

6.4.1 Differential Angular Reflectivity

With the measurement scheme, the differential angular reflectivity curves were examined and its trends were analysed with the support of the theoretical approaches we discussed. First, we employed the quasi-CW pump scheme to prove the expected behaviour of ΔR from the two silver thicknesses, 34 nm and 76 nm in the regions of interest we want to identify and compare. The distinctively different behaviour of differential angular reflectivity curves for the two silver thickness cases are shown in figure 6.12. The measured values were calibrated using C_2 (~ 11.5) as discussed previously. The thinner silver film (blue dots) presented positive ΔR values over whole observation angles and the thicker film had a negative ΔR values especially around the resonant coupling angle. These ΔR trends are closely same as the expectation (c.f. figure 6.1).

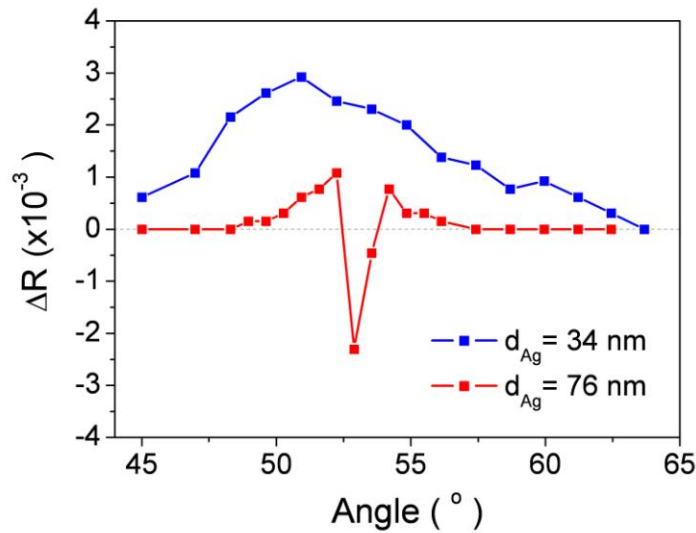


Figure 6.12 Measured differential reflectivity curves for silver thicknesses of 34 nm (blue dots) and 76 nm (red dots) using the quasi-CW pumping scheme.

Experimental investigation of differential angular reflectivity curves ΔR were moved to the single pulse pumping condition that gives better stability for the polymers. ΔR curves were measured for three different silver thicknesses of 34 nm, 53 nm and 76 nm and then material gains g_m were extracted by comparing the theoretical estimate of ΔR . Figure 6.11 shows experimentally measured angular reflectivity and differential reflectivity curves for

three silver thicknesses of 34 nm, 53 nm, and 76 nm in the two-layer structures along with their theoretical estimations under the pump energy density of 1 mJ/cm². In the presence of optical gain in the polymer layer, the negative imaginary part of its dielectric constant $\Delta\epsilon_p''$ are assumed to be generated. In essence, polymer permittivity, $n_p^2 + i \Delta\epsilon_p''$ were used for the calculation ($n_p=1.862$).

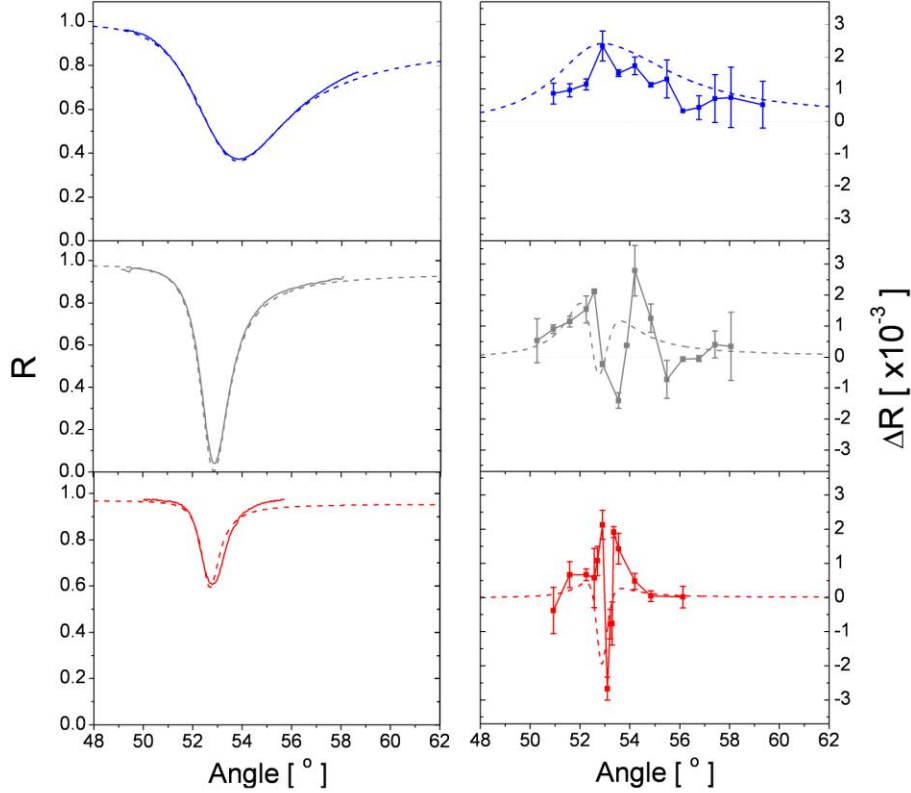


Figure 6.13 Measured angular reflectivity and differential reflectivity curves for three silver thicknesses of 34 nm, 53 nm, and 76 nm in the two-layer structures, which are fitted with theoretical curves (dotted lines). 34 nm, 53 nm, and 76 nm thicknesses are indicated as different colours of blue, grey, and red, respectively. For the ΔR calculation for each silver thickness, $\Delta\epsilon_p'' = -5.5 \times 10^{-4}$ is used.

The experimental curves are in good agreement with the theoretical ones. The theoretical curves of ΔR for all the three silver thicknesses, were produced using $\Delta\epsilon_p'' = -5.0 \times 10^{-4}$. As expected through the analysis using loss components (c.f. section 6.2.1), the two cases of 37 nm and 76 nm thicknesses exhibit distinctively different signs of ΔR over the observed angle range. 37 nm thick silver have only positive values over the entire angle range, while ΔR for 76 nm thick silver become negative at around the resonance angle. ΔR for 53 nm (close to the optimum thickness) is shown to have a little complicated pattern of

ΔR in angle, fluctuating around 0. Figure 6.14 shows theoretical angular reflectivity and differential reflectivity according to $\Delta\epsilon_p''$ values of -4×10^{-4} , -7×10^{-4} and -10×10^{-4} . It is noted that absolute values of ΔR increases linearly with respect to $\Delta\epsilon_p''$ at any angle of incidence.

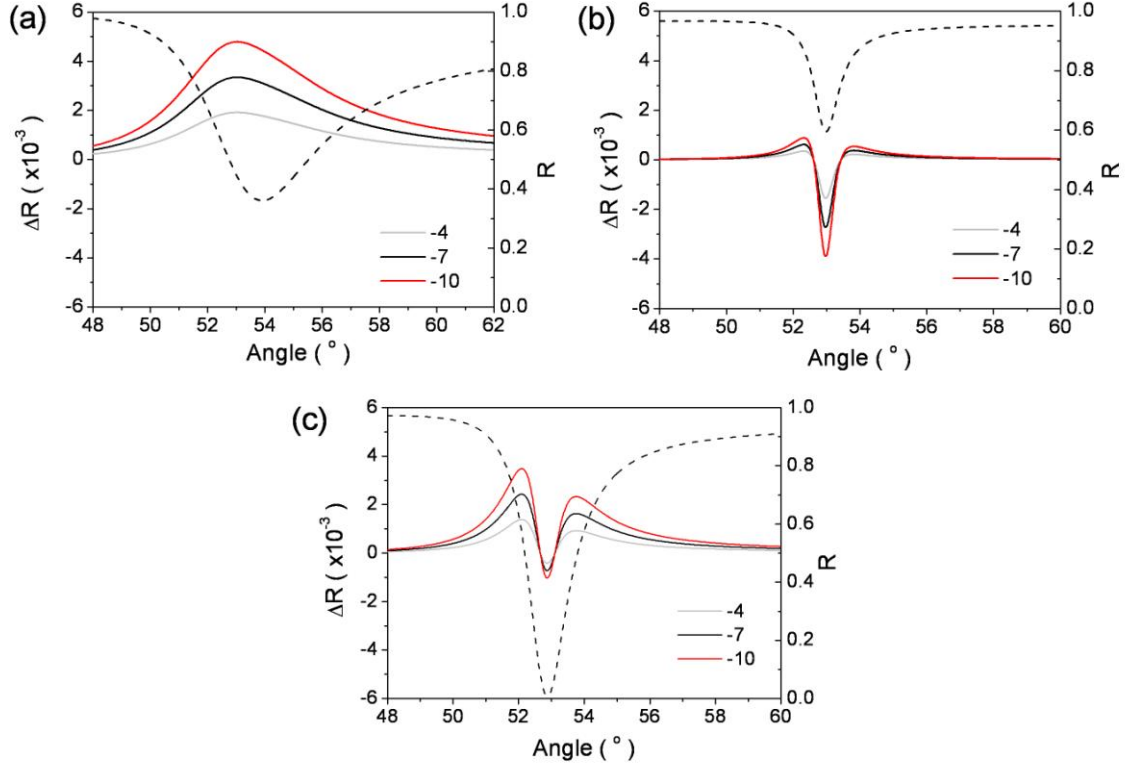


Figure 6.14 Theoretical angular reflectivity and differential reflectivity according to $\Delta\epsilon_p''$ ($\times 10^{-4}$) values (a) 34 nm thick silver film (b) 76 nm thick silver film (c) 53 nm thick silver film.

6.4.2 Other Effects

In this experiment, two effects on the differential reflectivity need to be addressed: thermal effect [24] and real value change of electric permittivity of the polymer via Kramers-Kronig relations [4]. Firstly, the high energy pump beam may possibly generate heat on the metal, thus creating the reflectivity change. To evaluate the possibility, a 53 nm thick single silver film on prism without a polymer film was examined as shown in figure 6.15. At three angle positions θ_0 , θ_1 and θ_2 of the measured reflectivity curve data in the figure 6.15 (a), The existence of the output signals at the lock-in amplifier 2 that corresponds to ΔR were recorded in time scale. As shown in the figure 6.15(b), there are no signals occurred under the pump beam exposure of the maximum energy density (1 mJ/cm^2) we were

capable of using.

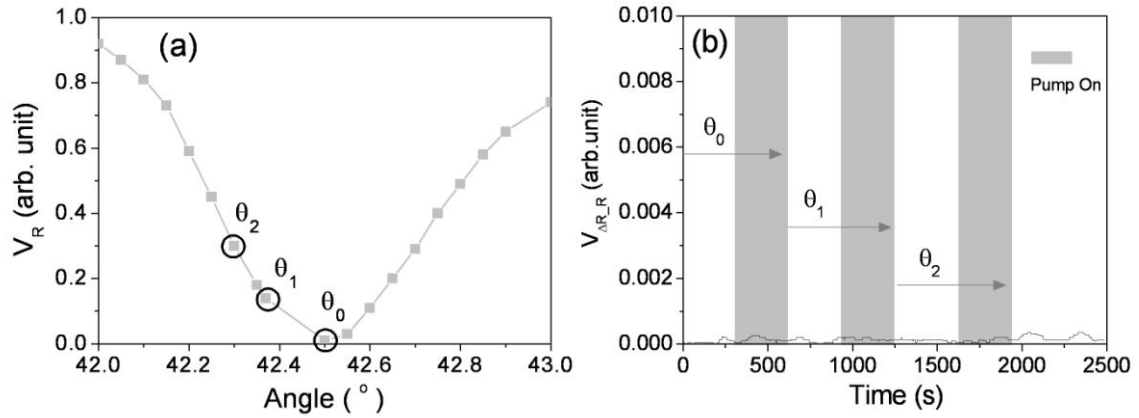


Figure 6.15 (a) Measured angular reflectivity curve from 53 nm thick silver films without Lumogen Red polymer film. Three incident angle positions of θ_0 , θ_1 and θ_2 are pointed out in the graph. (b) Time evolution of voltage signals at the lock-in amplifier 2 at three incident angles selected from the graph, which are associated with the ΔR .

Secondly, the $\Delta\epsilon_p''$ causes $\Delta\epsilon_p'$ which is main reason of shifting a resonance angle in $\Delta R(\theta)$ and $R(\theta)$. The angular shift from the transfer matrix calculations is predicted to be less than 0.25 degrees that comes from an assumed extreme condition, $\Delta\epsilon_p' / \Delta\epsilon_p'' = 1$ (Figure 6.16). Such a shift was not detected in our experiments. However, if the angular shape is more concerned, those situations need to be identified.

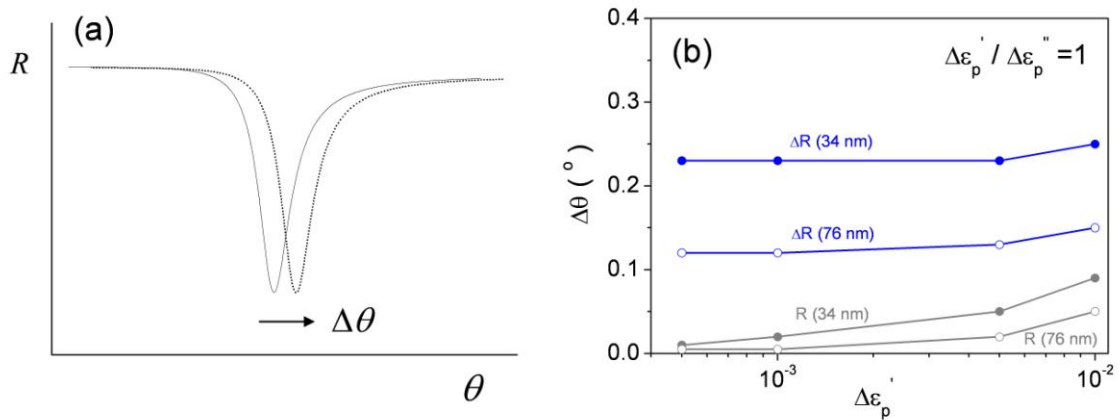


Figure 6.16 (a) Schematic of angular shift of a reflectivity curve due to variation of the real part of polymer permittivity, $\Delta\epsilon_p'$ (b) Calculated angular shift of R and ΔR curves for 34 nm and 76 nm silver thicknesses.

6.5 Extraction of Plasmonic Gain

Experimentally we can obtain the $\Delta\epsilon_p''$ value, which is inferred by comparing the experimental ΔR with theoretical ΔR , which produces a material gain g_m (c.f. equation 6.3). To precisely estimate the change of SPP modal propagation, however, an additional calculation needs to be performed. The calculation of the relevant propagation vector for each silver thickness is executed by inserting $\Delta\epsilon_p''$ into the numerical calculation of the transfer matrix method (c.f. Chapter 3). Thus, compensated *modal* gain in cm^{-1} can be obtained by subtracting the propagation loss in the absence of $\Delta\epsilon_p''$ from one in the presence of $\Delta\epsilon_p''$ as is made for ΔR calculation.

$$g_{\text{mod}} = 2(k_g'' - k_0'') \quad (6.10)$$

where k_g'' and k_0'' are the imaginary parts of propagation vectors in the presence and absence of a gain, respectively. The figure 6.18 is a diagram of the process for estimating plasmonic modal gain. Using the TMM as we did for ΔR estimates, the change of the imaginary part of the complex propagation vector of SPP mode due to the $\Delta\epsilon_p''$ value is calculated, finally yielding a compensated modal gain g_{mod} (c.f. equation 6.2).

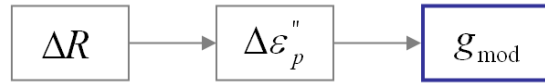


Figure 6.17 Extraction process of plasmonic modal gain g_{mod} from the factor ΔR observed in the Kretschmann configuration, which is based on the transfer matrix method theoretically estimating angular reflectivity changes and modal dispersion equation.

Figure 6.18(a) shows the calculated material gain g_m and modal gain g_{mod} as a function of $\Delta\epsilon_p''$. It was assumed that there is no change of real part of electric permittivity $\Delta\epsilon_p'$ of Lumogen Red polymer. Both g_m and g_{mod} increase linearly as the absolute value of $\Delta\epsilon_p''$ increases. An interesting observation is that g_{mod} does not depend on the silver thickness even though each thickness presents completely different ΔR shape. This indicates that different thicknesses experience virtually the same level of loss compensation. The reason of varying ΔR shapes can be attributed as the characteristic of leaky modes appeared in the Kretschmann geometry as discussed in the viewpoint of loss components. It may be speculated that if the near fields of the modes is observed directly via SNOM technique, we might get the same conclusion. In the figure, it is noted that the ratio of the material gain to the modal gain is about 31 %. In other words, actual gain of SPP modes emerged in

the multi-layer configuration is about 30% lower than the material gain from the configuration with around 40 nm thick polymer films irrespective of the metal film thickness.

To quantify the gain values under our pumping condition, measured material gains and corresponding modal gains for 34 nm, 53 nm and 76 nm thick silver film cases is plotted in Figure 6.17 (b). The measured value of $\Delta\epsilon_p'' = -5.7 \times 10^{-4}$ under the energy fluence of 1 mJ/cm² is indicated in figure 6.18(a). Average material gain g_m and modal gain g_{mod} are 29.4 cm⁻¹ and 9 cm⁻¹ respectively. The observed modal gain is a very small level of loss compensation compared to the propagation loss of the modes in the ‘two-layer’ structures ($>10^3$ cm⁻¹).

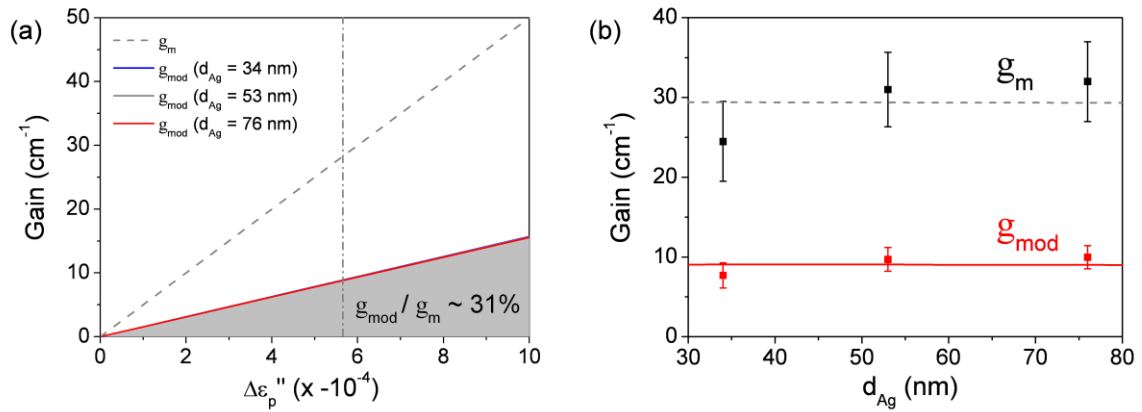


Figure 6.18 (a) Comparison of material gain g_m (grey dashed line) and modal gain g_{mod} for Ag thicknesses of 34 nm (black solid line), 53 nm (red solid line) and 76 nm (blue solid line). The g_{mod} lines for each thickness are overlapped among each others, which means that modal gains for any thickness are virtually same. The vertical dot-dashed line indicates the measured value of $\Delta\epsilon_p'' = -5.7 \times 10^{-4}$ under the energy fluence of 1 mJ/cm² (b) Measured material gain, g_m and plasmonic modal gain g_{mod} for 34 nm, 53 nm and 76 nm thick silver film cases under the energy fluence of 1 mJ/cm². Dotted lines are average values for g_m and g_{mod} .

The another point to be stressed is that the ratio is almost same as the calculated gain factors γ_p related to optical confinement factors for strongly confined TM modes at the same layer structure (see Section 5.3.1), confirming that the modal analysis is reliable for estimating propagation gain. For an example, Table 6.1 compares obtained modal gain g_c from calculated gain factors γ_p with the modal gain g_{mod} from the TMM. This implies that the gain factor approach gives quick and reasonable estimate of g_{mod} .

d_{Ag}	γ_p	$g_{mod} [cm^{-1}]$	$g_c (= \gamma_p \cdot g_m) [cm^{-1}]$
34 nm	0.297	7.69	7.27
53 nm	0.302	7.67	7.39
67 nm	0.280	7.63	6.86

Table 6.2 Calculated gain factors γ_p in the active polymer films for three silver thicknesses 34 nm, 53 nm, 76 nm, and comparison of the modal gains: g_c using γ_p and g_{mod} (from figure 6.16). This data are from the case of $\Delta\epsilon_p'' = -5.0 \times 10^{-4}$ ($g_m = 24.5 \text{ cm}^{-1}$). γ_p is calculated by using equation (5.2).

6.6 Effect of Spacer Layer

We have seen the evidence of interactions between excitons and plasmonic media and have successfully demonstrated optical gain in the plasmonic structures by introducing a thin gain medium. We now look to the optimization of plasmonic gain via structural modification. Studies to date have shown that the plasmonic interaction can be manipulated by changing the supporting geometry [Ch5.12]. Here, we also adopt the scheme to the two-layer structures we studied and show experimental demonstration of the improvement of modal gain.

Our key strategy is to insert a thin spacer layer (inert material) between a metal film and an active film, building on earlier studies within the group [25]. This preliminary work demonstrated a substantial decrease in the quenching of dipole energy [Ch5.1]. In our measurements the experiments were performed using the Kretschmann geometry, still maintaining the thickness of the polymer film as illustrated in figure 6.21. Lithium fluoride (LiF) was used as the spacer layer, which is known to be chemically strong. LiF films of nominal thickness of 11 nm were evaporated on silver films with varying thickness, followed by the polymer film deposition. LiF has relatively low refractive index of 1.39 at 675 nm. The thin films, nevertheless, affected angular reflectivity curves significantly (Figure 6.22). For both $d_{Ag} = 34 \text{ nm}$ and 76 nm , the resonance angles moved by around 2° , implying increased the effective indexes of the related modes, while the angular shapes did not change at all. The movement is exactly explained by the theoretical calculations (dotted lines).

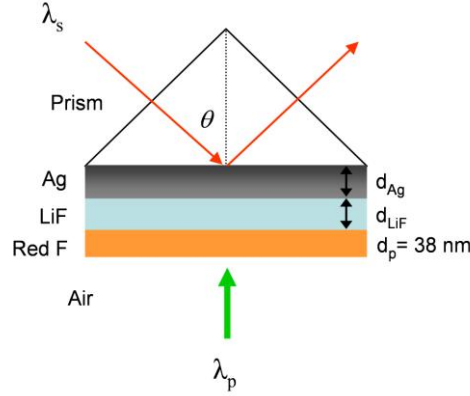


Figure 6.19 Layer configuration for improving the plasmonic gain by inserting the spacer layer of a LiF film between the silver (d_{Ag}) and the polymer film (38 nm). The thickness of the spacer layer d_{LiF} was nominally 11 nm.

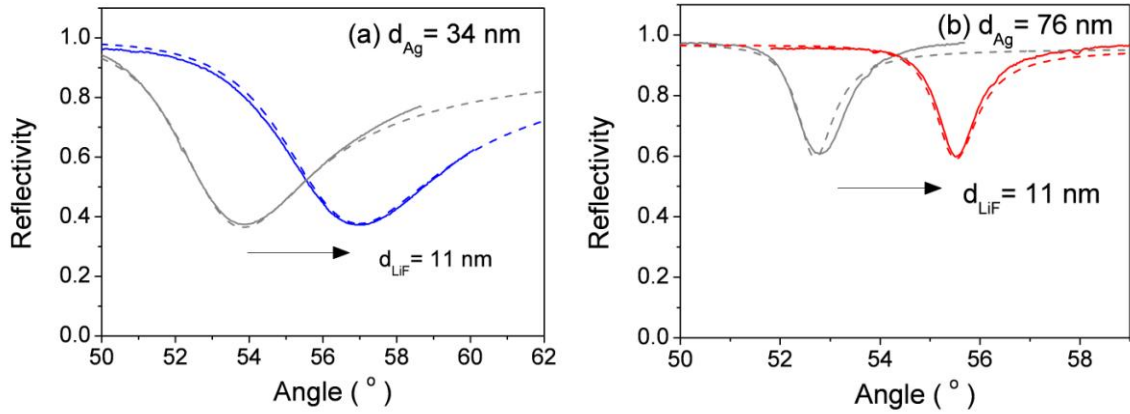


Figure 6.20 Measured angular reflectivity curves for three silver thicknesses of (a) 34 nm and (b) 76 nm in the two-layer structures, which are fitted with theoretical curves (dotted lines). Each silver thickness is indicated as different colours of blue, grey, and red, respectively.

To study the effect of LiF films on plasmonic gain, the differential angular reflectivity curves were measured using the same detection scheme (single pulse pumping condition) as shown in figure 6.23. For the presence of the LiF films, angular positions where maximum ΔR occur also moved to larger positions than the case without the LiF films as appeared in R curves, and overall trends of ΔR depending on d_{Ag} were same except that maximum ΔR values were increased, meaning that higher $\Delta\epsilon_p''$ were obtained. Inferred $\Delta\epsilon_p''$ values were -7.0×10^{-4} that corresponds to a modal gain g_{mod} of 11 cm^{-1} . This is about 30% improvement and clearly demonstrates the spacer layer, reduces the quenching and helps to improve plasmonic gain.

Further evidence of the role the spacer layer plays in terms of the energy dissipation

can be found from the fluorescence lifetime measurement and photoluminescence quantum yield measurement. The fluorescence lifetimes were found to increase for both $d_{\text{Ag}} = 34$ nm and 76 nm (c.f. figure 6.24), implying that total dissipation rate is substantially reduced, presumably because dipoles are now positioned further from the metal layer experience less quenching. For Ag 70 nm case, it is observed that the LiF film improves PLQE by 30 %.

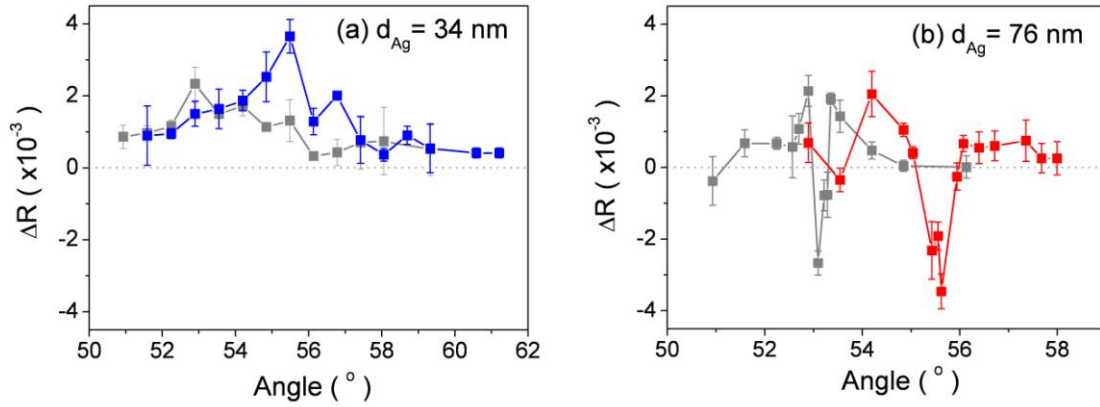


Figure 6.21 Measured differential reflectivity curves for two silver thicknesses of (a) 34 nm and (b) 76 nm in the two-layer structures. Each silver thickness is indicated as different colours of blue, grey, and red, respectively. For the ΔR calculation of each silver thickness, $\Delta \epsilon_p'' = -7.0 \times 10^{-4}$ is used.

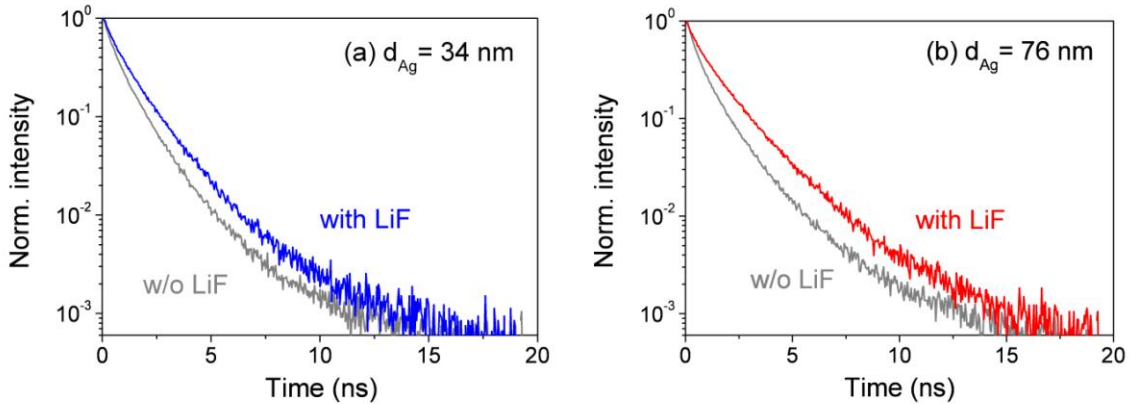


Figure 6.22 Effect of the LiF spacer layer on fluorescence lifetime (normalized) from BK7 plain glass / silver (d_{Ag}) / LiF / Lumogen Red (38 nm) / air multilayer configuration (a) for $d_{\text{Ag}} = 34$ nm, Inserting LiF layer leads to a variation of fluorescence decay time $\langle \tau \rangle$ from 1.20 ns to 1.44 ns (20% increase) (b) for $d_{\text{Ag}} = 76$ nm, LiF layer changes fluorescence lifetime $\langle \tau \rangle$ from 1.28 ns to 1.68 ns (30% increase)

6.7 Towards Active Plasmonic Devices

To achieve the gain function in plasmonic waveguides, there are three key factors we must take into account; waveguide structure with lower loss, efficient coupling of dipole energy to plasmonic modes and smaller design with sub-micrometre scale. Here, we focus on more low-loss waveguide cross-section design. As we discussed, the one-dimensional Kretschmann geometry is not ideally suited for practical application except possibly for applications based around sensing and imaging applications. For information processing perspectives, two-dimensional or three-dimensional structures with design flexibility may be more suitable and essential as many kinds of structure have been suggested, for instance, dielectric loaded surface plasmon polaritons waveguides (DLSPPW) [26], long-range surface plasmon waveguides (LRSPW) [27,28] and hybrid plasmonic waveguides [29,30]. Such the structures manage their electric field to distribute more in dielectric than metallic layer, which yield less propagation loss. This strategy gives not only efficient use of active materials incorporated into the structures, but also could lead to realistic devices with high practicality.

We examine the possibility of loss management by introducing plasmonic waveguides with a metallic stripe surrounded by the active polymer material we employed in this thesis. It is known that a metallic element in as close as symmetric environment has better performance in terms of propagation loss [27,31]. An investigated structures (figure 6.23) has a finite thick polymer slab film ($H_p = 100$ nm) that symmetrically surround a metal stripe of a thickness d_{Ag} and a width W . Specifically it is noted that the polymer film in combination with the metal stripe support no waveguide modes, reflecting our intention to support only plasmonic modes. An infinite W case corresponds to a one-dimensional structure (slab waveguide). Using the cross-section design, the conceptual schematic of an all-optical functional waveguide for a signal light (λ_{probe}), driven by the pump light (λ_{pump}) is shown on left in figure 6.23. By externally supplying energy into the structures, the input signal can be modulated or amplified. To estimate the potential active function, we employed a numerical method as mode solver.

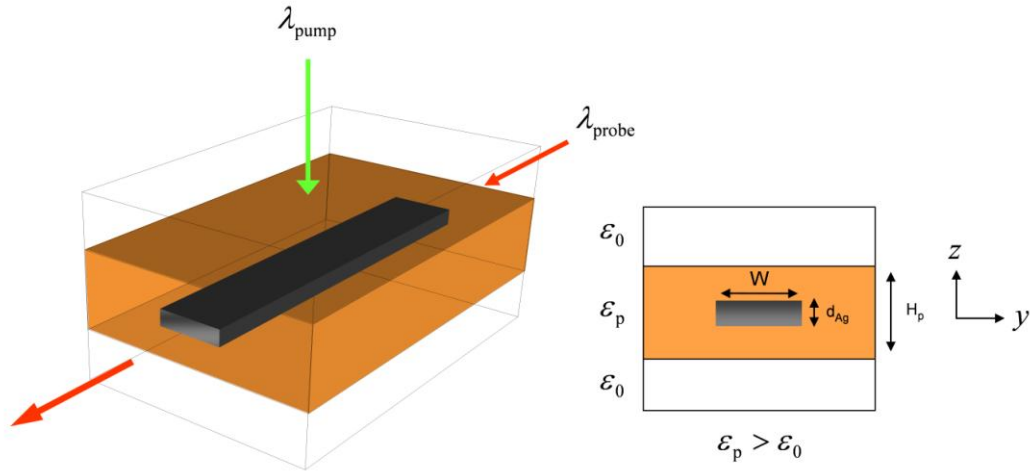


Figure 6.23 A possible design of cross-section of active plasmonic waveguides based on a metal (silver) stripe with a thin thickness incorporating a finite thick active polymer medium. The specific design parameters including stripe thickness (d_{Ag}), polymer film thickness (H_p) and varying metal stripe width, W are used as depicted. The cross-section geometry lies in the z - y plane (mode propagation direction is x -axis). Polymer permittivity ϵ_p is usually higher than glass materials' ϵ_0 . Using the cross-section geometry, input signal (λ_{probe}) modulation concept via optical pumping at λ_{pump} is described. (c.f. on left figure)

For the numerical investigation of supported mode behaviour, finite element calculation was performed using a commercial tool (COMSOL, Co. Ltd.). For the calculation, a defined area is divided into sub-elements with triangular shape, which is 'meshing' procedure (figure 6.24), and then the relevant partial differential equations are solved for propagation constants and corresponding field distributions. The size of the mesh is usually non-uniform, which should be smaller for sections of interest (c.f. the metal stripe and the polymer region, where most of energy of supported modes is expected to reside, have more fine meshing elements than the glass region.). The boundary condition along the outside of the whole structure is perfect magnetic conductor setting magnetic field to be zero. The mode calculation is made in the y - z plane and the wave propagation is in the x direction. The mode wave (e.g. magnetic field) has the form of

$$H(y, z) = f(y, z) \cdot e^{-i \frac{2\pi}{\lambda} (n_{eff} + i k_{eff}) x} \quad (6.11)$$

Where $f(y, z)$ is a transverse field distribution at $\lambda = \lambda_{probe}$, and n_{eff} and k_{eff} are the real and imaginary part of an effective propagation vector of a supported mode. The Helmholtz equation is solved for the effective propagation vectors and the corresponding fields. Propagation loss of the modes L is determined by $Loss = (4\pi / \lambda) k_{eff}$.

For the given structures, supporting modes are in general hybrid modes comprised of both TE and TM modes, and among electric and magnetic field components, E_z component is most dominant [27]. In figure 6.25, the calculated fundamental transverse modes with symmetric and asymmetric E_z field distribution across the y-axis (for $W = 2 \mu\text{m}$) are displayed in terms of power distribution P_x and the line distribution of E_z field. The visual comparison between both modes helps understand their propagating behaviour. It is clear that compared to the asymmetric mode, the symmetric mode has larger field size and its field distribution lies more in the lossless glass areas, implying less propagation loss.

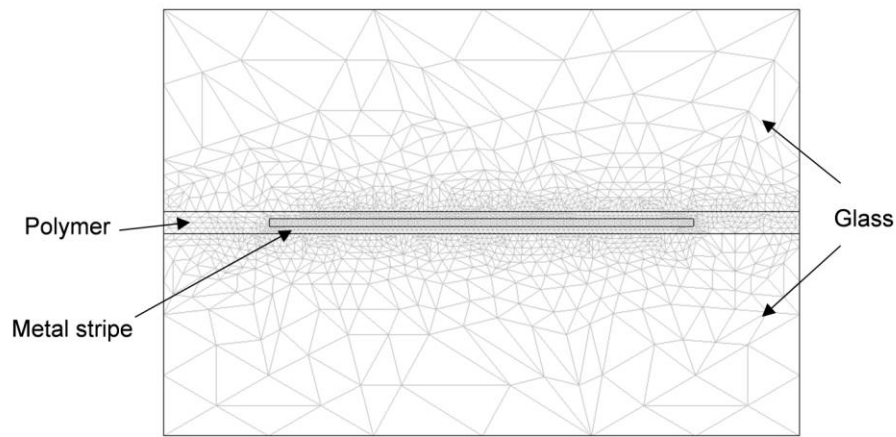


Figure 6.24 An example of meshing for the structure ($W = 2 \mu\text{m}$) we concern for finite element calculation in COMSOL commercial tool. The non-uniform meshing is distributed in the two-dimensional plane for calculating the modal propagation vectors and the distributions of electric and magnetic field components across the cross-section. Each meshing segment is a triangular shape, getting smaller (finer) around the area particularly concerned, where propagating modes of interest is excited (around the metal stripe).

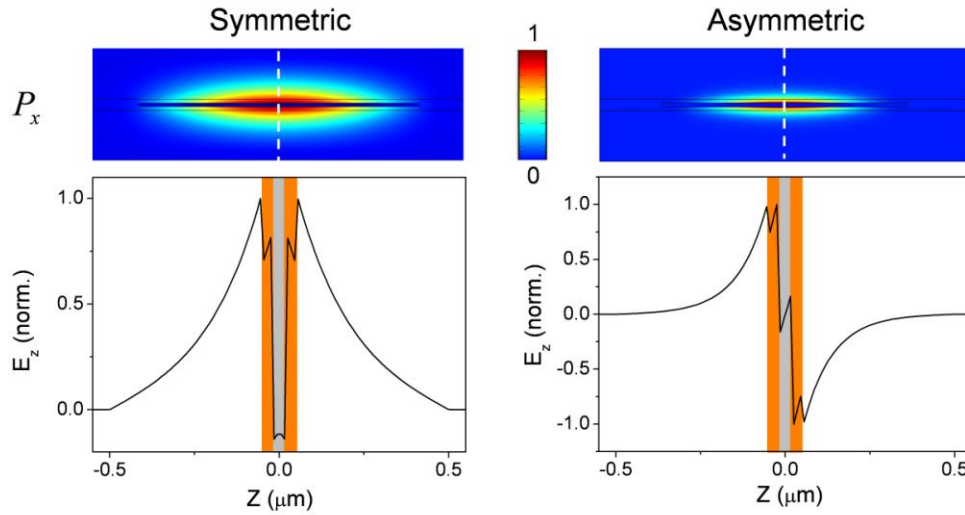


Figure 6.25 Normalised power P_x and electric field E_z distributions of transversely symmetric and asymmetric modes that the structure ($W=2\ \mu\text{m}$) supports. E_z distributions were taken along z -axis at $y=0$ (white dashed lines).

Furthermore, systematic analysis of both modes against the varying W strongly indicates strategic direction about the loss management. Figure 6.26 shows effective index and propagation loss of both modes as a function of W . The index difference between the polymer ($n_p=1.86$, Lumogen Red polymer) and glass ($n_0=1.514$) as indicated in the figure is set to $\Delta n \sim 0.35$, which is another important factor in determining mode behaviour. The symmetric modes have much lower effective indexes whose indices are close to the glass index, which also means their fields are more in glass (c.f. figure 6.27). It is noteworthy that the trend shows a big difference of the loss factor by more than a factor of 10. The other finding is that as W decrease, the effective indexes of both are steadily reduced, and at less than $W=1\ \mu\text{m}$, the loss of asymmetric modes begin to rise while the symmetric modes become less lossy. Therefore, one can expect that the symmetric modes with lower propagation losses are desirable for signal processing if the selective excitation of the modes may be possible [27]. As a next step, to estimate how optical gain affects on the modes, related quantitative analysis is necessary. For this, we also examine the change of propagation loss under optical gain by inserting a realistic value of the imaginary part of polymer permittivity $\Delta\epsilon_p''$ into the numerical calculation (c.f. dotted lines for each modes in the loss trend of figure 6.28). The used $\Delta\epsilon_p''$ was -1×10^{-3} , which corresponds to a material gain of about $50\ \text{cm}^{-1}$. This material gain value is easily achievable for conjugated polymer materials. The gain value basically leads to reduced propagation loss for both the modes. However the asymmetric mode case looks negligible, while the symmetric mode gets bigger impact.

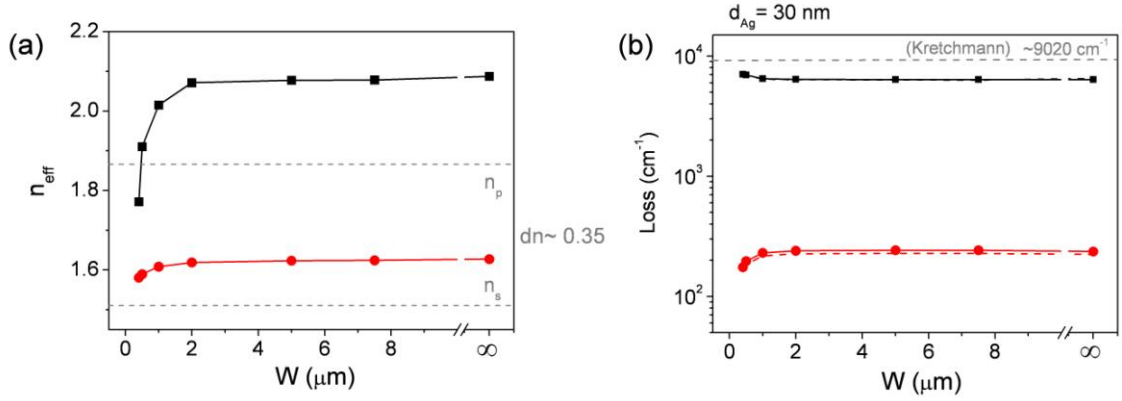


Figure 6.26 Stripe width dependence of plasmonic modes. (a) calculated effective indexes, n_{eff} and (b) propagation losses of symmetric (red color) and asymmetric (black color) plasmonic modes for the case of $\Delta n \sim 0.35$ as a function of the stripe width, W . In the ‘loss’ graph, the dotted lines are for the polymer layer that has a material gain of 50 cm^{-1} . The calculated loss is the unit of cm^{-1} .

It is certain that the metal stripe thickness is a factor in determining mode properties (Figure 6.27). In particular decreasing the thickness improves propagation loss property for the symmetric mode. For instance, a stripe of $d_{\text{Ag}} = 10 \text{ nm}$ has a reduced loss of 30 cm^{-1} , which is an order of magnitude lower than for $d_{\text{Ag}} = 30 \text{ nm}$ (the vertical dotted line indicate the thickness position). Our concern is to design efficient waveguides with lower propagation loss, which potentially give higher signal control capability (extinction ratio) under a given optical gain. To assess the capability, the fractional change ratio of propagation loss due to gain were introduced and analyzed, which is given as $r(\%) = (L_0 - L_g)/L_0$ where L_0 and L_g is propagation losses in the presence and absence of gain, respectively. Reduced propagation losses for each modes (the dotted lines in figure 6.27) were calculated by applying the same material gain of 50 cm^{-1} and then the fractional change ratio $r(\%)$ were analyzed as can be seen in figure 6.27 (b). the asymmetrical can hardly obtain more than 1% ratio. In contrast, the symmetric modes are shown to possess up to 40 %. This is because of decreased proportion of field distribution in metal.

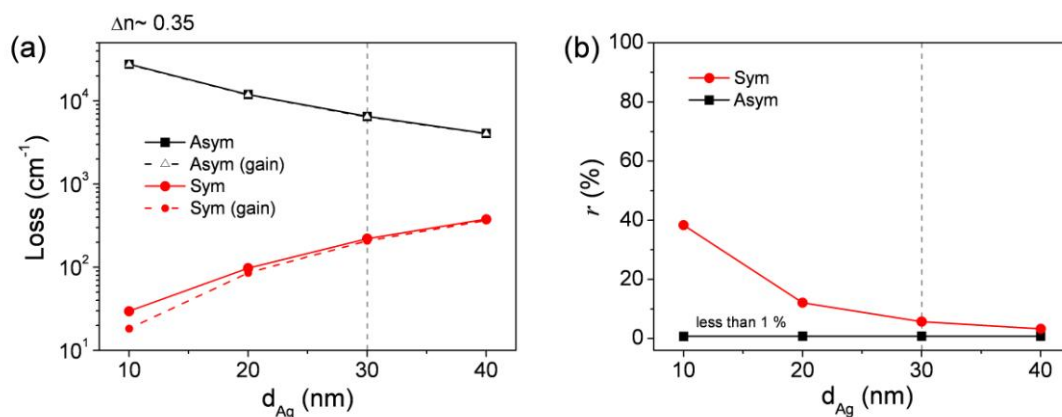


Figure 6.27 Effect of stripe metal thickness d_{Ag} on propagation loss (a) propagation losses of symmetric (red color) and asymmetric (black color) plasmonic modes for the case of $\Delta n \sim 0.35$ as a function of the stripe silver thickness d_{Ag} . The dotted line indicates the investigated condition $d_{Ag} = 30$ nm (c.f. figure 6.26) (b) Fractional change ratio (r) of propagation losses of symmetric and asymmetric plasmonic modes due to the polymer gain as a function of the stripe silver thickness d_{Ag} . The dotted lines are for the polymer layer that has a material gain of 50 cm^{-1} . The calculated loss is the unit of cm^{-1} .

In addition, the influence of the refractive index difference $\Delta n (=n_p - n_0)$ between the active polymer material and the surroundings (SiO_2) on the propagation loss were examined because refractive index distribution determines photon mode density (density of photon states) and field distribution. It is shown in figure 6.28 (a) that propagation losses are clearly reduced as Δn decreases, and at the same gain condition of 50 cm^{-1} , the degree of loss compensation is correspondingly improved (c.f. figure 6.28(b)), showing up to 90% signal change ($\Delta n \sim 0.35$, $d_{Ag} = 10$ nm). Hence, it is suggested that index difference must be taken into consideration as a design parameter. In practice, one may be able to control Δn by mixing gain materials with an inert material in a certain ratio [5,8], for our case, conjugated polymers in Poly(methyl methacrylate) (PMMA) matrix. r value has a very practical meaning for active function. For instance, $r = 100\%$ means that an active device can switch an input signal on and off completely, and in other words, the input signal can be recovered without degradation as it were. The loss compensation value obtained in our one-dimensional asymmetric layer configuration (grey dotted line) gives only 0.1% signal compensation (for the case, $d_{Ag} = 30$ nm). However, the symmetric structure, despite the fact that the mode selection process is necessary, could achieve more than 90 % signal variation under the same gain. If one of high gain polymeric materials currently available [32,33] is introduced into the guiding structure, we could easily accomplish more than 100% signal compensation, giving rise to plasmonic lasing.

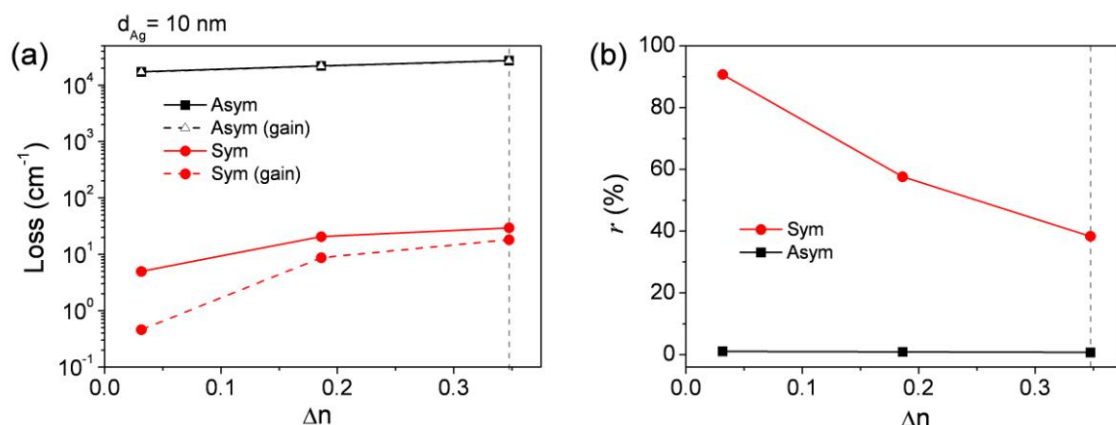


Figure 6.28 Improvement of plasmonic waveguides in terms of propagation loss by tuning the refractive index difference $\Delta n (=n_p - n_0)$ (a) propagation losses of symmetric (red color) and asymmetric (black color) plasmonic modes for $d_{Ag} = 10$ nm as a function of the refractive index difference, Δn . (b) Fractional change ratio (r) of propagation losses of symmetric and asymmetric plasmonic modes due to the polymer gain as a function of the refractive index difference, Δn .

6.8 Summary

Thin organic film-based plasmonic gain was investigated experimentally using the prism coupling technique and was carefully analyzed via the transfer matrix method. Angular reflectivity and differential angular reflectivity curves were measured using the ATR configuration in association with the double cascaded lock-in detection technique using short pulsed pump beams. Verification of the technique was presented as far as its signal process is concerned. We found that the thickness of silver film in the ATR geometry governs the plasmonic mode behaviour with gain, which is clearly identified shape of the reflectivity change curves and the related theoretical estimation.

We clearly identified that the propagation gain in a plasmonic waveguide can be created using optically excited thin light emitting polymers, and the achieved plasmonic modal gain from the configuration was 9 cm^{-1} . From the experimental observation, and with support from the modeling, it is suggested that the actual gain for different silver thicknesses are the same despite the fact that the angular differential reflectivity curves have different shapes. In addition, we showed that plasmonic gain may be improved (by around 30%) through the introduction of a thin optically inert spacer layer.

Based on our knowledge we learned from the one-dimensional structure, we also investigated the possibility of practical active plasmonic waveguides with two-dimensional

cross-section geometry of a metal stripe embedded in a thin polymer film, capable of signal processing with high extinction ratio (close to 100%). This design could form the basis of a range of guided-wave plasmonic devices, e.g. applied to filter or resonator designs.

References

- [1] I. Avrutsky, R. Soref, and W. Buchwald, "Sub-wavelength plasmonic modes in a conductor-gap-dielectric system with a nanoscale gap," *Opt. Express* **18**, 348-63 (2010).
- [2] Ş. Kocabaş, G. Veronis, D. Miller, and S. Fan, "Modal analysis and coupling in metal-insulator-metal waveguides," *Phys. Rev. B* **79**, 1-17 (2009).
- [3] L. H. Smith, M. C. Taylor, I. R. Hooper, and W. L. Barnes, "Field profiles of coupled surface plasmon-polaritons," *J. Mod. Opt.* **55**, 2929-2943 (2008).
- [4] J. Seidel, S. Grafström, and L. Eng, "Stimulated emission of surface plasmons at the interface between a silver film and an optically pumped dye solution," *Phys. Rev. Lett.* **94**, 177401 (2005).
- [5] M. Noginov, V. Podolskiy, G. Zhu, M. Mayy, M. Bahoura, J. Adegoke, B. Ritzo, and K. Reynolds, "Compensation of loss in propagating surface plasmon polariton by gain in adjacent dielectric medium," *Opt. Express* **16**, 1385-92 (2008).
- [6] M. Ambati, S. H. Nam, E. Ulin-Avila, D. A. Genov, G. Bartal, and X. Zhang, "Observation of stimulated emission of surface plasmon polaritons," *Nano lett.* **8**, 3998-4001 (2008).
- [7] I. De Leon and P. Berini, "Amplification of long-range surface plasmons by a dipolar gain medium," *Nature Photon.* **4**, 382–387 (2010).
- [8] J. Grandidier, G. C. des Francs, S. Massenot, A. Bouhelier, L. Markey, J.-C. Weeber, C. Finot, and A. Dereux, "Gain-assisted propagation in a plasmonic waveguide at telecom wavelength," *Nano lett.* **9**, 2935-9 (2009).
- [9] M. A. Noginov, G. Zhu, A. M. Belgrave, R. Bakker, V. M. Shalaev, E. E.

Narimanov, S. Stout, E. Herz, T. Suteewong, and U. Wiesner, "Demonstration of a spaser-based nanolaser," *Nature* **460**, 1110-2 (2009).

[10] R.-M. Ma, R. F. Oulton, V. J. Sorger, G. Bartal, and X. Zhang, "Room-temperature sub-diffraction-limited plasmon laser by total internal reflection," *Nature Mater.* **9**, 1-4 (2010).

[11] R.F. Oulton, V.J. Sorger, T. Zentgraf, R.-M. Ma, C. Gladden, L. Dai, G. Bartal, and X. Zhang, "Plasmon lasers at deep subwavelength scale," *Nature* **461**, 629-632 (2009).

[12] M. C. Gather, A. Kohnen, and K. Meerholz, "White organic light-emitting diodes," *Adv. Mater.* **23**, 233-248 (2011).

[13] A. Yariv, *Optical Electronics in Modern Communication* (Oxford University Press, 1997)

[14] A. E. Siegman, *Lasers* (University Science Books, 1986).

[15] S. V. Frolov and Z. V. Vardeny, "Double-modulation electro-optic sampling for pump-and-probe ultrafast correlation measurements," *Rev. Sci. Instrum.* **69**, 1257 (1998).

[16] D. Ionascu, F. Rosca, F. Gruia, A. Yu, and P. M. Champion, "Optical scanning instrument for ultrafast pump-probe spectroscopy of biomolecules at cryogenic temperatures," *Rev. Sci. Instrum.* **77**, 064303 (2006).

[17] P. L. Boulanger, J. Doualan, S. Girard, and J. Margerie, "Excited-state absorption spectroscopy of Er^{3+} -doped $\text{Y}_3\text{Al}_5\text{O}_{12}$, YVO_4 , and phosphate glass," *Phys. Rev. B* **60**, 11380-11390 (1999).

[18] R. Burdett, "Amplitude modulated signals: The lock in amplifier," in *Handbook of Measuring System Design* (John Wiley & Sons, Ltd, 2005).

[19] Signal recovery with PMTs (Application note, Standard Research System. Inc)

[20] High Speed Silicon Detector DET36A (Operating manual, Thorlabs. Inc)

[21] SR830 DSP lock-in amplifier (Operating manual, Standard Research System. Inc)

- [22] D. Bugg, *Electronics: Circuits, Amplifiers and Gates* (Taylor & Francis, 2006).
- [23] SR844 DSP lock-in amplifier (Operating manual, Standard Research System. Inc)
- [24] M. van Exter and A. Lagendijk, "Ultrashort surface-plasmon and phonon dynamics," *Phys. Rev. Lett.* **60**, 49-52 (1988).
- [25] Matthew Y. K. Ng, "Coupling of excited molecules to surface plasmon and other modes of dielectric/metal structures," Imperial College London, Ph. D Thesis (2010)
- [26] J. Grandidier, S. Massenot, G. des Francs, A. Bouhelier, J.-C. Weeber, L. Markey, A. Dereux, J. Renger, M. González, and R. Quidant, "Dielectric-loaded surface plasmon polariton waveguides: Figures of merit and mode characterization by image and Fourier plane leakage microscopy," *Phys. Rev. B* **78**, 1-9 (2008).
- [27] P. Berini, "Plasmon-polariton waves guided by thin lossy metal films of finite width: Bound modes of symmetric structures," *Phys. Rev. B* **61**, 10484-10503 (2000).
- [28] P. Berini, R. Charbonneau, and N. Lahoud, "Long-range surface plasmons along membrane-supported metal stripes," *IEEE J Sel. Top. Quant.* **14**, 1479-1495 (2008).
- [29] D. Dai, Y. Shi, S. He, L. Wosinski, and L. Thylen, "Gain enhancement in a hybrid plasmonic nano-waveguide with a low-index or high-index gain medium," *Opt. Express* **19**, 12925–12936 (2011).
- [30] R. F. Oulton, V. J. Sorger, D. A. Genov, D. F. P. Pile, and X. Zhang, "A hybrid plasmonic waveguide for subwavelength confinement and long-range propagation," *Nature Photon.* **2**, 496-500 (2008).
- [31] G. Winter, S. Wedge, and W. L. Barnes, "Can lasing at visible wavelengths be achieved using the low-loss long-range surface plasmon-polariton mode?," *New J. Phys.* **8**, 125-125 (2006).
- [32] T. Okamoto, F. H'Dhili, and S. Kawata, "Towards plasmonic band gap laser," *Appl. Phys. Lett.* **85**, 3968 (2004).

[33] M. C. Gather, K. Meerholz, N. Danz, and K. Leosson, "Net optical gain in a plasmonic waveguide embedded in a fluorescent polymer," *Nature Photon.* **4**, 457-461 (2010).

7 Conclusion

In this chapter, we summarise this work and suggest future research and applications. The key results of each chapter are restated. One of the main goals of this research is to demonstrate stimulated emission of SPPs using an active material on the sub-wavelength scale. To do this, both theoretical and experimental approaches were conducted. To initiate this work, the objectives listed below were addressed.

- To demonstrate the optical characteristics of the SPP modes in planar asymmetric metal/dielectric layer configurations using the prism-coupling method.
- To elucidate how a *thin* polymer film adjacent to a metallic layer determines the SPP modes.
- To show the optical properties of conjugated polymer films as optical gain.
- To describe how the SPP modes in the Kretschmann geometry interact with the active medium.
- To experimentally demonstrate plasmonic gain in metallo-organic multilayer structures incorporating the thin polymer film.

As a first step, the main materials comprising the planar SPP waveguides were introduced and their physical properties were shown along with the experimental methods for characterisation.

Metal/organic materials for plasmonic layer configurations (Chapter 2)

- To characterise plasmonic ingredients: silver as a metallic material and fullerene-based conjugated polymer as an active material.
- To show the basic optical properties of silver and conjugated polymers and highlight their pros and cons for plasmonic waveguides.

We clarified the role of multiple layers for SPP propagation, determining the propagation vector, propagation loss and their field distribution. It was clearly shown that varying silver films in a prism-based configuration sensitively determines the quantity of the propagation loss of the supported leaky modes, changing radiation loss. The loss components were also closely linked to the angular reflectivity curves that were experimentally observed. In addition, it was found that the physical variations of polymer films, e.g., specifically refractive index and thickness, play a great role in SPP behaviours.

Passive functions of SPP waveguides (Chapter 3 and 4)

- To implement the prism-coupling system and establish the fabrication of SPP structures.
- To obtain knowledge related to designing multilayer structures for plasmonic propagations by exploiting modal analysis and angular reflectivity curves.
- To probe and manipulate SPP characteristics by varying the geometrical dimension on a nanometre scale
- To establish the prediction of SPP properties using three theoretical approaches in terms of angular reflectivity curves and the propagation vectors of guided SPP modes.

Based on the establishment of passive functions of SPP modes, we moved to the active functions of SPPs in the metal/polymer layer structures. For this, we conducted direct measurement of optical gain using amplified spontaneous emission, giving clear evidence that thin active polymer films can possess strong optical gain by stimulated emission. It has been proven that oscillating dipoles via optical pumping can supply external energy to SPP modes through surface plasmon coupled emission (SPCE). Analysing the out-coupling light with respect to spectral components and angular distributions explained SPP-mediated emission well. We generated a solid foundation for knowledge about SPP interactions with gain medium, bridging the concept of SPP modes with plasmonic gain, which is our ultimate goal.

Active function of SPP waveguides (Chapter 5)

- To understand the SPP coupling via oscillating dipoles in a thin active film and show its unique emission properties.
- To present the systematic evaluation of the surface plasmon coupled emission and suggest a practical way of generating plasmon-mediated light out-coupling considering the emission bandwidth of Red F polymers.
- To examine the optical gain that arises in normal waveguide geometry using an active polymer film as a guiding layer.

Lastly, the demonstration of plasmonic gain using thin conjugated polymer films was presented. Thin conjugated polymer film-based plasmonic gain was investigated experimentally using prism coupling and was carefully analysed via the transfer matrix method. Angular reflectivity and reflectivity change curves were measured through the ATR configuration supported by a modified double cascaded lock-in detection technique. We found that the thickness of silver film in the ATR geometry determines the plasmonic

mode behaviour with gain, which is clearly identified by investigating the reflectivity change curves and the related theoretical estimation. We identified that the propagation gain in a plasmonic waveguide can be created through optically excited light-emitting polymers, and that apart from an option of selecting other promising gain materials, we could also improve the structure relating to the position of an active layer in any complex plasmonic configuration to optimise gain properties. In addition, we suggested a waveguide design to achieve complete compensation of loss, where the thickness level of an active polymer layer is to be kept at no more than 100 nm.

Plasmonic gain in SPP waveguides (Chapter 6)

- To introduce the modified double-modulation technique for precisely measuring plasmonic gain signals.
- To demonstrate plasmonic gain in the planar SPP waveguides incorporating thin films for the first time.
- To suggest a new waveguide cross-section design exploiting the thin polymer films.

This work showed only partial compensation of a propagation loss of SPP modes. Still, this provides useful information on the interaction between the SPP modes and a gain medium, and suggests a clear way of designing optimum SPP waveguides for gain which comprise multiple layers of different materials. This study resulted in two findings: 1) the ATR method is a feasible tool to effectively probe gain-assisted surface plasmon polaritons; and 2) conjugated polymers are a very promising material as a plasmonic gain medium from the viewpoint of the gain value itself, as well as the production process. Thus, this work provides a practical guide for developing novel active plasmon-based applications.

Future Work

We have demonstrated the SPPs' behaviours using the prism-coupling system, which allows us to study near-field effects very accurately by means of far-field excitation and detection. Furthermore, the system has been proven capable of investigating active as well as passive functions of SPPs. Using this platform could indeed allow many interesting subjects to be studied. In this work, we have only dealt with silver as a metallic layer. SPP-related study can be extended to many kinds of materials possessing metallic properties beyond the noble metals, for instance, transparent oxide materials (ZnO, InSn₂O₃), metallic molecules (PEDOT-PSS), carbon-based materials (carbon nanotubes and graphene), etc. These new materials have been widely used and studied for a new generation of electrode materials in the range of optoelectronic devices, and in any devices using those materials,

surface plasmon effects continue to be inescapable. For SPP-based sensing applications, finding new materials is a possible solution to improve detection resolution. Hence, investigating SPP properties for those materials will give valuable information for the design of optical devices.

As mentioned previously, for nanophotonic applications, waveguide design is important when it comes to achieving nanoscale field confinement with less propagation loss. The geometry using a single metallic layer discussed in this work obviously has the limitation of manipulating light for waveguiding applications. Guided SPP modes in complicated structures with more degrees of freedom need to be investigated, specifically metal/dielectric/metal (MDM), dielectric/metal/dielectric (DMD) and metal/dielectric/dielectric (MDD) structures. The momentum view (angular response) by prism coupling can allow us to separate each SPP mode that the structures can possibly possess and study their properties individually. It is obvious that characterising specific SPP modes is a prerequisite for the development of potential devices.

The plasmonic gain discussed in chapter 6 was demonstrated using the red-emitting material, Red F conjugated polymer. It is necessary to conduct the same study with different visible frequencies and even other frequency ranges. Conjugated polymers are known to cover the whole visible frequency range. It is therefore expected that the colour study of SPP modes, especially in view of SPCE and plasmonic gain, will provide more solid evidence of SPP characteristics and useful knowledge to other scientists to exploit for their SPP-related research.

Our ultimate goal in this work is to demonstrate complete loss compensation and even nano-lasing. For this, among many challenges, choosing appropriate gain materials is crucial in terms of achievable gain and the fabrication method.

Appendix

A. Power Dissipation Density Calculation

The nature of dipole energy dissipation to various channels including surface plasmon polaritons, arising in a multi-layer structure and the strength of coupling to the channels can be studied by using the semiclassical approach of Ford and Weber [Ch5.1]. When an oscillating point dipole in a gain medium is positioned in multi-layer structures as depicted in figure A.1, emitting fields of the dipole oscillation interact with its reflected fields from stacked optical multi-layer structures. Decay rate γ rate at which a dipole moment p of the oscillator with the angular frequency ω does work on the resultant field E of superposition of dipole field itself E_{dipole} and reflected fields E_r at the upper and lower interfaces from the dipole position is expressed by

$$\gamma = \frac{\omega}{2} \text{Im}(p^* \cdot E) \quad (\text{A.1})$$

Normalized decay rate with respect to the decay rate in infinite active medium may be expressed by

$$\hat{\gamma} \equiv \frac{\gamma}{\gamma_{free}} = 1 - \eta + \eta \int_0^\infty I_{\perp,\parallel}(k_{\parallel}) \cdot dk_{\parallel} \quad (\text{A.2})$$

where $k_{\parallel}$ is the in-plane wavevector and η is the internal quantum efficiency of free dipole, which is an probability of emitting photons under the competition with non-radiative decay channels. The integrand $I_{\perp,\parallel}$ is the normalized power dissipation density for perpendicular and parallel dipole orientations.

The power dissipation density of the dipole oriented at an angle α from the normal to the interfaces is given as

$$I_{\perp,\parallel} = \frac{1}{P_{free}} \frac{dP}{dk_{\parallel}} = I_{\perp} \cos^2 \alpha + I_{\parallel} \sin^2 \alpha \quad (\text{A.3})$$

$$I_{\perp,\parallel} = \frac{3}{2} \frac{1}{k_e^3} \frac{k_{\parallel}^3}{q_e} \frac{[1 + r_-^P \exp(2iq_e d_-)] \cdot [1 + r_{e+}^P \exp(2iq_e d_+)]}{1 - r_-^P r_+^P \exp(2iq_e D)} \quad (\text{A.4a})$$

$$I_{\perp,\parallel} = \frac{3}{4} \frac{1}{k_e^3} \frac{k_{\parallel}}{q_e} \left(k_e^2 \frac{[1 + r_-^S \exp(2iq_e d_-)] \cdot [1 + r_+^S \exp(2iq_e d_+)]}{1 - r_-^S r_+^S \exp(2iq_e D)} + q_e^2 \frac{[1 - r_-^P \exp(2iq_e d_-)] \cdot [1 - r_+^P \exp(2iq_e d_+)]}{1 - r_-^P r_+^P \exp(2iq_e D)} \right) \quad (\text{A.4b})$$

where $k_e = 2\pi\sqrt{\varepsilon_e}/\lambda$ wavevector in the gain material and $q_e = (k_e^2 - k_{\parallel}^2)^{1/2}$ is the perpendicular (out-of-plane) wavevector and $r_+^{S,P}$ and $r_-^{S,P}$ are effective TE and TM polarized reflectivities at lower and upper layers, respectively.

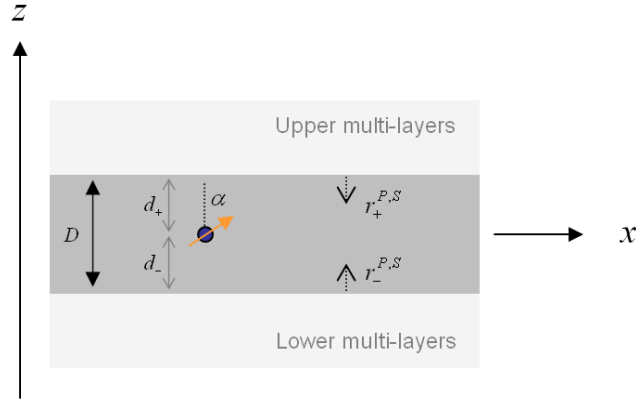


Figure A.1 Description of an oscillating dipole in the multi-layer structures. The dipole is assumed to be located at the distance d_+ from the upper interface and the distance d_- from the lower interface in the active medium of thickness $D = (d_+ + d_-)$.

B. Angular Radiation Distribution

Angular radiation distribution of an oscillating dipole in a multi-layer structure can be modeled by the theoretical method based on the Lorentz reciprocity theorem []. We here reproduce the theoretical descriptions that Luan, et al., derived in their publication []. This method can determine p and s-polarized normalized power distribution, $P^P(\theta, \varphi)$ and $P^S(\theta, \varphi)$ for a dipole oriented at a polar angle α from the normal to the layer interfaces at the azimuth angle φ and polar angles θ .

$$\begin{aligned} P^P(\theta, \varphi) &= \cos^2 \alpha \cdot P_{\perp}^P(\theta) + \sin^2 \alpha \cdot \cos^2 \varphi \cdot P_{\parallel}^P(\theta), \\ P^S(\theta, \varphi) &= \sin^2 \alpha \cdot \sin^2 \varphi \cdot P_{\parallel}^S(\theta) \end{aligned} \quad (\text{B.1})$$

This is generalized expressions considering dipole orientation and angular emission direction. If dipoles are randomly oriented, one has

$$\begin{aligned} P^P(\theta, \varphi) &= 1/3 \cdot P_{\perp}^P(\theta) + 1/3 \cdot P_{\parallel}^P(\theta), \\ P^S(\theta, \varphi) &= 1/3 \cdot P_{\parallel}^S(\theta) \end{aligned} \quad (\text{B.2})$$

As basic ingredients of the equation (B.1), $P_{\parallel}^P(\theta)$ and $P_{\parallel}^S(\theta)$ are p- and s-polarized radiation signals for dipoles oriented parallel to the interfaces, and $P_{\perp}^P(\theta)$ a p- polarized radiation signal for dipoles oriented perpendicular to the interfaces (perpendicular orientation contributes only to p-polarization). The superscripts represent polarization of light and the subscripts represent dipole orientation.

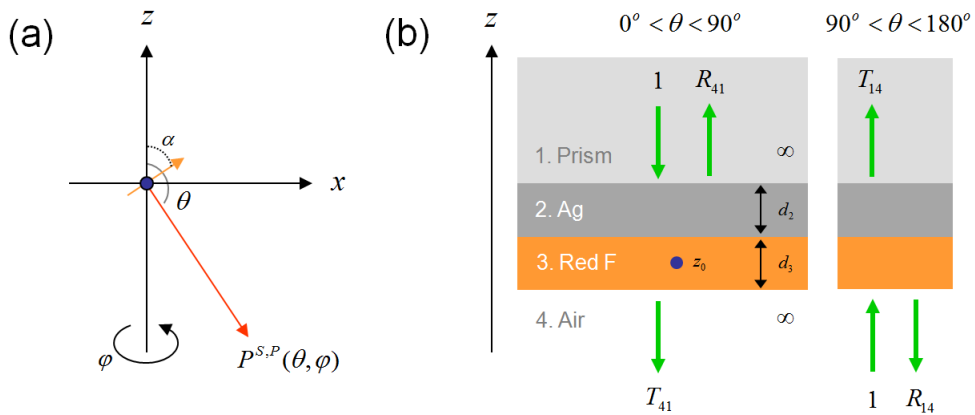


Figure B.1 (a) Description of dipole orientation and angular radiation direction (b) Layer configuration and the transfer matrix calculation direction according to the emission angle range

To derive $P_{\parallel}^P(\theta)$, $P_{\parallel}^S(\theta)$ and $P_{\perp}^P(\theta)$ on the basis of the Lorentz reciprocity theorem, we calculate electric fields $E^{S,P}(z_0)$ at the dipole position z_0 with respect to incoming fields $|E_{in}|=1$ propagating from infinity, which experience interference in multiple layers, by using the transfer matrix method. $E^{S,P}(z_0)$ is a combination of forward and backward propagating electric fields, $E_+^{S,P}(z_0)$ and $E_-^{S,P}(z_0)$, respectively. The transfer matrix that consists of the Fresnel transmission and reflection coefficients and the phase matrix are

$$\begin{aligned} M_{i+1,i} &= \frac{1}{t_{i+1,i}} \begin{bmatrix} 1 & r_{i+1,i} \\ r_{i+1,i} & 1 \end{bmatrix}, \\ \Phi_i(z_0) &= \begin{bmatrix} \exp(ik_i z) & 0 \\ 0 & \exp(ik_i z) \end{bmatrix} \end{aligned} \quad (\text{B.3})$$

The layer configuration we are interested in is the metallo-organic multi-layer structures as depicted in figure B.1(b). For the prism side incoming light ($90^\circ < \theta < 180^\circ$), we have

$$\begin{bmatrix} T_{41} \\ 0 \end{bmatrix} = M_{43} \Phi_3 M_{32} \Phi_2 M_{21} \begin{bmatrix} 1 \\ R_{41} \end{bmatrix} = \begin{bmatrix} M(1,1) & M(1,2) \\ M(2,1) & M(2,2) \end{bmatrix} \begin{bmatrix} 1 \\ R_{41} \end{bmatrix} \quad (\text{B.4})$$

which yields $R_{41} = -M(2,1)/M(2,2)$ that is inserted into the following equation.

$$\begin{bmatrix} E_+^{S,P}(z_0) \\ E_-^{S,P}(z_0) \end{bmatrix} = \Phi_3(z_0) M_{32} \Phi_2 M_{21} \begin{bmatrix} 1 \\ R_{41} \end{bmatrix} \quad (\text{B.5})$$

For the air side incoming light ($0^\circ < \theta < 90^\circ$), the same procedure is used. The expressions of the p- and s-polarized radiation signals according to the dipole orientation are given as

$$\begin{aligned} P_{\parallel}^S(\theta) &= \frac{3}{8\pi} n |E_+^S(z_0) - E_-^S(z_0)|^2, \\ P_{\perp}^P(\theta) &= \frac{3}{8\pi} n |E_+^P(z_0) - E_-^P(z_0)|^2 |\cos \theta_0|^2, \\ P_{\parallel}^P(\theta) &= \frac{3}{8\pi} n |E_+^P(z_0) + E_-^P(z_0)|^2 |\sin \theta_0|^2 \end{aligned} \quad (\text{B.6})$$

where θ_0 is refracted angle in the gain medium and n is refractive index of air and prism for the air and prism side, respectively.

C. Mathematical description of the signal process in dual-cascaded lock-in amplifiers for pump-probe experiments (faster probe modulation frequency: $\omega_e \ll \omega_p$)

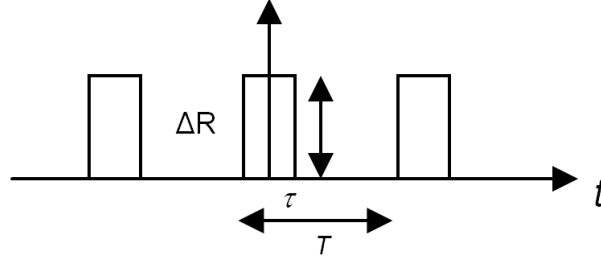


Figure C.1 Depiction of pulsed signals of a pump beam in time scale, which has a duration time τ and a repetition time $T = 1/\omega_e$, where ω_e is a modulation frequency of the pump beam.

Here, we present the derivation of the signal process in dual-cascaded lock-in amplifiers associated with pump-probe beam interactions. We focus the case of the excitation beam with much shorter duration time τ than half of a repetition time T (the duty cycle is less than 50%). The pump signals can be expressed in the Fourier analysis by

$$f(t) = \sum_{n=1}^{\infty} \frac{2\tau}{T} \sin c m \frac{2\pi\tau}{T} \cdot \cos(n\omega_p t + \theta_p) = \sum_{n=1}^{\infty} a_n \cdot \cos(n\omega_p t + \theta_p) \quad (C.1)$$

A pump beam is modulated at a frequency ω_p and a probe beam is at a frequency ω_s .

The probe beam experiences additional amplitude modulation (stimulated emission), and fluorescence light (spontaneous emission) without correlation with the probe beam modulates at the pump frequency ω_p .

$$V_{stim} = [R_v + \Delta R_v \cdot \sum_{n=1}^{\infty} a_n \cdot \cos(n\omega_p t + \theta_{\Delta R})] \cdot \cos(\omega_s t + \theta_s) \quad (C.2)$$

$$V_{spont} = A_F \cdot \sum_{n=1}^{\infty} a_n \cdot \cos(n\omega_p t + \theta_p) \quad (C.3)$$

where R_v is the amplitude of probe beam, ΔR_v is the amplitude of probe beam variation induced by pump beam and A_F is the amplitude of fluorescence. $R_v, \Delta R_v$ and A_F are

functions of incident angle. Correspondingly, all the signals through following process are a function of angle.

$$\begin{aligned}
V_{sig} &= V_{stim} + V_{spont} = R_v \cos(\omega_s t + \theta_s) + \Delta R_v \cdot \sum_{n=1}^{\infty} a_n \cos(n\omega_p t + \theta_{\Delta R}) \cdot \cos(\omega_s t + \theta_s) \\
&\quad + A_F \cdot \sum_{n=1}^{\infty} a_n \cos(n\omega_p t + \theta_p) \\
&= R_v \cos(\omega_s t + \theta_s) + A_F \cdot \sum_{n=1}^{\infty} a_n \cos(n\omega_p t + \theta_p) \\
&\quad + \frac{\Delta R_v}{2} \cdot \sum_{n=1}^{\infty} a_n \left\{ \cos[(\omega_s + n\omega_p)t + \theta_s + \theta_{\Delta R}] + \cos[(\omega_s - n\omega_p)t + \theta_s - \theta_{\Delta R}] \right\}
\end{aligned} \tag{C.4}$$

Total signals, V_{sig} contain four frequency components of ω_p , ω_s , $\omega_p + \omega_s$ and $\omega_p - \omega_s$.

A first lock-in amplifier locking ω_s components takes a demodulation process by multiplying V_{sig} by V_{r1} that is a reference signal with the frequency ω_s , producing $V_{\otimes 1}$ and then overall signals experience a phase-shift θ_{shift} in a digital signal processor including calculation of signal amplitude and phase difference between the input signals and the reference signal.

$$\begin{aligned}
V_{\otimes 1} &= V_{r1} \times V_{sig} = V_{r1} \cos(\omega_s t + \theta_1) \cdot V_{sig} \\
&= \frac{V_{r1} R_v}{2} [\cos(\theta_s - \theta_1) + \cos[2\omega_s t + \theta_s + \theta_1]] \\
&\quad + \frac{V_{r1} A_F}{2} \sum_{n=1}^{\infty} a_n \left\{ \cos[(\omega_s + n\omega_p)t + \theta_p + \theta_1] + \cos[(\omega_s - n\omega_p)t + \theta_p - \theta_1] \right\} \\
&\quad + \frac{V_{r1} \Delta R_v}{4} \sum_{n=1}^{\infty} a_n \left\{ \cos[(2\omega_s + n\omega_p)t + \theta_s + \theta_1 + \theta_{\Delta R}] + \cos[(2\omega_s - n\omega_p)t + \theta_s + \theta_1 - \theta_{\Delta R}] \dots \right. \\
&\quad \left. + \cos[n\omega_p t + \theta_s - \theta_1 + \theta_{\Delta R}] + \cos[n\omega_p t - \theta_s + \theta_1 + \theta_{\Delta R}] \right\}
\end{aligned} \tag{C.5}$$

And then $V_{\otimes 1}$ passes through a mixer and a low pass filter, being averaged in a time period of a time constant ($2\pi / \omega_s \ll T_{c1} < 2\pi / \omega_p$).

$$V_{avg\otimes 1} = \frac{1}{T_{c1}} \int_t^{t+T_{c1}} V_{\otimes 1} \cdot dt \tag{C.6}$$

The first term of equation C.6 is

$$\begin{aligned}
& \frac{1}{T_{c1}} \cdot \frac{V_{r1} R_v}{2} \int_t^{t+T_{c1}} (\cos(\theta_s - \theta_1) + \cos[2\omega_s t + \theta_s + \theta_1]) \cdot dt \\
&= \frac{1}{T_{c1}} \cdot \frac{V_{r1} R_v}{2} \left[\cos(\theta_s - \theta_1) t + \frac{1}{2\omega_s} \sin[2\omega_s t + \theta_s + \theta_1] \right]_t^{t+T_{c1}} \\
&= \frac{V_{r1} R_v}{2} [\cos(\theta_s - \theta_1) + 2 \cdot \sin c 2\omega_s T_{c1} \cdot \cos(2\omega_s t + \omega_s T_{c1} + \theta_s + \theta_1)] \\
&= \frac{V_{r1} R_v}{2} \cos(\theta_s - \theta_1) = \frac{V_{r1} R_v}{2} \cos \theta_{s1}
\end{aligned}$$

where θ_{s1} is a phase-difference between the probe signals and its reference signal, which can be adjusted to be 0 in the lock-in amplifier. The second term is derived as

$$\begin{aligned}
& \frac{1}{T_{c1}} \cdot \frac{V_{r1} A_F}{2} \sum_{n=1}^{\infty} a_n \int_t^{t+T_{c1}} \{ \cos[(\omega_s + n\omega_p)t + \theta_p + \theta_1] + \cos[(\omega_s - n\omega_p)t + \theta_p - \theta_1] \} \cdot dt \\
&= \frac{1}{T_{c1}} \cdot \frac{V_{r1} A_F}{2} \sum_{n=1}^{\infty} a_n \left[\frac{1}{\omega_s + n\omega_p} \sin[(\omega_s + n\omega_p)t + \theta_p + \theta_1] + \frac{1}{\omega_s - n\omega_p} \sin[(\omega_s - n\omega_p)t + \theta_p - \theta_1] \right]_t^{t+T_{c1}} \\
&= \frac{V_{r1} A_F}{2} \cdot 2 \sum_{n=1}^{\infty} a_n \left[\sin c \frac{(\omega_s + n\omega_p)T_{c1}}{2} \cdot \cos[(\omega_s + n\omega_p)t + (\omega_s + n\omega_p)T_{c1}/2 + \theta_p + \theta_1] \right. \\
&\quad \left. + \sin c \frac{(\omega_s - n\omega_p)T_{c1}}{2} \cdot \cos[(\omega_s - n\omega_p)t + (\omega_s - n\omega_p)T_{c1}/2 + \theta_p - \theta_1] \right] \\
&= V_{r1} A_F \cdot \sum_{n=1}^{\infty} a_n \left(n = \frac{\omega_s}{\omega_p} \right)
\end{aligned}$$

And the third term is given as the following

$$\begin{aligned}
& \frac{1}{T_{c1}} \cdot \frac{V_{r1}\Delta R_v}{4} \sum_{n=1}^{\infty} a_n \int_t^{t+T_{c1}} \left\{ \cos[(2\omega_s + n\omega_p)t + \theta_s + \theta_1 + \theta_{\Delta R}] + \cos[(2\omega_s - n\omega_p)t + \theta_s + \theta_1 - \theta_{\Delta R}] \dots \right. \\
& \left. + \cos[\omega_p t + \theta_s - \theta_1 + \theta_{\Delta R}] + \cos[\omega_p t - \theta_s + \theta_1 + \theta_{\Delta R}] \right\} \cdot dt \\
& = \frac{1}{T_{c1}} \cdot \frac{V_{r1}\Delta R_v}{4} \sum_{n=1}^{\infty} a_n \left[\frac{1}{2\omega_s + n\omega_p} \sin[(2\omega_s + n\omega_p)t + \theta_s + \theta_1 + \theta_{\Delta R}] + \right. \\
& \quad + \frac{1}{2\omega_s - n\omega_p} \sin[(2\omega_s - n\omega_p)t + \theta_s + \theta_1 - \theta_{\Delta R}] + \\
& \quad + \frac{1}{n\omega_p} \sin[n\omega_p t + \theta_s - \theta_1 + \theta_{\Delta R}] \\
& \quad \left. + \frac{1}{n\omega_p} \sin[n\omega_p t - \theta_s + \theta_1 + \theta_{\Delta R}] \right] \Big|_t^{t+T_{c1}} \\
& = \frac{V_{r1}\Delta R_v}{4} \cdot \sum_{n=1}^{\infty} a_n \left[\sin c \frac{(2\omega_s + n\omega_p)T_{c1}}{2} \cdot \cos[(\omega_s + n\omega_p)t + (\omega_s + n\omega_p)T_{c1}/2 + \theta_s + \theta_1 + \theta_{\Delta R}] \right. \\
& \quad + \sin c \frac{(2\omega_s - n\omega_p)T_{c1}}{2} \cdot \cos[(\omega_s + n\omega_p)t + (\omega_s + n\omega_p)T_{c1}/2 + \theta_s + \theta_1 + \theta_{\Delta R}] \\
& \quad + \sin c \frac{n\omega_p T_{c1}}{2} \cdot \cos[n\omega_p t + n\omega_p T_{c1}/2 + \theta_s - \theta_1 + \theta_{\Delta R}] \\
& \quad \left. + \sin c \frac{n\omega_p T_{c1}}{2} \cdot \cos[n\omega_p t + n\omega_p T_{c1}/2 - \theta_s + \theta_1 + \theta_{\Delta R}] \right] \\
& = \frac{V_{r1}\Delta R_v}{4} \sum_{n=1}^{\infty} \left[a_n \left(n = \frac{2\omega_s}{\omega_p} \right) + 2a_n \cdot \sin c \frac{n\omega_p T_{c1}}{2} \cdot \cos(n\omega_p t + n\omega_p T_{c1}/2 + \theta_{\Delta R}) \cdot \cos \theta_{s1} \right]
\end{aligned}$$

Therefore, the averaged signals are

$$\begin{aligned}
V_{avg\otimes 1} & = \frac{V_{r1}R_v}{2} \cos \theta_{s1} + V_{r1}A_F \cdot \sum_{n=1}^{\infty} a_n \left(n = \frac{\omega_s}{\omega_p} \right) \\
& + \frac{V_{r1}\Delta R_v}{2} \sum_{n=1}^{\infty} \left[a_n \left(n = \frac{2\omega_s}{\omega_p} \right) + 2a_n \cdot \sin c \frac{n\omega_p T_{c1}}{2} \cdot \cos(n\omega_p t + \frac{n\omega_p T_{c1}}{2}) \cdot \cos \theta_{s1} \right] \\
& = \frac{V_{r1}R_v}{2} + \sum_{n=1}^{\infty} \left[V_{r1}A_F \cdot a_n \left(n = \frac{\omega_s}{\omega_p} \right) + \frac{V_{r1}\Delta R_v}{2} \cdot a_n \left(n = \frac{2\omega_s}{\omega_p} \right) \right] \\
& + \frac{V_{r1}\Delta R_v}{2} \sum_{n=1}^{\infty} \left[2a_n \cdot \sin c \frac{n\omega_p T_{c1}}{2} \cdot \cos(n\omega_p t + \frac{n\omega_p T_{c1}}{2} + \theta_{\Delta R}) \cdot \cos \theta_{s1} \right]
\end{aligned} \tag{C.7}$$

and a display output $V_{Displ} (= V_{avg\otimes 1} \cdot \frac{2}{V_{r1}})$ is produced.

$$V_{Displ} = R_v + c + \Delta R_v \sum_{n=1}^{\infty} \left[2a_n \cdot \sin c \frac{n\omega_p T_{c1}}{2} \cdot \cos(n\omega_p t + \theta_{D1} + \theta_{\Delta R}) \cdot \cos \theta_{s1} \right] \quad (C.8)$$

Where $c \equiv \sum_{n=1}^{\infty} \left[2A_F \cdot a_n \left(n = \frac{\omega_s}{\omega_p} \right) + \Delta R_v \cdot a_n \left(n = \frac{2\omega_s}{\omega_p} \right) \right]$ is a constant and

θ_{D1} corresponds to a phase delay occurred in the low-pass filter. The amplified output signal V_{lock1} is directly transferred to the second lock-in amplifier.

$$V_{lock1} = g_1 \cdot V_{Displ} \quad (C.9)$$

where $g_1 (= 10(V)/sens.1(V))$ is a signal gain obtained from lock-in amplifier 1.

The demodulation process of the second lock-in amplifier locking ω_p components is described by a following equation. The multiplication with the ω_p reference signals gives

$$\begin{aligned} V_{\otimes 2} &= V_{r2} \cos(\omega_p t + \theta_2) \cdot V_{lock1} \\ &= V_{r2} r_1 \cdot (R_v + C) \cos(\omega_p t + \theta_2) \\ &\quad + V_{r2} r_1 \Delta R_v \sum_{n=1}^{\infty} a_n \sin c \left(\frac{n\omega_p T_{c1}}{2} \right) \\ &\quad \times [\cos(\omega_p (n-1)t + \theta_{D1} + \theta_{\Delta R} - \theta_2) + \cos(\omega_p (n+1)t + \theta_{D1} + \theta_{\Delta R} + \theta_2)] \cdot \cos \theta_{s1} \end{aligned} \quad (C.10)$$

Then the signal is averaged.

$$\begin{aligned} V_{avg\otimes 2} &= \frac{1}{T_{c2}} \int_t^{t+T_{c2}} V_{\otimes 2} \cdot dt \\ &= \frac{V_{r2}}{2} \cdot r_1 \Delta R_v \sum_{n=1}^{\infty} a_n \left[\sin c \left(\frac{n\omega_p T_{c1}}{2} \right) \cdot \sin c \left(\frac{\omega_p (n-1)T_{c2}}{2} \right) \right. \\ &\quad \times \cos(\omega_p (n-1)t + \theta_{D1} + \theta_{D2} + \theta_{\Delta R} - \theta_2) \\ &\quad + \sin c \left(\frac{n\omega_p T_{c1}}{2} \right) \cdot \sin c \left(\frac{\omega_p (n+1)T_{c2}}{2} \right) \\ &\quad \times \cos(\omega_p (n+1)t + \theta_{D1} + \theta_{D2} + \theta_{\Delta R} + \theta_2) \left. \right] \cdot \cos \theta_{s1} \end{aligned} \quad (C.11)$$

After the low pass filter with the other time constant ($T_{c2} \gg 2\pi / \omega_p$), V_{Disp2} is produced, reflecting ΔR , assuming $\theta_{s1} = 0$ and $\theta_2 = 0$.

$$V_{Disp2} = g_1 \Delta R_v C \cdot \cos \theta_T \quad (C.12)$$

$C = C_1 \cdot C_2$ is a total calibration factor, where $C_1 \approx \sum_{n=1}^{\infty} \sin c(\frac{\omega_p T_{c1}}{2})$ and $C_2 = a_1$, and $\theta_T = \theta_{D1} + \theta_{D2} + \theta_{\Delta R}$ is a total phase-shift, where $\theta_{D1} = 0^0$ and $\theta_{D1} = 90^0$ for a signal with $\sim 25 \mu s$ duration passing through the low-pass filters in the lock-in amplifiers used in this work. The final process for retrieving angular reflectivity R and differential reflectivity ΔR is given as

$$R = \frac{V_{Displ}(\theta)_{avg}}{V_{Displ}(ref)_{avg}} \quad (C.13)$$

$$\Delta R = \frac{1}{g_1} \frac{V_{Disp2}(\theta)}{V_{Displ}(ref)_{avg}} \quad (C.14)$$

PUBLICATIONS

Journal Publications

1. Hong Yoon, Stefan A. Maier, Donal D.C. Bradley, and Paul N. Stavrinou, "Surface plasmon coupled emission using conjugated light-emitting polymer films [Invited]," *Opt. Mater. Express* 1, 1127-1138 (2011).
2. Hong Yoon, Stefan A. Maier, Donal D.C. Bradley, and Paul N. Stavrinou, "Plasmonic gain in planar multi-layer structures incorporating a thin conjugated polymer film," to be submitted.

Refereed Conference Publications

1. Hong Yoon, Stefan A. Maier, Donal D.C. Bradley, Paul N. Stavrinou, "Plasmonic gain in planar multi-layer structures incorporatiing a thin conjugated polymer film," *SPIE Photonics Europe (EPE 10) Nanophotonics Conference*, 12-16 April (2010).
2. Hong Yoon, Stefan A. Maier, Donal D.C. Bradley, Paul N. Stavrinou, "Surface plasmon coupled fluorescence from conjugated polymers," *Fourth International Conference on Surface Plasmon Photonics (SPP4)*, 21-25 June (2009).