Electron Harvesting and Dynamics at a Metal-Semiconductor Interface

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In this thesis, optical measurements are combined with theoretical modelling to evaluate the viability of metal-semiconductor interfaces for use in plasmonic applications. Firstly, the optical response of metals and metallic nanoparticles is presented with emphasis placed on relating the observable optical properties to the underlying electronic processes. This is then extended to describe metal-semiconductor heterojunctions in the context of light-induced electron transfer between the metal and the semiconductor. An overview of the experimental methods used in this work is given along with how the relevant optical properties of a given sample are extracted from the collected data. The key material system of this work, titanium oxynitride, is introduced in the context of the developed models. Ultrafast pump-probe spectroscopy is then performed on various titanium oxynitride thin films. Unlike the femtosecond decay expected from density function theory calculations, the transient signal of the titanium oxynitride film persists on the scale of nanoseconds. This is shown to be a result of energetic electrons excited in the metal transferring into the surface oxide and remaining at the surface. The knowledge gained from this is then applied to titanium oxynitride nanostructures where the role of plasmon-enhanced electron harvesting is explored using pump-probe spectroscopy. Interestingly, the electron harvesting efficiencies into the titania surface oxide layer is shown to exceed what is expected by plasmon-enhanced absorption alone as a result of additional damping due to the encapsulating oxide layer. Finally, the thermal resistance of titanium oxynitride is explored at high laser powers, which is a proposed advantage of titanium oxynitride over gold. As a result of the unique thermal, optical and electronic properties provided by the spontaneously occurring titanium oxynitride-titanium dioxide interface, it is likely to play a critical role in the future development of electron harvesting and photocatalytic applications.
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Brock Doiron
Declaration

I hereby certify that the work presented in this dissertation is the result of my own investigations during the PhD project. Text and results obtained from other sources are referenced and properly acknowledged.

Brock Doiron
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To my sister Skye,

who helped me more than she will ever know.
Publications and Conferences

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Primary Author Articles


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Chapter 1

Introduction

1.1 Motivation

The field of plasmonics has brought about unprecedented capabilities in light manipulation and concentration. With the enhanced light-matter interactions of the free electrons in metals comes a proportionate increase in losses. Over the past decade, researchers have attempted to mitigate these losses through increasingly complex measures. Recently, there has been a paradigm shift with the proposition of hot electron and local heating applications where absorption is harnessed for productive purposes. Along with this increase in absorption comes an increase in operation temperatures. As many noble metals suffer from low melting temperatures, many have been exploring thermally stable alternative materials.

One of the most promising thermally stable material is titanium nitride, which has comparable optical properties to gold [1] but resistant to high temperatures and compatible with industrial semiconductor fabrication techniques [1, 2]. However, titanium nitride is extremely difficult to produce reliably due to its susceptibility to oxygen diffusion especially if the film is polycrystalline [3]. As such, to fully understand realistic titanium nitride, the properties of titanium oxynitride must also be well-understood. Titanium oxynitride has many of the same properties as titanium nitride but with an easily tunable carrier concentration by varying the relative oxygen content. Understanding, quantifying and integrating this material into plasmonic applications will be a primary focus of this work. A meticulous process of material characterisation will be presented along with insights into how a novel material can be most
efficiently integrated to give the highest performance result. Using purely optical measurements to probe the electron’s response to light, it is possible to extract a wide range of physical, electronic, optical and thermal properties for a thorough material characterisation.

1.2 Thesis Structure

This thesis begins with an introduction to existing literature as well as the relevant theoretical considerations in Chapter 2. Both the optical and electronic properties of both metals and semiconductors are developed from a microscopic picture to macroscopic material properties with emphasis placed on those relevant to plasmonic applications. Chapter 3 reviews the experimental methods used in the investigation of metal-semiconductor interfaces as well as the motivation to use them. The metal-semiconductor interface considered in this work is primarily that of titanium oxynitride and its titanium dioxide surface oxide layer. This material system is analysed rigorously in Chapter 4 including its deposition-tunable optical properties as well as the fabrication and measurement of fabricated nanoparticles.

Using pump-probe differential reflectivity the ultrafast electron dynamics in titanium oxynitride thin films are investigated in Chapter 5. In this, the role of the surface oxide in harvesting excited carriers is quantified using a trap-mediated recombination model. This model is applied to several titanium oxynitride films to demonstrate the use of oxygen to control the electron dynamics at the interface and the observation of high-energy electrons at the film surface. This coupled behaviour is paralleled in other naturally-oxidising material systems including Pd/PdO and NbN/NbO. The behaviour of the three systems are quantified to compared the potential benefits for hot electron chemistry. With a good understanding of the thin film system, the model is extended to nanopatterned titanium oxynitride in Chapter 6 to investigate the role that surface plasmon resonances play in the collection of electrons at the metal-semiconductor surface. Finally the high-temperature behaviour of these particles is studied to determine how physical changes in the material influence the observed electron dynamics.
Chapter 2

Background Theory

This chapter presents the theoretical background behind the optical and electronic properties of metal-semiconductor interfaces and describes how these properties can be observed experimentally. The study begins by quantifying the interaction of metals with incident photons over a range of frequencies and explaining how free conduction electrons in metals can give rise to resonant absorption and scattering conditions called surface plasmon resonances. The dynamics of electron excitation by photon absorption and subsequent relaxation are analysed in the context of electron temperature, which can be detected experimentally through ultrafast optical measurements. Finally, the physics of metal-semiconductor heterojunctions are examined, specifically in the context of charge transfer at the interface. Recent literature is reviewed to explore how these heterojunctions are being used in the areas of photocatalysis and opto-electronic devices.

2.1 Introduction

Over the past century, the study of material properties at the atomic level has deepened the understanding of how light interacts with matter. It developed from a purely academic pursuit into a quest to manipulate light for targeted applications. This has resulted in such pervasive devices as light-emitting diodes and photovoltaic cells. This progression is supported by the field of plasmonics, which has gained tremendous popularity over the past decade. Plasmonics has provided unprecedented sub-diffraction light confinement and guiding abilities by coupling light to the oscillation of conduction electrons in metals. This coupling incites the resonant
driving of the free electrons of the metal in a surface plasmon (SP).

As plasmonic phenomena are constrained to metal-dielectric interfaces, these resonant electron oscillations provide a means for enhancing the interaction between a material and its electromagnetic environment. Indeed, the dielectric environment regulates the surface charges generated by plasmon resonances, which directly influences the plasmonic resonant frequency [4, 5]. This sensitivity of plasmonic response to environmental conditions provides the basis for the development of SPP-based sensors [6] and the field of *active plasmonics*. This field has since expanded to encapsulate a wide range of external (environmental) control mechanisms for ultrafast opto-electronic devices [7] and plasmonic lasers [8, 9]. However, large losses from material defects and intrinsically rapid scattering still hinder plasmonic devices from competing with commercially available semiconductor and photonic devices [10].

This fundamental connection between plasmon resonances and environment also comes into play as energy is dissipated from the decaying oscillations. As a surface plasmon resonance decays, all energy that is not lost radiatively is retained by the electrons of the system through transitions to higher energy states. These electrons subsequently lose energy through scattering with lower-energy electrons and lattice phonons ultimately converting their increased kinetic energy to thermal energy of the lattice. This heat diffuses throughout the metal and ultimately the surrounding media. This heat transfer motivates the field of thermoplasmonics, where plasmonic antennas are exemplified as nanoscale heat sources [11]. However, recent work has shown that energetic electrons, also known as *hot electrons*, can be extracted as a photocurrent if removed faster they can thermalise with the lattice [12]. Many hot electron applications rely on metal-semiconductor [13] or metal-adsorbate [14] interfaces to collect the energetic electrons prior to thermalisation. Given the new opportunities, a range of semiconductors as well as alternative plasmonic materials are currently being investigated [15, 16].

In spite of the abundant time and effort being devoted to the development of these applications, there has yet to be a significant impact in industrial-scale applications. At this point, an objective examination of the advantages and limitations of plasmonics is imperative for the commercialisation of these applications currently restricted to academic research. What draws so many optics and solid state researchers to plasmonics is the flexibility provided by the free electrons in metals. These electrons can interact strongly with an applied field despite the
limited penetration depth of the light. This results in an enhanced local electromagnetic field as well as resonant scattering and absorption. Thus, it is possible to develop efficient plasmonic devices by focusing on applications that exploit the intrinsic strengths offered by plasmonic modes.

2.2 Light-Metal Interaction

A thorough understanding of the underlying interactions between light and matter is a critical first step to be able to manipulate light for productive purposes. There are several frameworks used to describe the physical processes from the quantum mechanical microscopic picture of individual photon-electron interactions to the macroscopic electromagnetic treatment describing the aggregate response of a material. For example, as light propagates through a dielectric material, although there is no bulk absorption, the light is slowed by scattering off bound electrons. This slowing is a result of coherent scattering by fixed-energy quantum states, which is dependent on the wavelength of light (i.e. dispersion). This is commonly expressed as a wavelength-dependent refractive index \( n(\lambda) \), which describes the reduction to the speed of light in the material relative to the speed of light in vacuum \( (n(\lambda) = c/v(\lambda)) \). In more complex processes such as the free carrier intraband absorption of light in semiconductors and metals, a microscopic approach is not feasible. However, the individual events of electrons gaining energy (photon absorption) as well as gaining or losing momentum (phonon absorption/emission) do produce observable features in the absorption and reflection spectrum. Through understanding these underlying physical processes, rigorous materials models can be developed for use in device engineering and experimental setup design. The experiments in this work reveal macroscopic properties, which are then related to microscopic theory.

2.2.1 Quantifying Light-Metal Interactions

The frequency-dependant optical response is a quantitative description of a material's electronic response to incident electromagnetic waves. The electrons bound to lattice atoms respond to the applied field by being polarised and forming microscopic dipole moments with the positive lattice atom and negative electron density driven in opposite directions. The cumulative
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Figure 2.1: (a) The real and imaginary components of a Lorentz oscillator with amplitude $A$ centred at an energy $E_0$. This is used to represent interband transitions where the width of the curve (related to $\Gamma$) determines with bandwidth of the absorption. (b) The real and imaginary components of a Drude Oscillator model, equivalent to a Lorentz oscillator centred at $E_0 = 0$. This is used to represent the intraband transitions, where $\Gamma$ is related to the electron scattering rate.

(macrosopic) effect is a net polarisation ($\vec{P}(\vec{r},t)$) being driven along the light’s polarisation axis and bound charges ($\rho_B$) accumulating at the surface ($\vec{P}(\vec{r},t) = -\nabla \cdot \rho_B = \chi \epsilon_0 \vec{E}(\vec{r},t)$ for a homogeneous, linear, and isotropic medium). The fields in the following discussion are all functions of $(\vec{r},t)$, but the dependencies are dropped for brevity. The susceptibility $(\chi)$ quantifies a material’s degree of polarisability in response to a field $\vec{E}$. Expanding the electric displacement field ($\vec{D} = \epsilon_0 \vec{E} + \vec{P}$) in terms of the previous expression for the induced polarisation yields:

$$\vec{D} = \epsilon_0 \vec{E} + \chi \epsilon_0 \vec{E} = \epsilon_0 (1 + \chi) \vec{E} = \epsilon_0 \epsilon_r \vec{E}$$

(2.1)

where $\epsilon_r \approx 1 + \chi$ is defined as the material-dependent permittivity used to characterise a materials optical response. This parameter provides a direct relationship between the electronic and optical properties of a material. In general, theories that describe $\chi$ are frequency-dependent, such that $\epsilon_r(\omega) \approx 1 + \chi(\omega)$.

For metals, in addition to the bound electrons, there are delocalised conduction electrons. Although there is some degree of Coulomb interaction between these electrons and the positive lattice atoms, the screening due to the valence (bound) electrons allows these to be treated effectively as free electrons [17]. The optical response of the free electrons in a metal can be described reasonably well by the Drude model for electrical conduction where these electrons
undergo frequent collisions with phonons, impurities and lattice defects. In an oscillating field, the conduction electron density will oscillate about the positive atoms to a maximum amplitude of \( \vec{x}_0 \) and induce an additional polarisation on the material \( \vec{P}_{\text{Drude}} = -n e_0 \vec{x}_0 \), where \( n \) is the electron number density and \( e \) the charge of the electron. Through the Drude model of AC conductivity [17], the maximum amplitude can be related to the driving electric field via the effective mass \( m^* \) and Drude damping term \( \gamma \):

\[
\vec{P}_{\text{Drude}} = -\frac{ne^2}{m^*(\omega^2 - i\omega\gamma)} \vec{E}
\]

Combining Equation 2.1 for the response of the bound electrons and 2.2 for that of the free electrons yields:

\[
\vec{D} = \epsilon_0 \epsilon_r \vec{E} - \frac{ne^2}{m^*(\omega^2 - i\omega\gamma)} \vec{E} = \epsilon_0 \left( \epsilon_r - \frac{ne^2}{\epsilon_0 m^*(\omega^2 - i\omega\gamma)} \right) \vec{E}
\]

\[
\vec{D} = \epsilon_0 \left( \epsilon_r - \frac{\omega_p^2}{\omega^2 - i\omega\gamma} \right) \vec{E} = \epsilon_0 \epsilon_D \vec{E}
\]

The plasma frequency of the material is defined as \( \omega_p^2 = ne^2/\epsilon_0 m^* \). This parameter describes the intrinsic bulk oscillation frequency of electron density about the lattice. It is also used to determine the crossover of the permittivity from positive (dielectric behaviour) to negative (metallic behaviour).

Finally, consider the interaction of light with electrons that are optically excited between bands (interband transitions). These states are modelled as a number \( N \) of Lorentz oscillators with particular amplitudes \( f_j \) and widths \( \Gamma_j \). Combining each of these electron-light interaction processes yields the Drude-Lorentz model for the electric permittivity:

\[
\epsilon(\omega) = \epsilon_\infty + \sum_{j=1}^{N} \frac{f_j \omega_0^2}{\omega_0^2 - \omega^2 + i\Gamma_j \omega} - \frac{\omega_p^2}{\omega^2 - i\omega\gamma}
\]

Note that equation 2.5 is complex valued, conventionally separated as \( \epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \).

The magnitude of the real component describes the ease of polarising the medium. A larger value suggests that, for a given applied electric field, there is a greater induced polarisation within the material. This is captured in the relationship between the electric field and electric displacement \( (\vec{D} = \epsilon \vec{E}) \). In materials that possess free conduction electrons (i.e. metals and
2.2. Light-Metal Interaction

Figure 2.2: (Left) When a linearly polarised electric field is applied across a metal particle, the electrons move in an opposing direction to the electric field. This accumulation of charges results in a polarity of particles. When applying an oscillating electric field (i.e. light), the rapid alternation of polarity results in the particle acting like a dipole source. (We show that it is possible to achieve such a situation by using bit-flips induced by double-sided as well as single-sided Rowhammer attacks.) Far field radiation pattern of a spherical metal particle excited on resonance simulated using finite-difference time-domain (FDTD) software.

heavily n-doped semiconductors) the permittivity will be negative in some spectral range. This arises when the induced electric displacement is 180° out of phase with the applied electric field due to the negative charges moving opposite of the electric field vector. The imaginary part quantifies the amount of absorption inside the medium ($\kappa = \frac{\epsilon_2}{2n}$ is the standard absorption coefficient) as the light propagates with a larger value signifying more absorption (loss). Loss can arise from both interband and intraband electron transitions (UV-visible-near IR) as well as phonon absorption further into the infrared [18].

2.2.2 Localised Surface Plasmon Resonances

The field of plasmonics is often concerned with nanoscopic metal structures. If a metal region is smaller than the wavelength of light, all of the free electrons in this region could be driven coherently. The resultant accumulation of electrons at the surface of this metal particle provides a restoring force, resulting in electron oscillatory behaviour. If the frequency of the incident field approaches the frequency of the natural restoring oscillation, the electrons can be resonantly driven in what is termed a localised surface plasmon resonance (LSPR). This is distinguished by an enhanced field inside the particle, leading to higher absorption, and a strong electric field surrounding the particle. The coherent oscillation of negatively charged electrons acts as
a dipole-like source, which can radiate to the far-field and be detected experimentally. The induced dipole moment is proportional to the polarisability $\alpha(\omega)$ of the particle,

$$\vec{p} = \varepsilon_0 \varepsilon_m \alpha(\omega) \vec{E}$$  \hspace{1cm} (2.6)

For a sphere of radius $a$ with permittivity $\varepsilon(\omega)$ in a host dielectric medium with approximately constant permittivity $\varepsilon_s(\omega) \approx \varepsilon_s$ in the quasi-static approximation ($a \ll \lambda$) the polarisability is given by [19]:

$$\alpha(\omega) = 4\pi a^3 \frac{\varepsilon(\omega) - \varepsilon_s}{\varepsilon(\omega) + 2\varepsilon_s}$$  \hspace{1cm} (2.7)

From this, it can be seen that a resonant condition arises when the denominator approaches zero ($\varepsilon(\omega) = -2\varepsilon_s$) called the Fröhlich condition. The condition also depends on the particles geometry in general. In real metals, the denominator never reaches zero due to losses (the imaginary part of the permittivity) being nonzero. This leads to a reduction of intensity and broadening of the frequency range where this resonant enhancement occurs. This spectral range defines where plasmonic enhancements can be best exploited.

As the incident light (an electromagnetic field) is driving the free electrons of the material, the interaction area of a metallic particle with light will extend beyond its physical cross section. As a result, plasmonic particles have the ability to scatter and absorb more power than is directly incident on them. Considering an incident power density $S_0 [W/m^2]$, one can define effective scattering, absorption, and extinction cross sections ($\sigma_{\text{Scat}}$, $\sigma_{\text{Abs}}$, $\sigma_{\text{Ext}}$ respectively) by normalising the respective powers ($P_{\text{Scat}}$, $P_{\text{Abs}}$, $P_{\text{Ext}}$) by the incident power density:

$$\sigma_{\text{Scat}} = \frac{P_{\text{Scat}}}{S_0} \hspace{1cm} \sigma_{\text{Abs}} = \frac{P_{\text{Abs}}}{S_0} \hspace{1cm} \sigma_{\text{Ext}} = \frac{P_{\text{Ext}}}{S_0}$$  \hspace{1cm} (2.8)

which directly quantifies the extent of interaction of the particle with the incident light with units of area. The total extinguished power from the incident beam (which can be measured using the difference between incident and transmitted power) is simply the sum of the scattering and absorbed power ($P_{\text{Ext}} = P_{\text{Scat}} + P_{\text{Abs}}$). However, with this measure it is difficult to compare particles of varying size as the total power will scale with the geometric cross section ($\sigma_G$) of the particle.

To quantify the efficiency of the respective processes due to the plasmonic modes, one
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Figure 2.3: (Left) The variation of the wavelength-dependent scattering cross-section ($Q_{\text{Scat}}$) of the dipolar mode of a gold sphere with various radii under the electrostatic (ES) approximation. (Right) The same variation of scattering cross-section from Mie theory calculations showing a pronounced red-shift and broadening for larger particle sizes (shown with dotted lines) due to radiative damping. The failure of the electrostatic approximation is clearly observed beyond 20 nm.

This directly quantifies the degree of plasmonic enhancement irrespective of size. With respect to an incident power of $P_0$: 

$$Q_{\text{Scat}} = \frac{P_{\text{Scat}}}{P_0}, \quad Q_{\text{Abs}} = \frac{P_{\text{Abs}}}{P_0}, \quad Q_{\text{Ext}} = \frac{P_{\text{Ext}}}{P_0}$$ (2.9)

For simple geometries with convenient symmetry conditions, such as spheres and ellipsoids, these efficiencies can be calculated analytically. The framework was termed Mie theory after its introduction by Gustav Mie in 1908 [20]. To do this, the incident, scattered and internal electric fields are expanded using an infinite series of vectorial spherical harmonic (VSH) functions. The size and wavelength-dependent expansion coefficients describe the relative contributions of the dipolar, quadrupolar and higher order modes on the scattering and absorption of the particle. The governing equations of this method are described in detail in Appendix A. In Figure 2.3, exemplary calculations of the scattering efficiency of gold spheres between the radii of 10 nm and 150 nm are shown using the electrostatic approximation and the dipolar mode of first order Mie theory. Unlike the electrostatic approximation, Mie theory has the ability to predict the red-shifting and broadening of the plasmon resonance with increasing size due to radiation damping, characteristic of LSPR modes [21].
Surface Plasmon Decay

The surface plasmon excitation can be seen as a light-induced disturbance of the electron density within the metal. There is a distribution of surface plasmon energies related to the overlap of the broad spectrum of the surface plasmon resonance and the exciting beam. The energy gained by the electrons is dissipated on timescales of tens of femtoseconds due to dephasing of the collective oscillation and subsequent scattering with bound electrons. The energy distribution of the excited plasmons correspond to a range of electron oscillation frequencies. Higher energy plasmons have higher oscillation frequency and vice-versa for lower energy plasmons, causing the oscillations to gradually grow out of phase.[22] There are two pathways for the energy to be dissipated: radiative decay, involving re-emission of a photon and non-radiative decay, generating an electron-hole pair through interband or intraband transitions. The dominant decay channel is closely related to the size of the particle involved with larger particles favouring radiative damping and smaller particles tending to dissipate energy non-radiatively [23].

2.2.3 Alternative Plasmonic Materials

Although the potential of many plasmonic applications has been demonstrated experimentally, they have yet to be integrated into widespread industrial settings. This is primarily a result of the incompatibility with industrial fabrication techniques due to the relatively low melting temperatures of conventional plasmonic metals. This can cause diffusion into silicon [24] during deposition, for example, which is detrimental to electrical performance. Additionally, it is difficult to pattern inert metals using gas phase chemical etching typically used in semiconductor fabrication [25]. Furthermore, the large absorptive losses at visible wavelengths result in pronounced heating, which can speed up the degradation of surrounding components [26]. Recently, there has been particular interest in alternative materials and diversification of applications [27, 28] to exploit the strengths of plasmonics.

We divide the diverse range of materials currently being investigated into four classes: noble metals, refractory (high-temperature stable) metals, transition metal nitrides, and conductive oxides. The extensive range of physical properties (hardness, heat tolerance, thermal dissipation) and electronic characteristics (free carrier concentration, effective mass) are taken
2.2. Light-Metal Interaction

into account to examine which will facilitate plasmonic devices that can be efficiently implemented across the ultraviolet (UV), visible and infrared (IR) regimes. The summary of the operation ranges and advantageous properties is summarised in Table 2.1.

The most widely used and well-studied materials in plasmonics are silver (Ag), gold (Au), and copper (Cu). These noble metals were originally preferred due to their stability and high conductivity resulting in sharp resonances. Although in bulk these materials are relatively robust to high temperatures, when fabricated into nanostructures the melting temperature decreases considerably, reaching only a few hundred degrees in Au and and Ag [29]. In addition, the fixed free carrier concentration restricts the operation to the ultraviolet and higher frequency end of the visible spectrum. Less common metals have been explored including palladium (Pd), magnesium (Mg), and yttrium hydride (YH2) for their sensitivity to particular gases (for example H2)[30, 31, 32] and rhodium (Rh) due to its comparable optical properties to Al but with resistance to oxidation.[33] In this group we also include aluminium (Al), which although not strictly a noble metal, has comparably low-loss and narrow resonances at higher optical frequencies.[34, 35]

For high temperature applications, the refractory metals molybdenum (Mo),[36] niobium (Nb),[37] nickel (Ni),[38] tungsten (W), [39] and titanium (Ti)[40] are being exploited in plasmonics for their high melting temperature and red-shifted resonances compared to the noble metals. However, due to the fixed carrier concentration in mono-atomic metals, tuning of the plasmon resonance requires change of the geometry for these materials.

A relatively new class of materials, transition metal nitrides, are conductive ceramics (XN, X=Ti, Zr, Hf, Nb) with variable stoichiometry allowing for tunable carrier concentration by varying deposition conditions in addition to high thermal stability.[41, 42] The ability to substitute nitrogen atoms with more electronegative oxygen atoms allows for tunable properties between metal and semiconductor, as has been observed with the intermediate titanium oxynitride (TiON) [43]. However, the transition metal nitrides have high optical losses, making them ideal broadband absorbers [15, 44] but poor light scatterers.

For low loss plasmonics, conductive metal oxides such as Al and Ga doped ZnO and ITO [2] are currently being explored; however, they are only metallic in the infrared (above 1500 nm). For visible and near-infrared applications, recent developments in strontium-based oxides
Table 2.1: Comparison of various plasmonic material categories: noble metals, refractory metals, transition metal nitrides and conductive oxides. They are analysed in terms of their physical properties (loss, thermal stability, tunable carrier concentration) and their respective operation regimes.

<table>
<thead>
<tr>
<th>Material Category</th>
<th>Low Loss</th>
<th>Thermal Stability</th>
<th>Tunable Carrier Concentration</th>
<th>UV</th>
<th>Visible</th>
<th>Near-IR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Noble Metals</td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Refractory Metals</td>
<td></td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Transition Metal Nitrides</td>
<td></td>
<td></td>
<td>✓</td>
<td>✓</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Conductive Oxides</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

including strontium molybdate (SrMoO3; SMO)[45], strontium niobate (SrNbO3; SNO)[46] and strontium ruthenate (SrRuO3; SRO)[47] have allowed for reduced loss while still maintaining plasmonic properties in the visible regime.

2.2.4 Evaluating Alternative Materials for Plasmonic Applications

With the rapid development of novel plasmonic applications and a growing library of materials to consider, a standardised method of comparing materials for specific applications is imperative for the continuity of the field. Using ellipsometry (Appendix B) in combination with Mie Theory calculations (Appendix A), application-specific figures of merit are proposed to quantify material performance [48]. The figures of merit extend beyond purely electromagnetic effects to incorporate the materials’ thermal properties, interactions with adjacent materials, and realistic illumination conditions. The approach is summarised in Figure 2.4. Materials are directly compared for each application using an optimised spherical geometry to make use of the analytical solutions available. The most promising plasmonic materials for key applications are shown along with benchmark comparisons to the current state-of-the-art in Appendix C.

2.3 Electron Dynamics in Metals

An electromagnetic driving field of a plasmon resonance introduces an electron transition probability between states of the metal. This transition probability from an initial state $|\psi_i\rangle$ to
2.3. Electron Dynamics in Metals

Figure 2.4: Overview of the calculation process for the application-specific figures of merit. Using the Drude-Lorentz model fitted to experimental ellipsometry measurements, a frequency-dependent permittivity is extracted for each material. The size and wavelength-dependent cross-sections (absorption, scattering and extinction) are calculated using Mie theory. Using these, and the relevant physical parameters found in literature the figure of merit is maximised for each material by varying particle size accounting for any experimental constraints.

A final state $|\psi_f\rangle$ from an interaction operator $\hat{V}$ can be described by Fermi’s golden rule:

$$P = \frac{2\pi}{\hbar}|\langle \psi_f | \hat{V} | \psi_i \rangle|^2 \rho,$$

where $\rho$ is the density of unoccupied final states [49].

The energy associated with a surface plasmon is generally insufficient to induce a significant amount of interband transitions due to the large energy needed to excite an electron to the Fermi level from the d-band (2.4 eV and 4 eV for Au and Ag, respectively) [50, 12]. However, intraband transitions are accessible if momentum is available to facilitate the transition, e.g. via phonon scattering to Landau damping [51]. As a result of an electron transition to the state $|\psi_f\rangle$, a hole is formed in state $|\psi_i\rangle$. If the difference between the energies of these states and the Fermi level is at least an order of magnitude higher than that of the thermal excitations, the carriers are termed hot carriers [52].

The term “hot” carrier stems from the fact that these energetic carriers are not in thermal equilibrium with the other electrons of the material. In the literature, there is some disagreement as some others define hot carriers as those that are at an elevated-temperature Fermi-Dirac distribution. However, in this work, the definition is strictly those that are out of
Chapter 2. Background Theory

thermal equilibrium and cannot be fit to a Fermi-Dirac distribution. Whether the hot electron or hot hole has more energy hinges on the band structure of the material, [10] and dictates how it is implemented in so-called hot carrier applications.

As high-temperature electrons spatially overlap with the non-excited electrons, electron-electron scattering distributes the excess energy amongst the states of the metal until an elevated-temperature ($T_e$) Fermi distribution is achieved. This increased electron temperature distribution attains a quasi-equilibrium, but with an electron temperature higher that of the lattice at temperature $T_L$. A common temperature is eventually reached via heating of the lattice and cooling of the electrons. This may be described by a two-temperature model [53], which is presented in full detail in this section. As a result of these thermalisation processes, plasmon-excited hot carriers have a finite lifetime, $\tau$. This limited lifetime enforces a temporal window in which hot carriers can be exploited for practical purposes.

2.3.1 Absorption in Metal Nanoparticles

Both linear (single-photon) and nonlinear (multi-photon) absorption pathways exist simultaneously in response to an incident field. In direct interband transitions of many noble metals (Cu, Au), few useful hot carriers are generated as the electron is excited to just above the Fermi level and the poor mobility of holes in the d-band limits their effectiveness as energy carriers in many conventional metals [54]. Although intraband transitions can occur at lower energies, they require the transfer of additional momentum to the electrons. One means of satisfying this requirement is through phonon-mediated photon absorption. In this, momentum $\vec{q}_{ph}$ is transferred from a phonon to the electron ($\vec{k}_2 - \vec{k}_1 = \pm \vec{q}_{ph}$) resulting in the generation of hot carriers.

The periodicity of the lattice, with reciprocal lattice vector $\vec{G}$, allows for electron transitions to occur to different Brillouin zones, satisfying momentum conservation ($\vec{k}_3 - \vec{k}_1 + \vec{k}_4 - \vec{k}_2 = \vec{G}$) termed Umklapp scattering. Each absorption mechanism is shown in Figure 2.5 taken from [54].

Landau damping allows the decaying plasmon to contribute the momentum of the plasmon ($\Delta \vec{k}_0$) needed for an electron to transition above the Fermi level. The sub-wavelength plasmon modes will result in large spatial frequencies and in turn momentum larger than $\Delta k_0$. This contribution becomes comparable to the bulk absorption of the material for particles on
2.3. Electron Dynamics in Metals

Figure 2.5: Mechanisms of electron excitation in metals where vertical transitions represent changes in electron potential energy and horizontal transitions represent changes in momentum. (a) Phonon- or defect-assisted where the momentum $\vec{q}_{ph}$ is transferred to the electron. (b) Umklapp scattering where two electrons are excited but transfer opposite momentum so there is no net change of momentum. (c) Plasmon-assisted transitions involve the electron gaining momentum from a decaying localised plasmon resonance ($\Delta k_0$) (d) Interband transition where enough energy is provided to change bands, with no change in electron momentum. Reproduced from Ref [51].

The absorbed energy, $h\omega$, from the incident field can be sufficient to produce hot carriers within the metal. In some metals, such as aluminium, the separation of the d-band and the s-band can overlap with the energy associated with the surface plasmon [10]. The shape of the excited distribution is governed by the relative position of the d-band. For example, in copper and gold the large separation of the d-band and the Fermi energy inhibit the generation of hot electrons so the energy is concentrated in the holes of the material. This is not the case in aluminium with an almost even energy distribution between electrons and holes [10].

The relatively low probability of exciting hot carriers via single-photon absorption
processes can be overcome by nonlinear processes such as two-photon absorption, which permit the excitation of d-band electrons to energies well above the Fermi level. The enhanced near field associated with the excitation of a surface plasmon increases the probability of multi-photon absorption [55]. It was first shown that second [56, 57, 58, 59] and third harmonic generation [60] are possible, confirming the coherent multi-photon absorption by the electrons of the metal. In addition, incoherent multi-photon absorption processes have been observed with linearly-inaccessible transitions occurring with the decay of three or four plasmons contributing to a single electron transition [61, 62]. However, this requires several pulses within the timescales associated with the redistribution of energy via electron-electron scattering. This emphasises why long hot electron lifetimes are desirable, as small lifetimes can prevent the nonlinear interband transitions required for significant hot carrier densities to be achieved.

2.3.2 Extended Two Temperature Model

Following the initial absorption of photons, electron and phonon scattering events return the electron and phonon systems to mutual thermodynamic equilibrium. The redistribution of this finite amount of energy absorbed by the system is described by the extended two temperature model to account for nonthermal energy density as well as electron and phonon temperatures. The electronic system following laser excitation is comprised of two separate distributions: the thermal distribution, $f_T(E, T_e)$, which follows a Fermi-Dirac distribution at a temperature $T_e$ and the nonthermal distribution, $f_{NT}(E)$, which cannot be fit to a Fermi-Dirac distribution. The exact shape of the nonthermal distribution depends on the overlap between the laser pulse energy and the band structure of the material.

On very short timescales, the electron distribution is nonthermal. As such, the energy absorbed by these electrons cannot be described by a single temperature. On longer timescales (tens of femtoseconds), the excess energy in the nonthermal electrons is distributed amongst the available states via electron-electron scattering events. This results in the heating of the thermal electron population and decay of the nonthermal population. The decay of the nonthermal electron distribution can be described by Fermi liquid theory [63] using a thermalisation time, $\tau_{Th} = \alpha^{-1}$, where $\alpha$ is the electron gas heating rate. In terms of the energy difference from the
2.3. Electron Dynamics in Metals

Figure 2.6: Schematic of the three interacting thermal bodies in a metal. Initially, a small portion of electrons are excited, that cannot be described by a Fermi-Dirac distribution and are thus termed nonthermal. Through electron-electron scattering the thermal electrons, following a Fermi-Dirac distribution, increases in temperature until all electrons are in thermal equilibrium. The phonons of the system are then heated by electron-phonon scattering events. This results in a cooling of the thermal electron population and heating of phonons until they reach thermal equilibrium. Following this, the electrons and phonons cool together by losing energy to phonon-phonon scattering and diffusion or radiation of heat to the metal’s surroundings.

Fermi level, for an excitation energy $E$ this is given by [63]:

$$\tau_{Th}(E) = \frac{128}{\pi^2 \sqrt{3} \omega_p} \left( \frac{E_F}{E - E_F} \right)^2 = \alpha^{-1} \quad (2.10)$$

where $\omega_p$ is the (unscreened plasma frequency) and $E_F$ the Fermi energy. This process is described by the following coupled differential equations:

$$\frac{\partial N}{\partial t} = -\alpha N \quad (2.11)$$

$$C_e \frac{\partial T_e}{\partial t} = \alpha N \quad (2.12)$$

The second expression describes the temperature evolution of the thermal electron distribution with volumetric heat capacity, $C_e$.

As the thermal electrons heat via electron-electron interactions, there are correspondingly more collisions between those electrons and the lattice atoms which have a different
temperature. This is associated with the concurrent heating of the lattice (increase in $T_l$) and cooling of the electron system (decrease in $T_e$) via electron-phonon scattering. This is known to occur at a rate proportional to the temperature difference between the two systems, with material and temperature-dependent proportionality factor, $G$, termed the electron-phonon coupling strength [64].

A larger value of $G$ indicates stronger coupling between the electrons and phonons and, in turn, a faster electron cooling. In addition, the generated temperature gradients of both electron and lattice temperature can result in thermal diffusion away from heated areas. The ability of a material to conduct heat is described by a thermal conductivity, $\kappa$, and, in metals, is divided into a sum over free carrier, $\kappa_e$, and phonon, $\kappa_p$, contributions ($\kappa = \kappa_e + \kappa_p$). By ascribing a lattice temperature, $T_l$, and heat capacity, $C_l$, the extended two temperature model assumes the following form:

$$\frac{\partial N}{\partial t} = -\alpha N \quad (2.13)$$

$$C_E \frac{\partial T_e}{\partial t} = -\nabla \cdot (\kappa_e \nabla T_e) - G(T_e - T_l) + \alpha N \quad (2.14)$$

$$C_l \frac{\partial T_l}{\partial t} = G(T_e - T_l) - \nabla \cdot (\kappa_p \nabla T_l) \quad (2.15)$$

In these equations, the interaction between the nonthermal electrons and the phonons are neglected. The electron thermal diffusion is represented by the term $-\nabla \cdot (\kappa_e \nabla T_e)$, and the phonon thermal diffusion term is similarly $-\nabla \cdot (\kappa_p \nabla T_l)$. The exchange of energy between the electron and phonon systems is described by $G(T_e - T_l)$.

As optical measurements only respond to variations in the electron temperature, the role of nonthermal electron-phonon interactions can be included by adding a constant term to the solution of the lattice temperature as was done in previous work [65]. Furthermore, on timescales of several picoseconds, the phonon-phonon scattering is negligible due to the relatively infrequent collisions between phonons [66]. Thus, the interaction of the two systems can be effectively described by the difference of the last two equations. That is:

$$\frac{\partial(T_e - T_l)}{\partial t} = -G\left(\frac{1}{C_e} - \frac{1}{C_l}\right)(T_e - T_l) + \frac{\alpha}{C_e} N \quad (2.16)$$

The resulting differential equation resembles a two-body Newton cooling problem,
2.3. Electron Dynamics in Metals

Figure 2.7: A schematic of the energy pathways following surface plasmon resonance excitation. The plasmon mode can either decay radiatively resulting in the emission of a photon (green) or non-radiatively resulting in the generation of an electron-hole pair in the metal (purple). The excited carriers can be extracted using a metal-semiconductor or metal-graphene interface resulting in net charging of the metal (blue). If the carriers remain in the metal, the carriers relax through electron-electron, electron-phonon, and phonon-phonon scattering and the heat then diffuses into the surrounding media (red).

which is characterised by an electron-phonon lifetime $\tau_{ep}^{-1} \approx G(1/C_e - 1/C_l)$. This energy exchange continues until the electron and lattice temperatures approach the same value. Following this bottleneck, the electrons can only cool at a rate equal to the cooling of the lattice. On these longer time scales, an exponential cooling occurs following the phonon-phonon scattering lifetime, $\tau_{pp}$, which is related to the thermal conductivity of the material.

The three energy-transfer processes occur simultaneously, which is treated using a phenomenological approach. Due to the large difference in timescales of the independent processes ($\tau_{Th}$, $\tau_{ep}$, $\tau_{pp}$), each dominates in distinct temporal regimes. With such a model, it is possible to independently monitor the response of the electrons and phonons using laser pulses 100 fs duration even when electron heating and cooling processes are competing. The derivation of the phenomenological solution to this set of equations is shown in Appendix D.
2.3.3 Energetic Properties of Plasmon-Induced Hot Carriers

The generation and relaxation of hot carriers is inextricably linked to the band structure and density of states of the material. In addition to determining the dominant energy carrier, it also dictates the relaxation process and hot carrier lifetimes. In bulk plasmon excitation in metal films, momentum conservation limits the transitions to within a small energy range around the Fermi level. However in LSPR decay, a large range of energies are accessible by the electrons, through interaction with the nanoparticle walls [67, 68]. Consequently, size and geometry play a critical role in dictating the quantity and energy of plasmon-induced hot carriers.

In smaller particles (below 10nm, where quantum effects begin to play a role), although they have fewer electrons, the spatial confinement allows electrons to access higher energy levels. Conversely, larger particles allow for a larger number of hot carriers to be excited but closer to the Fermi energy. This is corroborated by a recent theoretical analysis of hot electron distributions with various carrier lifetimes and particle sizes [52]. This fundamental trade-off between hot carrier energy and quantity was addressed by introducing a figure of merit, $\eta_e(E)$, to describe the number of hot electrons generated over a certain threshold $E$ per plasmon generated given in terms of the absorbed power $P_{Abs}$ and plasmon resonance frequency $\omega_p$ by [52]:

$$\eta_e(E) = \frac{\hbar \omega_p \sum_{E_f > E} \gamma_e(E_f, \omega_p)}{P_{Abs}}$$

(2.17)

where $\gamma_e(E_e, \omega_p)$ is the electron transition probability per unit time calculated by the Fermi golden rule. This allows for a direct comparison between the use of different materials and geometries for hot electron applications. It should be noted that in the Drude model for metals, in vacuum ($\epsilon_s = 1$) the absorbed power depends on the permittivity $\epsilon(\omega)$ and diameter of the particle $D$, according to [52]:

$$P_{Abs} = \frac{\omega}{4} D^3 Im \left[ \frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} \right] E_0^2$$

(2.18)

Both the electron-electron and electron-phonon scattering are associated with finite lifetimes $\tau_{ee}$ and $\tau_{ep}$ respectively. In noble metals, $\tau_{ee}$ has been found to typically be less than 100 fs [69] [70, 67] where $\tau_{ep}$ can be longer, falling between 1 and 10 ps [71, 67]. Subsequently,
phonon-phonon interactions dissipate heat across the lattice in a time scale $\tau_{pp}$ on the order of 100 ps [71]. This finite lifetime varies between materials as Coulomb screening effects from d-band electrons can prolong the relaxation of the hot electrons [72]. Consequently in larger nanoparticles on the order of tens of nanometres, this finite lifetime broadens the range of accessible energies for each state enough for the density of states to become quasi-continuous. This smoothing effect gives rise to the relationship between the hot carrier lifetime and the hot carrier distribution [52].

### 2.4 Metal-Semiconductor Interfaces

At the interface between two different materials, the electronic states are modified due to the difference in the occupied energy states. At a metal-semiconductor junction this difference is characterised by an imbalance of the Fermi levels. The Fermi level in an intrinsic semiconductor ($E_{F,s}$) is situated halfway between the valence and conduction band edges. However, by doping the material, the Fermi energy can be shifted up (n-type) or down (p-type) to a degree dependent on the concentration of dopants used. The change in electron occupancy at metal-semiconductor heterojunctions depends on the relative Fermi levels. Through careful selection of materials, a potential energy barrier can be formed allowing for photo-induced charge separation. This charge separation underpins many advancements in photocatalysis and opto-electronic devices.

#### 2.4.1 Interfacial band-bending properties

Upon contacting a metal and semiconductor, the free electrons will transfer between the metal and semiconductor due to the difference in electron potential energies. Charge carriers will be exchanged until a constant Fermi level is achieved throughout the device. When the Fermi level of the metal is lower than that of the semiconductor, charge will flow to the metal causing the semiconductor Fermi level to decrease. By induction, positive charges will accumulate at the surface of the semiconductor, called a depletion layer. This induces an electric field at the interface; if a subsequent electron is to move from the semiconductor it must have enough energy to overcome this field. The energy band edges in the semiconductor shift continuously
due to the electric field between the semiconductor and the metal due to charge transfer. This process is called band bending.

The metal and semiconductor work functions are given by $\phi_m$ and $\phi_s$, respectively. If $\phi_m > \phi_s$, there is an upward bend and a downward bend if $\phi_m < \phi_s$. The magnitude of band bending is given by $v_{BB} = |\phi_m - \phi_s|$ and the electron affinity is given by: $\chi_s = E_{vac} - E_C$.

The difference in energy an electron would need to overcome to move into the semiconductor $(\phi_M - \chi_s)$ is called the Schottky Barrier [73].

When the Fermi level of the metal is higher than that of the semiconductor, charges will flow to the semiconductor causing the metal Fermi level to decrease causing the electrons to accumulate at the semiconductor surface. This is called the accumulation layer. The electric field is now the opposite direction, allowing semiconductor electrons to move more easily into the metal. This is characterised by a downward bend of the conduction band of the semiconductor. This is the case of Ohmic Contact [73].

Similar arguments apply at the interface between a metal and an adsorbed molecule where the highest-occupied molecule orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) are analogous to the valence band and conduction band respectively [74]. In the perspective of holes, the arguments above are simply reversed. That is, an electron Ohmic contact forms a barrier for holes (hole Schottky contact). An electron Schottky contact forms an Ohmic contact for holes. Thus, the type of contact formed is dictated by the dominant carrier of the semiconductor being used (n- or p-type). Each case is summarised in Figure 2.8.

### 2.4.2 Separation mechanisms at the interface

Due to the ultra-short timescales involved, there is a disagreement in the literature regarding the transfer process of hot carriers from metals to adjacent media. Several mechanisms have been proposed and experimentally verified implying that charge carriers and energy are extracted from metals using a combination of pathways. The most prevalent mechanisms proposed thus far are direct electron transition (DET) over a Schottky barrier [75, 12], enhanced semiconductor absorption by the plasmon-induced local electromagnetic field (LEMF) [76, 77], resonant energy transfer (RET) [78] via dipole-dipole coupling, and chemical interface damping (CID) [79] due to surface states at the interface.
2.4. Metal-Semiconductor Interfaces

Figure 2.8: Band bending at a metal-semiconductor interface for several different cases of metal work function ($\phi_M$) and semiconductor electron affinity ($\phi_S$). (Top-Left) When $\phi_S < \phi_M$ in an n-type semiconductor, electrons accumulate at the semiconductor surface (accumulation layer). This results in an upward bend of the semiconductor’s conduction band forming an electron Schottky barrier. (Top-Right) When $\phi_S > \phi_M$ in an n-type semiconductor, electrons accumulate at the metal’s surface (depletion layer). This results in a downward bending of the semiconductor’s conduction band forming an Ohmic contact. (Bottom-Left) When $\phi_S < \phi_M$ in a p-type semiconductor, electrons accumulate at the semiconductor surface (accumulation layer). This results in an upward bend of the semiconductor’s valence band forming an Ohmic contact for holes. (Bottom-Right) When $\phi_S > \phi_M$ in a p-type semiconductor, electrons accumulate at the metal’s surface (depletion layer). This results in a downward bending of the semiconductor’s valence band forming a hole Schottky barrier.
Direct Electron Transfer

As shown in Figure 2.8, a Schottky barrier can form at the interface between a metal and a semiconductor if the Fermi level of the metal is below that of the semiconductor. This provides a way of capturing hot electrons with energies greater than the barrier height while preventing back-flow of electrons via the intrinsic electric field at the junction. The efficiency of the electron transfer across the Schottky barrier ($\Phi_S$) is given by a modified Fowler formula [80] accounting for thermionic emission from the metal to the semiconductor.

$$\eta = \frac{(h\nu - e\Phi_S)^2}{4E_Fh\nu}$$

Since the efficiency depends on both the Schottky barrier height and the Fermi level of the metal ($E_F$), the choice of material is critical for the optimisation of hot electron applications. It should be noted that an analysis of the electronic structure at the interface between Au nanoclusters and TiO$_2$ showed a hybridisation of electronic states of both materials. This was expressed by a broadening of the peaks in the density of states compared to the isolated particles making transitions more easily accessible [81]. This is observed experimentally as an increase in absorption at the associated wavelengths. Thus far, TiO$_2$ has been a commonly used electron-accepting semiconductor for gold and silver with 1 eV and 0.91 eV Schottky barriers formed respectively [82, 83]. However, it was found that energies below the Schottky barrier can also allow electron transfer via quantum tunnelling [84], enhancing the overall photocurrent measured in the semiconductor. A schematic diagram of this process is shown in Figure 2.9.

Resonant Energy Transfer

First proposed as a means of electron transfer by Scott Cushing et al. in 2012 [78], resonant energy transfer (RET) is a non-radiative energy transfer mechanism through the coupling of electrons in an adjacent material to a dipole. It is known that energy can be passed between two closely spaced charge distributions via dipole-dipole interactions in a process called Förster resonance energy transfer [85]. In the case of semiconductors, the dipole excited via the surface plasmon mode decays and transfers its energy to the electrons of the semiconductor, resulting in the formation of an electron-hole pair. As such, the efficiency of this process is directly related
2.4. Metal-Semiconductor Interfaces

Figure 2.9: Direct electron transfer schematic diagram at a Schottky barrier interface. Due to the potential barrier formed by the accumulation of electrons at the semiconductor surface, only high energy electrons can traverse the interface. Low energy electrons are reflected by the electric field of the accumulation layer where high energy electrons can cross into the semiconductor and remain there.

to the overlap of the plasmon resonance and semiconductor absorption spectra. This process is not guided by the band structures of the material and as such, electrons can be excited both above and below the semiconductor bandgap.

In the study performed by Cushing [78], the contribution by RET was distinguished by that of direct electron injection by comparing the photocatalytic activity in $Cu_2O$ in both direct $Au/Cu_2O$ junctions and insulated junctions $Au/SiO_2/Cu_2O$ that inhibit the transfer of electrons. The insulated structure showed a higher photocatalytic efficiency than the bare $Au/Cu_2O$ particle even with the electron transfer blocked by the silica. This is attributed to the red-shifting of the plasmon resonance when the $Au$ is coated in $SiO_2$, increasing the overlap with the semiconductor absorption spectrum. This has since been further supported experimentally in core-shell and other metal-semiconductor structures [86, 87]. A schematic diagram of the process is shown in Figure 2.10.
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Figure 2.10: Schematic diagram of resonant energy transfer. Each dipole mode is shown as a crossed yellow arrow. The dipole-dipole coupling (requiring overlap of the metal’s emission spectrum and the semiconductor’s absorption spectrum) allows for the decay of the plasmon resonance to transfer energy into an electron in the semiconductor allowing it to be excited across the bandgap.

Chemical Interface Damping

At the interface between two materials, in this case the metal and adjacent semiconductor, the actual electronic states are not as simple as shown in the band bending schematics (Figure 2.8). The chemical bonds that form at the interface can introduce new electronic states near the Fermi energy that will influence the exchange of charges. Furthermore, as it is the surface electrons that play the operative role in surface plasmon resonances, these interfacial states can have a profound impact on the harvesting of electrons from optically driven metal nanoparticles. These surface states can provide additional decay channels, decreasing the plasmon resonance lifetime and increasing absorption.

This was initially proposed in the context of Au nanoparticles fixed to CdSe rods, which showed an internal quantum yield of up to 24%.[88] This work paralleled what was being done on interfacial charge transfer processes between a metal and adsorbed molecule. The presence of the acceptor states of the molecule increased the rate of plasmon dephasing and increased absorption [89] In this context, it was widely termed chemical interface damping (CID). The electron transfer process was confirmed showing an inverse relation with the distance electrons need to travel to the surface [90]
Indeed, the similarities between the metal-molecule and its metal-semiconductor counterpart even prompted many to apply the term chemical interface damping to metal semiconductor systems [91]. This process provides insight to the observed photocatalytic activity beyond what is expected from Fowler-like crossing of a potential energy barrier. The decay of the surface plasmon leaves a hole in the metal and electron in the semiconductor, leading to instantaneous charge separation. This often neglected mechanism works in tandem with the other mechanisms above to provide the plasmon-enhanced effects observed in experiments.

![Diagram of plasmon-enhanced interfacial charge transfer process](image)

**Figure 2.11:** Schematic diagram of the plasmon-enhanced interfacial charge transfer process. The dipole mode is represented as a crossed yellow arrow. The presence of a surrounding media damps the plasmon resonance and through interfacial states an electron can be instantaneously excited directly into the semiconductor’s conduction band, leaving a hole remaining in the metal.

### 2.4.3 Plasmon-Enhanced Hot Carrier Applications

The ability to excite and separate electrons at junctions between p- and n-type semiconductors underpins such pervasive devices as the transistor, photovoltaic cell, and photodetector. Similarly at metal-semiconductor junctions, metals can act as the electron source. This is currently a very active area of research, particularly in exploiting surface plasmon resonances in nanostructures to increase the hot carrier generation and harvesting rates. Beyond the exploitation of plasmon resonances, a key advantage in using metals over semiconductors is the ability to generate energetic carriers at low photon energies below the bandgap of semiconductors.
Plasmon-enhanced hot carrier applications include: hot carrier photocatalysis, sub-bandgap photodetection and plasmon-enhanced solar energy conversion.

**Hot Carrier Photocatalysis**

The hot carriers generated in metals can participate in photochemical reactions if utilised before they thermalise with the lattice. Energetic carriers can diffuse to the surface of a particle or adjacent semiconductor and participate in catalytic reactions at the active sites by depositing energy into the chemical bonds of the surrounding media or an adsorbed material [92, 93]. As the Fermi level of the metal is typically higher than the valence band of the semiconductor, it allows sub-bandgap photons to excite electrons that can participate in catalytic reactions [82].

The photocatalytic abilities of semiconductor/metal hybrid particles is greater than that of the metal or semiconductor alone due to plasmon-enhanced absorption and hot electron generation processes as outlined above. This was shown in both Au/\(SiO_2/Cu_2O\) [78] and Au/\(Fe_2O_3\) [94] core-shell structures. Furthermore, the additional energy of hot electrons can effectively reduce the activation energy of chemical processes such as the dissociation of adsorbed \(H_2\) [95]. Furthermore, the energetic electrons and holes have an associated reduction and oxidation potential respectively [96, 97]. Using this, large-scale photo-reduction of silver ions in solution was demonstrated at distances of several beam diameters away from the illumination spot [98]. By reduction of silver ions to silver atoms (\(Ag^+ \rightarrow Ag\)) and subsequent adsorption, clusters were formed on a flat substrate surface.

The development of plasmon enhanced photo-chemistry has spawned an interest in artificial photosynthetic technology. For example, clean energy could be produced by converting solar energy into chemical energy. The idea relies on the dissociation of water by plasmonic catalysis using solar radiation, producing \(H_2\) gas [99]. The chemical process relies on both energetic electrons and holes and proceeds as follows:

\[
H_2O + 2h^+ \rightarrow 2H^+ + \frac{1}{2}O_2 \quad (2.20)
\]

\[
2H^+ + 2e^- \rightarrow H_2 \quad (2.21)
\]

The resultant hydrogen gas bubbles can be collected and used as fuel. An autonomous device
was developed by Mubeen et al [100]. based on Au nanorods in $TiO_2$. The top surface is coated in $Pt$ nanoparticles, which are responsible for the reduction of $H^+$ to $H_2$ gas. This device showed stability for over 60 hours and an external quantum efficiency of 0.25%. $Au-TiO_2$ remains the standard system for such devices with a plethora of additional studies looking to enhance the $H_2$ generation rate [101, 102, 103, 104].

One significant problem in hot electron photocatalysis is the charging of the metal following the transfer of electrons to an adjacent material. This then increases the potential barrier for subsequent hot electron transfer. To remedy this, an electron source or hole transporting material must be included to maintain charge neutrality. This has been performed using $Fe^{2+}$ and the redox couple $I^-/I_3^-$ with the fastest regeneration time measured to be 20 ns with Au immersed in $I^-$ [12, 105, 106]. This has also been accomplished using an ITO film as a transparent electrode to replenish extracted charges in gold nanoparticles [107].

Sub-Bandgap Photodetection

Conventional semiconductor-based photodetectors are a staple in most optics and photonics applications and rely on an incident photon exciting an electron across the bandgap of the semiconductor. As such, only photons whose energy is above the bandgap are detected, restricting the operation range. For silicon detectors this cutoff is at wavelengths above 1100 nm, preventing any detection at telecommunication wavelengths (1530-1565 nm). This can be circumvented by exploiting the band-bending behaviour at metal-semiconductor interfaces. Schottky barriers formed at these interfaces can be used to harvest high energy electrons in the metal where the interfacial energy barrier assures electrons do not return to the metal [73].

Schottky barrier photodetectors have been used for over a decade,[108, 109] but in 2011 the collection of hot electrons resulting from the decay of plasmon resonances in gold nanoparticles was experimentally demonstrated [110]. Using the Schottky barrier formed between an n-Si substrate and Ti adhesion layer, the excited electrons are harvested as a photocurrent at photon energies below 1650 nm. However, the responsivity (photocurrent extracted per unit of input laser power) was much lower when the plasmon resonance is tuned into the IR simply to the weaker absorption of gold and overlap with the Schottky barrier height. Nevertheless, this spawned an enthusiastic response with the application of this concept to different metals (Ag
Chapter 2. Background Theory

[111], Al [34, 112]) and many different geometries [110, 112, 113, 42]. A recent comprehensive review of hot electron photodetectors [28] also explain 2D materials for electron collection.

2.4.4 Transition Metal Oxide semiconductors

Transition metal oxides (TMOs) are a class of materials that are comprised of a metal bonded with one or more oxygen atom. Many of the physical, chemical, and optical properties of this diverse range of materials depends on the relative difference between the electronegativity of the metal (low 1.3-1.65) and the oxygen (high, 3.44) leading to diverse bonding properties. In transition metal oxides, the limited overlap between the valence d-orbitals of the metal and oxygen p-orbital leads to narrow electronic bands between 1-2 eV compared to 5-15 eV for metals [114]. In many cases, this narrowing of the conduction band introduces a range in energies with no possible electronic states (bandgap) giving transition metals their characteristic semiconducting properties. Well-known examples of TMOs are titanium dioxide (TiO$_2$), zinc oxide (ZnO), and vanadium oxide (V$_2$O$_5$) widely used in catalysis, manufacturing, and UV absorption in sunscreen.

The photocatalytic abilities of TMOs were first discovered with UV-excitation of titanium dioxide in the early 1970s [115] and have since been applied to photocatalysis in both liquid [116] and gas phases [117, 118] and using other TMOs [119]. As excitation generates electron-hole pairs with an electron being excited to the conduction band and hole remaining in the valence band, both reduction and oxidation are possible to stabilise environmental contaminants. TMOs also form on the surfaces of many transition metals once exposed to air. The dangling metal bonds remaining following deposition leaves the surface susceptible to oxidation in air. TMOs formed in either process are also highly susceptible to defects such as interstitial metal implantation or oxygen vacancies that can act as electron traps and introduce states within the bandgap. This has the potential to decrease the bandgap energy as has been observed in titanium dioxide [120].
2.5 Summary

The static and dynamic properties of metals alone as well as interfaced with a semiconductor were studied and related to experimentally observable parameters. This ranged from the macroscopic permittivity to ultrafast electron scattering and injection. With an intuition of the interconnected nature of the optical and electronic properties of a material, it is now possible to use optical measurements to probe the harvesting and recombination of hot carriers at metal-semiconductor interfaces. This is extremely powerful as optical measurements are much more sensitive to small signals and can be performed at extremely fast timescales. This allows new physical process to be studied that would not be possible with purely electronic measurement techniques. Optical measurements combined with theoretical models are exploited throughout this work to provide physical bases of the unique behaviour of novel materials systems.
Chapter 3

Experimental Methods

This chapter presents the optical measurement techniques and how they are used in tandem with theoretical modelling to determine the properties of a given material. Transient pump-probe spectroscopy is used to observe the temporal response of an electronic system. The evolution of the reflectivity over time is then related to the energy dissipation mechanisms discussed in the previous section. For the linear optical properties, spectroscopic ellipsometry is used. The polarisation-dependent reflection amplitudes and phase delays are used to relate the measured values to the electronic properties using a Drude-Lorentz model. Multi-layer models are also developed to account for the interference of reflected beams from multiple interfaces.

3.1 Transient Pump-Probe Spectroscopy

The free electrons in metals travel at the Fermi velocity ($\tilde{v} \approx 10^6 \text{ m/s}$), experiencing collisions over distances of the mean free path (tens of nanometers [121]). Collisions occur at rates of $\approx 10^{14} \text{s}^{-1}$ or on timescales on the order of 10 femtoseconds. Electronic measurement techniques cannot resolve these process even with the current state-of-the-art fibre optic photodetectors with bandwidths of 100 GHz. All-optical detection methods are required where the temporal resolution is only limited by the pulse width of the laser. This section discusses all-optical time domain measurements capable of resolving $\approx 100 \text{fs}$. Although this is not fast enough to directly observe electron-electron scattering, it is sufficient to observe electron-phonon interactions, which occur on the order of single picoseconds for conventional metals[122].

An established measurement technique, called transient pump-probe spectroscopy, uses
two ultrafast pulses with tunable relative optical path lengths to observe the evolution of the reflection or transmission of a given sample over time. The first pulse, termed the pump pulse, arrives and excites the sample through electron absorption processes. The second pulse, termed the probe, travels along a variable path controlled with a motorised delay stage producing a time delay between the two pulses. The probe, typically at a lower power than the pump, is reflected by (or transmitted through) the pump-excited system. By mechanically “chopping” the pump, the difference in reflection (or transmission) with and without the pump can be determined. This can then be directly related to changes in the optical properties of the sample and, in turn, the electronic properties.

The achievable temporal resolution of pump-probe spectroscopy has established it as a standard characterisation technique and is presently used in a wide range of disciplines from cancer diagnosis [123] to monitoring chemical reactions [124, 125, 126] and device characterisation [127]. In photonics, the development of sub-ten femtosecond and attosecond lasers has made it possible to resolve ultrafast processes with pump-probe spectroscopy that were not previously possible. This includes, scattering of nonthermal electron populations, [128, 129, 130] the decay of surface plasmon resonances [131, 132] and nonlinear optical properties of materials [133].

The ability to tune the wavelengths of the pump and probe allows for comprehensive investigations of materials, e.g. by accessing the desired transitions of a materials band structure. However, there is a fundamental trade-off between the temporal and spectral resolution of a setup. An ultra-short laser pulse of temporal width ($\tau$) must have spectral bandwidth ($\Delta \nu$), such that $\tau \Delta \nu \geq c_B$, where $c_B$ is a constant depending on the pulse shape [134]. A 10 fs pulse will have a bandwidth $\Delta \nu \geq c_B / \tau \approx 10$ THz. At optical frequencies, this is comparable to the bandwidth of plasmon resonances and limits the wavelength selectivity of material resonances. Thus there is a distinct advantage in working with optical pulse widths on the 100 fs timescale.

### 3.1.1 Experimental Setup

A schematic of the experimental setup and its relevant components are shown in Figure 3.1. Initially, a 180 fs pulse is generated with a possible spectral range of 700-900 nm, which pumps an optical parametric oscillator (OPO). The seed pulse is split into two using a beam splitter,
Figure 3.1: Experimental setup of the transient pump-probe spectroscopy technique. An ultrafast near infrared pulse (pump) is generated using the Ti:Sapphire laser, which is then split into two. One pulse pumps an optical parametric oscillator (OPO) to generate infrared (1000-1550 nm) probe pulses. The pump pulse is chopped using a mechanical chopper and the probe is guided onto a delay stage to control the relative path lengths between the pump and probe. The pulses are then collimated and directed to the sample. The reflection is guided to a photodetector where the remaining pump signal is filtered out. Using a lock-in amplifier connected to the mechanical chopper a differential reflectivity signal is measured.

Detection of the small pump-induced changes to the reflectivity in metals is challenging due to the large intensity of the reflected beam. However, through use of the mechanical
chopper, the pump beam is modulated at the frequency $\omega_L$. As the reflected intensity of the probe beam is dependent on the presence of the pump, the probe beam intensity is also modulated at the same frequency but with a phase shift $\phi$. Through use of a lock-in amplifier, the intensity modulation of the probe can be extracted as a function of pump-probe delay ($\tau$) $(\Delta I(\tau) = I_{\text{Pump}}(\tau) - I_{\text{NoPump}}(\tau))$. As there are many pump pulses for a single “on” phase of the chopper, the measured modulation of the probe is the average over many given pulses.

To account for this accumulation of pulses for a given measurement, the average power is measured simultaneously $(I_0(\tau) = \frac{1}{2}(I_{\text{Pump}}(\tau) + I_{\text{NoPump}}(\tau)))$. This is used to normalise the measured data, explained in more detail in the subsequent section. The change in intensity $(\Delta I(\tau))$, average intensity $(I_0(\tau))$, and relative phase $(\phi)$ are measured simultaneously using an automated LabView program that controls the motorised delay stage and data acquisition.

### 3.1.2 Differential Reflectivity

The degree to which the ground state electronic system is perturbed by the absorption of the pump pulse is inferred from the differential reflectivity $\Delta R/R$ (the percent change of the reflected intensity of a probe pulse with and without the pump). The absorption (and, in turn, the reflection) from a metal surface is dependent on the electron energy distribution. This depends on both the Fermi-Dirac occupation probability $f(E, T_e)$ and the density of electron states $\rho(E)$. The probability of an electron transition from an energy $E_0$ to $E_0 + \hbar \omega_{\text{probe}}$ depends on the probability of there being an occupied state at energy $E_0$ and an unoccupied state at $E_0 + \hbar \omega_{\text{probe}}$. That is,

$$P(E_0 \rightarrow E_0 + \hbar \omega_{\text{probe}}) \propto f(T, E)[1 - f(T, E_0 + \hbar \omega_{\text{probe}})] \quad (3.1)$$

The total probability of absorption of a photon of energy $\hbar \omega_{\text{probe}}$ is the integral over all such energies, $E_0$.

$$P_{\text{Abs}}(\hbar \omega_{\text{probe}}) \propto \int P(E \rightarrow E + \hbar \omega_{\text{probe}})dE \quad (3.2)$$

The excitation of the electron population by absorbing energy from the pump pulse results in a modification of the electron distribution function and a corresponding change to the absorption. To prevent any interaction of subsequent pump pulses, the repetition period of the laser should
be much larger than the response time of the electronic system. In this case, the repetition rate is 80 MHz (period of 12.5 ns), while the slowest processes considered are on the order of hundred of picoseconds. However lattice cooling may persist for microsecond timescales.

At negative time delays (probe arriving before the pump), there is no difference in absorption with or without the pump as reflection occurs before the arrival of the pump and the electronic system has recovered following previous pump pulse. However, for positive probe delays (probe arriving after the pump), the pump induced change to the electron distribution is observable by the change in reflected intensity of the probe.

The differential reflectivity is calculated as the percent change in intensity with and without the pump:

$$\frac{\Delta R}{R_0}(\tau) = \frac{I_{\text{Pump}}(\tau) - I_{\text{NoPump}}(\tau)}{\frac{1}{2}(I_{\text{Pump}}(\tau) + I_{\text{NoPump}}(\tau))}$$

(3.3)

As these are dynamic values with respect to the probe delay (\(\tau\)), it is critical to measure this over time to observe the changes in the energy density of the electrons, which is described using a time-dependent function \(\frac{\Delta R}{R}(\tau)\). At \(\Delta \tau = 0\), the pump and probe arrive at the same time. Before this (\(\Delta \tau < 0\)), the probe arrives before the pump and so there is no pump-induced changes observable by the probe (\(\frac{\Delta R}{R}(\tau) = 0\)). At positive delays (\(\Delta \tau > 0\)) the electron energy density increases and then subsequently decreases as the system relaxes back toward its ground state. By taking measurements at each time step, the full evolution of the electron energy density is extracted.

### 3.1.3 Measuring differential reflectivity with a lock-in amplifier

As metal surfaces are typically highly reflective, the pump-induced change to the reflected intensity is small relative to the total intensity (\(\Delta R/R \lesssim 10^{-5}\)). Lock-in amplification uses phase-sensitive detection to isolate the relevant signal based on a known AC reference. The background and noise, however, are not amplified in the signal convolution process. Therefore, there is a dramatic enhancement of the signal-to-noise ratio allowing for resolution of such small signals.

In this case, the chopper wheel is used to modulate the pump signal resulting in a corresponding modulation of the reflected probe signal. The chopper signal, with frequency
3.1. Transient Pump-Probe Spectroscopy

\( \omega_L \), is fed as an input to the lock-in amplifier where an AC reference voltage is generated as:

\[
V_{\text{ref}}(t) = V_L^0 \sin(\omega_L t + \theta_{\text{ref}}) \tag{3.4}
\]

where \( V_L^0 \) and \( \theta_{\text{ref}} \) are the amplitude and phase shift of the generated reference signal. \( V_L \) is controlled manually using the sensitivity settings on the control panel. The signal collected at the detector has the form:

\[
V_{\text{sig}}(t) = V_{\text{sig}}^0 \sin(\omega_L t + \theta_{\text{sig}}) \tag{3.5}
\]

where \( V_{\text{sig}}^0 \) is the measured wave amplitude and \( \theta_{\text{sig}} \) is the phase delay of the signal relative to the reference.

The lock-in amplifier used, the Stanford Research Instruments SR830 [135], then multiplies the signal and reference waves, and time averages the result over a time constant \( t_p >> 2\pi/\omega_L \):

\[
\langle V(t) \rangle = V_{\text{sig}}^0 V_L^0 \sin(\omega_L t + \theta_{\text{ref}}) \sin(\omega_L t + \theta_{\text{sig}}) = \frac{V_L^0 V_{\text{sig}}^0}{2} \langle \cos(\theta_{\text{sig}} - \theta_{\text{ref}}) \rangle \tag{3.6}
\]

to produce a DC signal. By adjusting the reference phase, we can make \( \theta_{\text{sig}} = \theta_{\text{ref}} \) and the cosine term becomes unity allowing for direct extraction of the measured signal amplitude. Alternatively, the first output is taken to be \( \langle V(t) \rangle = X \) and a second reference signal is generated, shifted by \( \pi/2 \) with respect to the first reference signal such that:

\[
V_{\text{ref},2} = V_L^0 \sin(\omega_L t + \theta_{\text{ref}} + \frac{\pi}{2}) \tag{3.7}
\]

Now a second output (Y) can be determined depending on the sine of the signal/reference phase difference:

\[
Y = \frac{V_L^0 V_{\text{sig}}^0}{2} \sin(\theta_{\text{sig}} - \theta_{\text{ref}}) \tag{3.8}
\]

It is straightforward to deduce the signal’s amplitude as \( R = \sqrt{X^2 + Y^2} = V_{\text{sig}} \) and the relative phase as \( \theta_{\text{sig}} - \theta_{\text{ref}} = \tan^{-1}(Y/X) \).
3.1.4 Fitting to Experimental Data

Following measurements of differential reflectivity at various delay times, a physical model is applied to the data to determine the underlying physical parameters. In this work, the Levenberg-Marquardt minimisation algorithm is used in Origin, a graphing and data analysis software package. The Levenberg-Marquardt algorithm accounts for the gradient of the minimisation curve, which better avoids stopping in local minima. Letting the discrete measured data be represented by a function \( y(\tau) \), which is a collection of \( M \) experimental values, a parameterised function \( f(\tau; \lambda_i) \) is proposed in terms of \( p \) parameters, \( \lambda_i \), with initially guessed values \( \lambda_i^0 \). The fitting proceeds through minimisation of a trial function \( S(\vec{\beta} + \vec{\delta}) \) for the set of parameters \( \vec{\beta} = \{\lambda_i\} \) and a perturbation \( \vec{\delta} \):

\[
S(\vec{\beta} + \vec{\delta}) = \sum_{j=1}^{M} (y(\tau_j) - f(\tau_j; \vec{\beta}) - \nabla_{\vec{\beta}}[f(\tau_j; \vec{\beta})] \vec{\delta})^2
\]  

(3.9)

The \( R^2 \)-value is the chosen value used to evaluate the quality of the fit, which is adjusted to account for the number of fitting parameters used. This is designed to prevent over-fitting as the \( R^2 \) value alone does not account for the number of parameters [136]. The adjusted \( R^2 \) is defined in terms of the conventional \( R^2 \) value:

\[
R^2_{\text{Adj}} = \frac{(1 - R^2)(M - 1)}{M - p - 1}
\]  

(3.10)

where the \( R^2 \) value is calculated using the formula:

\[
R^2 = 1 - \frac{\sum_i (y_i(\tau_i) - f_i(\tau_i; \lambda_i))^2}{\sum_i (y_i(\tau_i) - \bar{y})}
\]  

(3.11)

with \( y_i = y(\tau_i) \) and \( f_i = f(\tau_i; \lambda_i^f) \) in terms of the fitted parameters \( \lambda_i^f \). By definition the adjusted \( R^2 \) value lies between 0 and 1, with 1 being a perfect fit to experimental data and 0 signifying no correlation between the fitted curve and experimental data. Typically due to experimental noise, \( R^2_{\text{Adj}} = 1 \) is never obtainable but low-noise measurements are able to exceed \( R^2_{\text{Adj}} = 0.98 \) considered to be a very good fit. The uncertainties on the fitted parameters are taken to be one standard deviation on either side of the fitted value, giving relatively high certainty (68.2%) that the true value is within the range stated.
3.2 Spectroscopic Ellipsometry

As emphasised previously in Section 2.2, determining the optical properties of a material resolves a wide range of complex light-matter interactions. The dielectric permittivity quantifies both interband and intraband absorption processes, determines the plasmon resonance, and describes the dispersion of light through the material. As such, a systematic experimental method of determining the optical properties of a deposited thin film is invaluable in the exploration of novel materials. Spectroscopic ellipsometry is a conventional method for determining the optical property of thin films. It uses measured reflection spectra, with knowledge of the polarisation-dependent Fresnel equations and film thickness, to determine the dielectric permittivity.

3.2.1 Polarisation and Fresnel’s Equations

Ellipsometry uses linearly-polarised broad spectrum light generated from a lamp to measure reflection from a thin film surface. The generated light is some superposition of s-polarised light, also known as transverse electric (TE), and p-polarised light, also known as transverse magnetic (TM). According to Fresnel’s equations [137], the fraction of incident light reflected from an interface formed between one material with refractive index \(n_1\) and another with refractive index \(n_2\) as a function of incident angle \(\theta_i\) and transmitted angle \(\theta_t = \sin^{-1}\left[\frac{n_2}{n_1} \sin \theta_i\right]\) is:

\[
R_S = \frac{\left|n_1 \cos \theta_t - n_2 \cos \theta_i\right|^2}{\left|n_1 \cos \theta_t + n_2 \cos \theta_i\right|^2} \quad (3.12)
\]

\[
R_P = \frac{\left|n_1 \cos \theta_t - n_2 \cos \theta_i\right|^2}{\left|n_1 \cos \theta_t + n_2 \cos \theta_i\right|^2} \quad (3.13)
\]

The polarisation-specific reflection coefficient is shown as a function of incident angle in Figure 3.2 for light propagating through air reflecting off a surface with various refractive indices (1.2-2). The different reflection coefficients for s- and p- polarisations results in elliptically polarised light. The strong dependence of the reflected intensity on the polarisation and incident angle gives ellipsometry its high sensitivity. By looking at the two polarisations simultaneously, the optical properties can be reliably extracted.
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Figure 3.2: Angular dependence of the s-polarised (left) and p-polarised (right) reflection for indices of refraction ranging from 1.2 to 2 calculated using the Fresnel equations. This underpins the use of multi-angle measurements in spectroscopic ellipsometry for the determination of a sample’s refractive index.

3.2.2 Experimental Process and Theory

A schematic of the full experimental setup of the J.A. Woollam WVASE ellipsometer is shown in Figure 3.3. Initially, unpolarised light is generated (350-2000 nm) using a Quartz Tungsten Halogen (QTH) lamp. A variable-wavelength monochromator allows specific wavelengths to be selected for measurement. The beam is then linearly polarised using a polariser, reflectes off of the sample and then passes through a second polariser, termed an analyser, which is rotating at a fixed frequency (between 10 and 60 Hz). Finally, the photodetector (Si between 350-1340 nm, InGaAs between 1450-2000 nm) converts the signal into a voltage, which oscillates at the same frequency as the analyser rotation frequency.

Except for a very particular incident angle, termed Brewster’s angle, the reflected light from the surface will be a superposition of s- and p- polarisation of varying intensities resulting in elliptically polarised light. The exceptional condition can be seen with the minima in Figure 3.2 and more clearly in Figure 3.4. Several incident angles from this region are selected for reflection measurements due to the considerable difference between the two polarisations.

At each angle of incidence and wavelength, ratios between the two polarisation are measured. The ratio of the two amplitudes is characterised by an ellipsometric parameter $\tan(\Psi) = \sqrt{|r_p|^2/|r_s|^2}$. The phase difference is encapsulated by the second ellipsometric parameter $e^{i\Delta} = e^{i(\Delta_p - \Delta_s)}$. For simplicity, a single quantity $\rho$ is defined to be the product of the
3.2. Spectroscopic Ellipsometry

![Experimental setup of the varying angle spectroscopic ellipsometer. The lamp generates continuous light, which passes through a linear polariser to selective filter s- or p-polarisation. This polarised light is reflected off the sample as elliptically polarised light and then the magnitude of the reflected field is measured using a rotating analyser and photodetector.]

Two ellipsometric parameters containing both amplitude and phase information:

\[ \rho \equiv \tan(\Psi)e^{i\Delta} = \frac{r_p}{r_s}e^{i(\Delta_p - \Delta_s)} \quad (3.14) \]

In general, the voltage collected by the photodetector \((V(t))\) will have a DC offset \((V_0)\), which can be used to normalise the voltage:

\[ \frac{V(t)}{V_0} = 1 + \alpha \cos(2\omega t + \phi) + \beta \sin(2\omega t + \phi) \quad (3.15) \]

where \(\omega\) is the angular frequency of the analyser, and \(\phi\) the phase delay of the analyser. The coefficients \(\alpha\) and \(\beta\) are the Fourier expansion coefficients of the collected signal and are obtained using the Fourier transform. Using these coefficients and the angle of the input polariser axis with respect to 0° (P), the ellipsometric parameters can be retrieved using the following expressions[138]:

\[ \tan \Psi = \sqrt{\frac{1 + \alpha}{1 - \alpha}}|\tan P| \quad (3.16) \]

\[ \cos \Delta = \frac{\beta}{\sqrt{1 - \alpha^2}}|\tan P| \quad (3.17) \]
3.2.3 Modelling and Fitting

For single, homogeneous, isotropic, bulk materials, where multiple reflections can be neglected, the optical properties can be estimated using a pseudo-permittivity ($\langle \epsilon \rangle$) from the extracted parameters. This can be calculated as [41]:

$$
\langle \epsilon \rangle = \sin^2(\theta)[1 + \tan^2(\theta)(\frac{1 - \rho}{1 + \rho})^2]
$$  \hspace{1cm} (3.18)

For samples with surface roughness, multiple layers, or thin films, this approach is insufficient and one uniform permittivity from the measured parameters is meaningless. More complex regression analysis is required that leverages oscillators to represent optical transitions and account for the interference of multiple reflections.

In multi-layer thin films, a portion of light transmitted through the air-film interface can reflect off the substrate one or more times and interfere with other reflections. As such, the film thickness is a key parameter to accurately determine the optical properties of the film. In addition, the reflected intensity depends on the materials in the stack, thereby increasing the number of free parameters in a general model. Several fitting and analysis iterations are generally performed to find the best model, quantified by a minimisation of the mean-squared error (MSE). This value quantifies the difference between a series of N experimentally measured points ($\Psi_i^{Exp}$, $\Delta_i^{Exp}$) to those generated from a model with M free parameters ($\Psi_i^{Mod}$, $\Delta_i^{Mod}$).
The MSE is then calculated as follows:

\[
MSE = \sqrt{\frac{1}{2N-M} \sum_{i=1}^{N} \left[ \left( \frac{\Psi_{Mod}^{i} - \Psi_{Exp}^{i}}{\sigma_{\Psi,i}} \right)^2 + \left( \frac{\Delta_{Mod}^{i} - \Delta_{Exp}^{i}}{\sigma_{\Delta,i}} \right)^2 \right]}
\]  

(3.19)

where \(\sigma\) is the standard deviation of the experimentally measured values. The sum over the squares of the differences of the experimental and modelled values is conventionally known as the chi-squared \((\chi^2)\) value and the error is, thus, defined as:

\[
MSE = \sqrt{\frac{1}{2N-M} \chi^2}
\]  

(3.20)

Typically when creating the model one would start with a sample with a known thickness and substrate. This reduces the number of free parameters and increases the reliability of the model. Once this model is determined, more complex investigations can be performed. Through an iterative process of changing material starting points, number of parameters and even types of models, the MSE can be reduced to a minimum. It should be noted that many local minima of the MSE exist and a variety of models and starting points are required to assure that the fit is the most accurate.

The accuracy of a fit can be evaluated based on the square root of the mean squared error (root-mean-square deviation or RMSD), which has the same units as the estimated value. If the value is much smaller than the range of values of the measured data, the associated fit is considered to be good. For ellipsometry data, \(\Psi\) and \(\Delta\) vary between 20 and 180 degrees. As such, a rule-of-thumb is \(MSE < 10\) is considered a satisfactory fit and \(MSE < 1\) is ideal but not always possible due to systematic errors such as surface roughness or material defects which cause noise in the measurements. Figure 3.5 shows exemplary ellipsometric measurements \((\Psi, \Delta)\) of a 50 nm gold film on glass. In the ellipsometry modelling in this work, an increasing number of oscillators is introduced with careful observation of the physical parameters and MSE to assure over-fitting is avoided. Application of this method is shown explicitly in Section 4.2.

The proposed model consists of three Lorentz oscillators representing the interband transitions defined by an amplitude \((A)\), width \((B)\), and centre energy \((E)\). A single Drude oscillator (Lorentz oscillator centred at \(E = 0\)) is included to model the free electron contribution.
Figure 3.5: Ellipsometric fitting procedure to experimentally measured ellipsometric parameters $\Psi$ (top-left) and $\Delta$ (top-right). The dots represent experimentally measured data, the blue curve shows the initialised Drude-Lorentz model and the red curve shows the fitted curve with minimised mean squared error. Shown below are the real (bottom-left) and imaginary (bottom-right) components of the permittivity. The dots show the permittivity calculated directly from the measured data and the solid lines show the calculated values accounting for the substrate reflections before (blue) and after (red) the fitting procedure is performed.

The $\Psi$ and $\Delta$ of the initialised values are shown with the blue curve and deviate significantly below 600 nm. Upon fitting, the curves align very well with the measured data yielding a MSE of 5.9. In Figure 3.5, the permittivity generated from the fitted model (incorporating substrate and multiple reflections) is also shown alongside that of the initialised model and the directly extracted permittivity calculated from $\Psi$ and $\Delta$. There is a marked difference between the free electron absorption ($\varepsilon_2(\lambda > 600 \text{nm})$) between the fitted and calculated permittivities even with nearly identical $\Psi$ and $\Delta$. This emphasises the importance of physically accurate modelling in determining the optical properties of measured films.
3.3 Summary

The key experimental setups were explained in detail along with an introduction to the data analysis. Connections are drawn to the previous section where theoretical models, based on physical parameters are used to described the observed behaviour. Emphasis is placed on the fitting algorithms and fit evaluation techniques to determine the reliability of the fitted parameters. With both the experimental and theoretical approaches established, it is possible to examine novel materials without relying on existing models in the literature. Having a standardised approach developed from fundamental physics allows for a direct comparison between diverse material systems and will be applied to the various materials.
Chapter 4

Titanium Oxynitride for Plasmonic Applications

In this chapter, the experimental methods and theoretical models of Chapter 2 and 3 are applied to characterise the properties of titanium oxynitride. Titanium nitride has been of particular interest for high-power optical studies. However, it is difficult to fully eliminate oxygen in TiN, so understanding TiON is critical. Furthermore, TiON can be tailored to have a wide range of optical and electrical properties. With low oxygen, TiON is highly metallic (TiN-like) but becomes semiconducting with higher oxygen. A brief overview of the surface oxidation process and multi-layer ellipsometry model developed for this system is presented. To make the most metallic film possible, the deposition temperature, environmental composition and residual oxygen are varied to produce films that are then characterised by ellipsometry to determine losses and degree of metallic behaviour using the permittivity. With its metallic properties, TiON can be used as a plasmonic material if patterned into nanostructures. Two nano-patterning methods are compared: reactive ion etching (RIE) and chromium liftoff. The shape and optical properties of the particles are then compared to determine the optimal fabrication method. This systematic characterisation will act as the foundation for the subsequent investigation of electronic and plasmonic behaviour of titanium oxynitride thin films and particles.
4.1 Introduction

Although noble metals (Au, Ag) have underpinned the rapid development of plasmonics over the past decade, there are irreconcilable limitations that continue to prevent the widespread industrial integration of plasmonic devices. These problems stem from incompatibility with silicon manufacturing techniques due to low melting temperatures, lack of tunability over wide spectral ranges, as well as chemical instability. This has spurred a new branch of research into novel materials that could circumvent the problems of noble metals. A dominant class of materials are the transition metal nitrides, in particular titanium nitride (TiN) with optical properties that are claimed to be comparable to gold.[1] The stronger covalent bonds between the titanium and nitrogen atoms makes this metallic ceramic much more robust to higher temperatures to gold [139, 42].

There has thus been a surge of interest in using TiN for plasmonic applications. With its higher melting temperature, it was shown to be able to maintain its nonlinear (second harmonic generation) properties above $8 \text{GW/cm}^2$, where gold experiences irreversible degradation of its optical properties [140]. The potential benefits extend beyond structural integrity to enhanced hot electron generation [16] and photocatalytic ability [15]. As studied in this work, its diatomic unit cells allows for tunable stoichiometry to vary its optical properties [41]. However, variations in stoichiometry also leave the material more susceptible to the formation of defect centres that can lead to unpredictable or inhomogeneous behaviour.

Titanium oxynitride ($\text{TiO}_x\text{N}_y$ or simply TiON) can form naturally during the oxidation of titanium nitride as oxygen diffuses from the surface and substitutes nitrogen atoms in the lattice [141]. Alternatively, oxygen can be included during deposition for a more uniform inclusion of oxygen throughout the film [43]. Inclusion of oxygen within the lattice of titanium nitride allows for the control of the material’s free carrier concentration as the strong electronegativity of oxygen effectively acts as an electron trap to control carrier concentration (and in turn the optical properties) without the need of introducing defects.

With the inclusion of oxygen the material properties can be tuned over a wider range from metallic (low oxygen with similar behaviour to TiN) to fully semiconducting (high oxygen with similar behaviour to $\text{TiO}_2$). An earlier study of TiON protective coatings showed that
the physical (hardness and Young’s modulus) and chemical (bioreactivity) properties can be varied continuously through careful control of oxygen [142]. Indeed, we have also shown this to extend to the optical properties with both metallic and semiconducting behaviour in the near infrared achievable with an intermediate double epsilon near zero (ENZ) condition emerging at particular oxygen compositions [43].

4.2 Deposition and oxidation of thin films

A key advantage of the transition metal nitrides over conventional noble metals for use in plasmonics is the inclusion of different atoms in the lattice unit cell. The ability to vary the stoichiometry provides a straightforward method to tune the carrier concentration. Therefore, it is possible to engineer the properties of the material by carefully selecting the deposition conditions. For this work, titanium oxynitride films were deposited onto thin fused quartz substrates by Andrei Mihai from Imperial’s Department of Materials using Pulsed Laser Deposition (PLD).[43] A KrF excimer laser was used to ablate a titanium target into a plasma formed of a variable concentration between $N_2$ and $Ar$ gases. By controlling the nitrogen concentration and substrate temperature, the entire range of properties (metallic to semiconducting) could be achieved as shown by spectroscopic ellipsometry (Section 3.2). In addition, the residual atmospheric oxygen in the chamber was controlled by pre-sputtering of a titanium target for a variable amount of time as described in [43].

The accepted mechanism for surface oxidation proceeds as follows. $Ti^{3+}$ ions diffuse to the surface via interstitial sites [143] resulting in dangling $Ti$ bonds at the surface (Figure 4.1). Upon exposure to air, atmospheric oxygen can adsorb and dissociate at the film’s surface, which was shown to be exothermic [141]. This oxygen can readily bond with the surface titanium. During the oxidation process, it is also possible for oxygen to diffuse into the film and substitute nitrogen atoms. As oxygen atoms require energy to diffuse into the lattice, the probability of oxygen substitution decreases exponentially with depth [141, 144]. These processes continue until a self-limiting oxide later is formed at the surface of the film, typically on the order of a few nanometers [145, 14].

Shown in Figure 4.2 is a time-of-flight secondary ion mass spectroscopy (ToF-SIMS)
4.2. Deposition and oxidation of thin films

Figure 4.1: Oxidation process at the surface of a titanium nitride film. (1) Following the film deposition in vacuum, dangling titanium bonds remain exposed at the surface. (2) Atmospheric oxygen bonds with the surface titanium. (3) During the oxidation process, nitrogen may be displaced by the highly electronegative oxygen. (4) This continues until the surface is quenched with oxygen forming the titanium dioxide surface oxide layer. The layer is self-limiting in that no further nitrogen-oxygen exchange occurs once the diffusion barrier formed at the surface.

measurement of an exemplary TiON film, which was performed by Sarah Fearn at Imperial’s Materials Department. Using a focused ion beam of Bi\(_1^+\) ions to ablate the sample, both positively and negatively charged ions are collected and distinguished based on their charge-to-mass ratio. Through analysis of the collected species, it is possible to determine the atomic composition of the film from surface (\(t = 0s\)) to substrate (\(t = 625s\)). At the surface, there is a sharp increase in measured oxygen consistent with a TiO\(_2\) surface oxide layer (red shaded region). Below this (blue shaded region) there is a transitionary region due to the diffusion of oxygen into the film. Below this is the uniform film, estimated to be TiO\(_{0.2}\)N\(_{0.8}\), henceforth addressed as TiON 10%. Note the small amount of oxygen diffusion from the substrate side observed as an increase in oxygen between 500 and 625 s due to the interaction of titanium with the SiO\(_2\). Finally, at times beyond 625 sm the fused quartz coverslip substrate composition is recorded (grey shaded region).
Figure 4.2: Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) analysis of a titanium oxynitride film showing elemental composition as a function of sputtering time from surface (t=0) to substrate (t=625 s). The red region shows the surface oxide layer, blue region shows region of atmospheric oxygen penetration and grey region shows the substrate. ToF-SIMS measurements were performed by Sarah Fearn of Imperial’s Department of Materials.

4.2.1 Ellipsometry Model

To be able to controllably and reproducibly tune the properties of titanium oxynitride thin films, it is necessary to relate the changes in deposition conditions to physical changes both structural and optical. This can be accomplished using a rigorous physical model for ellipsometric measurements that accounts for the electronic properties of the individual layers. First, a bare fused quartz substrate is measured independently and fit to an established SiO$_2$ model to extract the refractive index. For the titanium oxynitride film, a Drude-Lorentz model consisting of Lorentz oscillators (with variable amplitude, width and energy) and a Drude oscillator (with variable amplitude and width) is used to describe the permittivity of the film (Section 3.2).

As a starting point, the model is fit to the experimental data as a single, uniform layer as described in Chapter 3. This neglects the surface oxide layer that is known to exist at the surface. Through variation of the model parameters, a reasonably good fit can be achieved (Figure 4.3) as seen between the experimental values (black dots) and the Drude-Lorentz fit (blue curve). The corresponding real and imaginary components of the permittivity are shown in 4.3 as well and the application of a single layer almost exactly reproduces the values directly calculated from the ellipsometric parameters. The fitted parameters are shown in Table 4.1,
and although the interband transition energies and permittivity are reasonable for reported values of titanium nitride, the negative value of $\epsilon_\infty$ casts doubt on the reliability of the model.

![Figure 4.3: Ellipsometric data $\Psi$ (top-left) and $\Delta$ (top-right) for measured values (dotted values) and two proposed models: Drude-Lorentz (blue) and Drude-Lorentz + oxide layer (red). Both models appear to fit the experimental data extremely well, however, the inclusion of an oxide layer dramatically alters the interpretations of the model. Shown below are the real (bottom-left) and imaginary (bottom-right) components of the permittivity. The simple Drude-Lorentz resembles the permittivity calculated directly from the experimental values (dotted values). The Drude-Lorentz + oxide layer, resembling the physical system, estimates much more metallic behaviour that the homogeneous approach.

As an extension to the Drude-Lorentz model, the $\text{TiO}_2$ surface oxide layer is added to account for the additional reflections collected by the detector. The optical properties of $\text{TiO}_2$ are well-characterised and assumed to be a constant for each of the measured films. However, the thickness of this layer is left as a fitting parameter to best minimise the mean-squared error. The fitted $\Psi$ and $\Delta$ are shown in Figure 4.3 appear to more accurately reproduce the experimentally measured values. Indeed, the MSE is calculated to be 5.6, almost half of that of the single uniform layer. The fitted parameters are shown in Table 4.1, with interband transition energies closer to reported literature values and a physically reasonable $\epsilon_\infty$. The corresponding
Table 4.1: Comparison of Drude-Lorentz fitting parameters with and without a TiO$_2$ native oxide layer. The unphysical $\varepsilon_\infty$ and large mean squared error (MSE) immediately casts doubt on the reliability of the fit that does not include a surface oxide layer.

real and imaginary components of the permittivity are shown as the red curve in Figure 4.3. Although the $\Psi$ and $\Delta$ of the two models are similar, this change of the model has a dramatic impact on the extracted optical properties. This again emphasises the importance of accurate material characterisation when applying ellipsometry to a novel material.

The optimised model consists of two Lorentz oscillators (representing two interband electron transitions) in addition to the single Drude oscillator (Lorentz oscillator centred at $E = 0$) as well as the TiO$_2$ oxide layer. This was decided systematically as described in Section 3.2. It is known that by increasing the number of fitting parameters (by increasing the number of oscillators), the MSE can be continuously reduced even with an unphysical number of oscillators. This phenomenon is termed “overfitting” and is a systematic problem in regression analysis. The black squares in Figure 4.4 show exemplary experimentally measured $\Delta$ at 70° along with the corresponding directly calculated imaginary component of the dielectric permittivity. Measurements were also performed at 65° and 75° and used in the fitting but omitted from the plot for clarity.

Table 4.2: The Drude and interband transition energies extracted from the fitted models along with the mean squared error (MSE). When the first two interband transitions are added, there is a significant reduction of the MSE. However, beyond that the third interband transition is fit as a second Drude term and has only slight reduction of the MSE, characteristic of overfitting. As such, a two-Lorentz model is used to describe titanium oxynitride thin films.

The modelling process began with a Drude oscillator term (no Lorentz oscillators) shown by the red curve in Figure 4.4. The fit does not adhere to the experimental data very well, suggesting an underfitting of the data, which is reflected in the large MSE (65.17). The
modelling proceeds by adding additional Lorentz oscillators to account for interband transitions. With no Lorentz oscillators, the high energy response is incorporated into the background permittivity ($\epsilon_\infty$). As this constant value does not account for the spectral variation of the electron interband transitions, this leads to an underestimation of the intraband (Drude) absorption at lower wavelengths.

When one Lorentz oscillator is added (fitted as $E_1 = 4.95$ eV), the mean squared error drops considerably (11.18) and the free electron behaviour ($\geq 500$ nm) is reproduced very well. However, at shorter wavelengths, the fitted curve deviates considerably from the experimental data. When two Lorentz oscillators are used (fitted as $E_1 = 5.64$ eV and $E_2 = 3.47$ eV), the MSE is reduced by more than a factor of 2 (5.60) with good fits across the measured spectral range. When an additional Lorentz oscillator is added there is a slight decrease in the MSE (5.22), and the first two oscillators do not change dramatically ($E_1 = 5.98$ eV and $E_2 = 3.54$ eV). However, the third oscillator appears to be redundant as it is degenerate with the Drude oscillator ($E_3 = 0$ eV). The produced imaginary parts of the permittivity are shown in Figure 4.4 and the fitted parameters for each step are summarised in Table 4.2. For all subsequent fitting, two Lorentz oscillators are used as well as a single Drude oscillator with the titanium dioxide surface oxide layer.

![Figure 4.4](image)

**Figure 4.4:** *(Left)* Minimised MSE fits to the experimental data for an increasing number of Lorentz oscillators. Beyond two Lorentz, oscillators, no significant improvement is observed. *(Right)* Corresponding imaginary component fits to the model showing the convergence to the true value at two Lorentz oscillators.
4.2.2 Optical and electronic properties

Titanium nitride gains its metallic properties from the unique bond formed between the titanium and nitrogen atoms. The partial hybridisation between the p-orbitals of nitrogen and d-orbitals of titanium results in one delocalised electron remaining per unit cell. The ionic-like bond formed between the two materials gives titanium nitride its robust physical properties and high thermal stability. The bond between titanium and oxygen does not result in a delocalised electron due to the complementary number of electrons in the oxygen valence orbital. As such, when oxygen is systematically substituted for nitrogen, as in titanium oxynitride, the overall free carrier concentration decreases. This can be characterised by a decrease in magnitude of the real part of the permittivity and red-shifting of the cross-over wavelength due to the inverse square-root dependence between the plasma frequency and carrier concentration.

By fitting spectroscopic ellipsometry to a Drude-Lorentz permittivity model as described in Section 3.2, the influence of oxygen on the electronic properties can now be investigated using the crossover wavelength (the wavelength where $\Re\{\lambda\}$ is zero). This is also called an epsilon-near-zero (ENZ) point in literature but can also refer to a spectral range where the total permittivity (real and imaginary parts) are minimum. Therefore, the term crossover wavelength is preferred to refer to the specific point where the real component is zero. The plasma frequency is proportional to the square root of the free carrier concentration ($N$). For TiON with an oxygen filling factor ($f$), the free carrier concentration as a function of oxygen filling factor is $N(f) = N(0)(1 - f)$. The oxygen-dependent permittivity $\epsilon(\omega, f)$ can then be approximated as:

$$\epsilon(\omega, f) \approx \epsilon_{\infty}(f) - \frac{[\omega_p(0)]^2}{\omega^2} = \epsilon_{\infty}(f) - \frac{[\omega_p(0)]^2(1 - f)}{\omega^2} \quad (4.1)$$

The frequency where the permittivity is zero can be solved as a function of the oxygen filling factor $f$:

$$\omega_0^2 = \frac{[\omega_p(0)]^2}{\epsilon_{\infty}(f)} (1 - f) \quad (4.2)$$

Rearranging this equation in terms of wavelength yields:

$$\lambda_0 = \lambda_p(0) \sqrt{\frac{\epsilon_{\infty}(f)}{1 - f}} \quad (4.3)$$
4.2. Deposition and oxidation of thin films

With three well-characterised titanium oxynitride films of increasing oxygen filling (f=0.1, 0.15, 0.25) as measured by ToF-SIMS measurements by Sarah Fearn, the measured crossover wavelength is compared to the values calculated using a fitted $\lambda_p(0)$ of 352 nm (Figure 4.5). This wavelength is substantially lower than what has been reported in literature for supposedly pure titanium nitride [41]. This suggests that most titanium nitride contains some degree of oxygen at the surface that is not considered in these experimental works. This emphasises the importance of thorough modelling when looking at such complex materials.

**Figure 4.5:** Comparison between the measured and calculated values of the crossover wavelength as a function of oxygen filling factor. The clear increase with wavelength (decrease in energy) is visible with increasing oxygen content and agrees very well with the theoretical model.

To gain some physical insight on the optical properties of the intermediate titanium oxynitride, we use a Maxwell-Garnet effective medium model [146] to calculate the effective permittivity ($\epsilon_{TiON}$) for titanium dioxide inclusions in a titanium nitride host, with filling factor $f$:

$$\frac{\epsilon_{TiON}(\omega) - \epsilon_{TiN}(\omega)}{\epsilon_{TiON}(\omega) + 2\epsilon_{TiN}(\omega)} = f \frac{\epsilon_{TiO_2}(\omega) - \epsilon_{TiN}(\omega)}{\epsilon_{TiO_2}(\omega) + 2\epsilon_{TiN}(\omega)}$$

It is straightforward to show that $f = 0$ would give $\epsilon_{TiON} = \epsilon_{TiN}$ and $f = 1$ gives $\epsilon_{TiON} = \epsilon_{TiO_2}$. Figure 4.6 shows the real component of the permittivity for filling factors between 0% and 100% in increments of 10%. This exhibits the predicted red-shifting of the crossover wavelength over a considerable range (<500 nm to >1200 nm) predicted for $TiO_2$ filling factors up to 60%. In addition there is a monotonic decrease of the magnitude of the real part of the permittivity with increasing oxygen associated with the decrease in metallic behaviour.
Figure 4.6: Maxwell-Garnett effective medium calculations for the optical properties of titanium oxynitride using titanium nitride inclusions in a titanium dioxide matrix (left) and titanium dioxide inclusions in a titanium nitride matrix (right).

4.2.3 Deposition-Tunable Properties

Equipped with a multi-layer ellipsometry model and an understanding of the interactions of the composition and optical properties of the two layers (TiON and TiO$_2$), it is possible to engineer the properties of the film. Temperature is one of the key means of controlling the properties of titanium oxynitride. By varying the substrate temperature during deposition, the crystallinity and migration of oxygen can be tailored. As films in this work are deposited onto glass substrates, with very low thermal conductivity, there is poor thermal contact between the substrate and the heated holder. As seen with the measured permittivity data in Figure 4.7, deposition onto the bare quartz substrate results in semiconducting behaviour across the entire measured spectral range (high oxygen). This is due to the small average grain size resulting in more oxygen penetration into the film and, in turn, almost complete oxidation. When Cr is deposited onto the backside of the film, the increased thermal contact allows for partial annealing during the deposition and the metallic behaviour emerges. This difference is clearly distinguishable from the red and black curves in Figure 4.7. The real part of the metallic TiN permittivity becomes negative beyond 500 nm and the Drude-like absorption is retrieved in the imaginary part.

The next mechanism of tailoring the film composition is controlling the gaseous environment in which the film is deposited. By varying the relative flow rates of nitrogen and argon gases, it is possible to alter the chemical make-up of the film. Figure 4.8 shows the
4.2. Deposition and oxidation of thin films

Figure 4.7: The real (left) and imaginary (right) components measured using spectroscopic ellipsometry of titanium oxynitride on fused quartz coverslip with and without a Cr layer deposited on the backside. The thermal contact between the holder and substrate allows for deposition to be performed at a higher substrate temperature and anneal the sample during deposition, preventing oxygen penetration as was observed with the bare quartz. Films were deposited by Andrei Mihai of Imperial’s Department of Materials.

The real and imaginary parts of the permittivity for four titanium oxynitride films deposited at high temperature (600 °C) with a Cr-backside thermal contact in atmospheres of 5%, 10%, 20% and 30% N₂ : Ar ratios. With lower nitrogen pressures, the amount of residual oxygen in the chamber during deposition (20 nTorr) becomes more significant during the deposition. This allows for continued oxygen substitution during growth as was observed in ToF-SIMS measurements (Figure 4.2). As the amount of oxygen is decreased further (by increasing the relative amount nitrogen) the film becomes more metallic exhibited by a monotonically decreasing (more negative) permittivity and higher carrier concentration as seen in the blue-shifting cross-over wavelength.

As a final means of controlling the film properties, the residual oxygen is reduced by performing a one hour pre-sputter of the titanium target. Titanium is a well known oxygen getter at high temperatures, [147] which will reduce the residual oxygen in the chamber. In Figure 4.9, we show the permittivity of two titanium oxynitride film deposited at high temperature (600 °C with Cr-backside thermal contact) in a 30% nitrogen to argon atmosphere.

The first, as in Figure 4.8, was deposited under high oxygen partial pressure (20 nTorr). The second, was after the 1 hour presputter reaching oxygen partial pressures below 5 nTorr, termed the low-residual oxygen sample. (This sample was the subject of investigation in the previous Section see Figure 4.2). This results in a highly metallic film, with the most metallic behaviour
ever reported for titanium oxynitride (TiON), even surpassing many reports of titanium nitride (TiN) in the literature [41]. For this reason, it is proposed that films that are not deposited epitaxially on lattice-matched substrates to titanium nitride (Si, MgO) [143, 148] inherently contain some degree of oxygen and thus, are not pure titanium nitride as claimed in previous literature [41]. As such, for most industrially-relevant deposition techniques, titanium oxynitride is the essential system to be investigated.

Figure 4.8: The real (left) and imaginary (right) components measured using spectroscopic ellipsometry of titanium oxynitride deposited at various nitrogen concentrations (5-20% with the remaining being Ar and residual oxygen). The higher the nitrogen, the less relative oxygen and more metallic behaviour observed. Films were deposited by Andrei Mihai of Imperial’s Department of Materials.

Figure 4.9: The real (left) and imaginary (right) components measured using spectroscopic ellipsometry of titanium oxynitride deposited with (red) and without (black) a 1 hour pre-sputter of titanium to reduce the residual oxygen in the deposition chamber. The reduction of oxygen leads to notably more metallic behaviour. Films were deposited by Andrei Mihai of Imperial’s Department of Materials.
4.2.4 Density functional theory calculations

Density functional theory (DFT) is a computational approach to calculate the lowest energy configuration of a system with many atoms. This is typically applied to molecules or unit cells of a crystalline material to determine the bulk behaviour of electrons. All DFT calculations were performed by Stefano dal Forno from Imperial’s Department of Materials. The calculated band structures of TiN and $\text{TiO}_{0.2}\text{N}_{0.8}$ (TiON 10%) are shown in Figure 4.10. Remarkably, no significant change is detectable even with such a large percentage of oxygen substitution.

As thermal electrons heat via electron-electron interactions, they collide with lattice atoms, exchanging energy with phonons. The electron-phonon interactions can be described by an electron temperature-dependent coupling parameter $G$. Lin et al [64]. derived the following expression for an arbitrary density of electronic states, $\rho(\epsilon)$ and electron distribution $f(E,T_e)$ as above:

$$G(T_e) \approx -\frac{\pi k_B \lambda \langle \omega^2 \rangle}{\hbar \rho(E_F)} \int \rho^2(\epsilon) \frac{\partial f(E,T_e)}{\partial E} \partial E$$

(4.5)

with $\lambda \langle \omega^2 \rangle$ being the electron-phonon mass enhancement parameter at the second moment of the phonon spectrum [149]. The calculated temperature-dependent electron-phonon coupling parameter, G, is shown in Figure 4.11. With the electron and phonon systems characterised, it is also possible to estimate the thermal properties of the material. This is done via the electron
and phonon thermal heat capacities defined by:

\[ C_e(T_e) = \int_{-\infty}^{\infty} dE \rho(E) E \frac{\partial f(E,T_e)}{\partial T_e} \]  

\[ C_l(T_l) = \int_{-\infty}^{\infty} dE P(E) E \frac{\partial n(E,T_l)}{\partial T_l} \]  

(4.6)  

(4.7)

where \( P(E) \) is the phonon density of states and \( n(E,T_l) \) the Bose occupation factor for the phonon system. Figure 4.11 shows the calculated heat capacities. As expected from the similarities of the band structures, the substitution of oxygen for nitrogen has little influence on the thermal properties.

Using the two temperature model solution (Section 2.3), the electron-phonon scattering time can be estimated from the rate of a two-body Newton cooling problem. That is,

\[ \tau_{e-p} \approx \frac{1}{G} \left( \frac{C_e C_l}{C_e + C_l} \right) \]  

(4.8)

The electron-phonon scattering time of TiN, two sub-stoichiometric \( TiN_{1-x} \) variants, and one stoichiometric TiON (\( TiN_{0.8}O_{0.2} \)) are compared in Figure 4.11 using DFT-calculated parameters. For all cases and temperatures up to 8000 K, the electron-phonon scattering time does not exceed 250 fs owing to the strong coupling between the electrons and phonons quantified by the parameter G. Remarkably, the substitution of oxygen has a much weaker effect on the electron-phonon lifetime than simply the removal of nitrogen.

### 4.3 Fabrication and Characterisation of TiON Nanstructures

Many of the favourable properties of titanium nitride and titanium oxynitride such as chemical stability and high melting temperature make it extremely difficult to pattern. The ion milling rate of titanium nitride using an argon ion gun was found to be 0.033 nm/s (1.98 nm/min) much slower than even silicon, (0.16 nm/s or 9.6 nm/min under identical conditions) [150]. Using a PMMA mask, which has an etch rate of 10 nm/min [151] would require 1 \( \mu \)m of PMMA to resist etching of 50 nm of TiN, which would restrict the particle quality and resolution achievable
Figure 4.11: DFT-calculated thermal properties of TiN (left) and TiO_{0.2}N_{0.8} (right). The temperature dependence of the electron-phonon coupling strength (G) and electron-phonon lifetime ($\tau_{ep}$) (top) as well as the electron and lattice heat capacity ($C_e$ and $C_l$, respectively) (bottom) are presented. No significant change is observed in the electron dynamics when oxygen is introduced in place of nitrogen. Calculations were performed and figures generated by Stefano dal Forno from Imperial’s Department of Materials.
Figure 4.12: DFT calculated electron-phonon scattering times (in picoseconds) for several different materials. Along with stoichiometric TiN, two sub-stoichiometric films (TiN$_{0.84}$ and TiN$_{0.91}$) are considered. A single titanium oxynitride (TiO$_{0.2}$N$_{0.8}$) is included as well. Each film, has a very short electron-phonon thermalisation time, less than 250 fs for electron temperatures up to 8000 K. The substitution on nitrogen and oxygen has little influence on the dynamics but the presence of nitrogen vacancies in the sub-stoichiometric films slow the dynamics considerably. Calculations were performed by Stefano dal Forno from Imperial’s Department of Materials.

with this technique. As such, wet and dry chemical reactive methods [152, 153, 154] have been explored to more efficiently fabricate titanium nitride nanostructures with some degree of success. A more unconventional fabrication technique has also been proposed in which titanium dioxide particles are first fabricated and then TiN is formed through annealing in a high nitrogen concentration environment in a process called nitridation [155]. However with this process, the degree of nitrogen penetration and residual lattice oxygen remains unclear.

4.3.1 FDTD Simulations of TiON Nanostructures

The finite-difference time-domain (FDTD) software Lumerical provides computational solutions to Maxwell’s equation by discretising a problem into sufficiently small unit cells. Computations progress with increments in time across the discrete cells by alternating between calculations of the electric and magnetic fields. Using short time steps and fine discrete meshing, solutions can approximate the true solution with a high degree of accuracy. By controlling the optical constants of individual cells, the behaviour of inhomogeneous optical structures can also be
simulated. In Lumerical, field properties can be extracted using frequency-domain field power monitors, which perform calculations across a preset boundary between cells to determine electric field intensity and direction of propagation.

Using a broadband (300-2000 nm) plane wave source, in a so-called total-field scattered-field (TFSF) configuration, the scattering and absorption can be quantified (process shown in Figure 4.13). The incident field is generated (blue box) and interacts with the particle with some light being absorbed by the particle ($P_{Abs}$), some being scattered ($P_{Sca}$) and the remaining being transmitted ($P_{Tr}$). Within the source box, a total field (TF) monitor is included which integrates the Poynting vector ($\vec{S} = \vec{E} \times \vec{H}/2$) flowing through all sides of the monitor ($\vec{S}_{Tot} = \vec{S}_{Inc} + \vec{S}_{Sca}$). Beyond the source box, the incident field is subtracted leaving just the scattered field ($\vec{S}_{Sca}$). As the scattered and incident fields are flowing in opposite directions the total field is the difference between the scattered and incident field: $\vec{S}_{Tot} = -|\vec{S}_{Inc}| + |\vec{S}_{Sca}|$, and by definition $\vec{S}_{Abs} = |\vec{S}_{Inc}| - |\vec{S}_{Sca}| = -\vec{S}_{Tot}$, giving a method to extract the power absorbed by the particle. To determine the total extinguished power, it is only required to sum the absorbed and scattered power $\vec{S}_{Ext} = \vec{S}_{Abs} + \vec{S}_{Sca}$.

FDTD calculations are an excellent first step in designing nanostructures. Using experimentally measured optical properties, it is possible to predict the plasmon resonance
Figure 4.14: FDTD Simulations of TiN (top) and Au (bottom) spheres of increasing radius using the TFSF technique. The corresponding scattering (left) and absorption (right) cross-sections corresponding to each material. The strong infrared absorption of titanium nitride is clearly visible.

behaviour by calculating the spectral dependence of the scattered and absorbed power. The first structure considered is a simple single disk with a fixed height of 50 nm and varying radius between 10 and 200 nm. Using the calculated spectra of the absorption and scattering cross-sections (defined as a percentage of incident power), a two-dimensional plot can be constructed of the red-shifting and broadening of the plasmon resonance. Shown in Figure 4.14, are the calculated scattering and absorption cross-sections using the measured optical data from the most-metallic titanium oxynitride film (“Low Residual Oxygen” in Figure 4.9). Titanium oxynitride nanostructures show a strong broadband absorption and relatively weak scattering, which is contrary to what is observed in the noble metals (strong scattering). The absorption is maintained for larger particles shifting into the near-infrared, which is difficult to achieve with gold with weak infrared absorption. The target radius $R = 100$ nm provides the most efficient scattering for detection with standard optical set-ups.
4.3. Fabrication and Characterisation of TiON Nanostructures

4.3.2 Fabrication of TiON nanostructures

Two methods, reactive Ion Etching (RIE) and Cr-Lift-off, are used to fabricate titanium oxynitride nanoparticles. The nanoscale resolution of these methods hinges on the use of electron beam lithography (EBL), which has a resolution of 10 nm using a focused electron beam. A pattern is created on commercial software and then traced out by the electron beam. Upon exposure to the electron beam, the polymer bonds of the negative tone resist (ma-N 2403) strengthen, leaving it resistant to the subsequent chemical development step. This leaves a mask of the original pattern from the resist that is used in the subsequent processing of the titanium oxynitride. The detailed steps of each method are shown in Figure 4.15. The exploration of patterning techniques was done with Yi Li, who also performed the majority of the lift-off patterning attempts.

Figure 4.15: (Top) Deposition procedure of reactive ion etching procedure (RIE) using a negative resist patterned by electron beam lithography. (Bottom) Deposition procedure of the Cr-mask liftoff procedure using a negative resist patterned by electron beam lithography.
Reactive Ion Etching

In reactive Ion Etching (RIE) a TiON film is deposited, followed by the spin-coating of the negative resist. Subsequently, the resist mask is patterned and developed using EBL. To pattern the film, a chemically-reactive inductively coupled plasma (ICP) is generated using flowing gas into the Surface Technology Systems ICP RIE chamber. Using a DC voltage, the high energy ions generated in the ICP are directed to the substrate-heated sample and proceed to react with the atoms at the surface. The newly formed compounds have a lower melting temperature than TiON and are easily evaporated off at the elevated temperatures. After removing the remaining resist, only the areas of TiON beneath the resist remain, yielding the designed pattern in titanium oxynitride. The first recipe attempted used chlorine gas as the reactive component, which is known to readily form titanium chloride ($\text{TiCl}_4$) [156], which has a much lower boiling temperature (136 °C [157]) than titanium oxynitride. Before the sample is introduced into the chamber, a purge and ceramic holding wafer cleaning is performed using a $\text{Cl}_2$ plasma for plasma 5 minutes to remove any organic residue on the surface.

The sample is then fixed to the ceramic wafer and loaded into the chamber. Etching is performed using a 10:30 sccm $\text{Cl}_2 : \text{Ar}$ at a pressure of 8 mTorr for 6 minutes. Following processing, the substrate is clearly visible and only the designed structures remain on the surface. Shown in Figure 4.16 are atomic force microscopy (AFM) scans of one such fabricated particle designed to be a disk of radius 200 nm and height of 100 nm. 100 nm of titanium oxynitride was deposited along with 250 nm of resist. However, the resultant particle has a

Figure 4.16: Cross-section (left) and two-dimensional scan (right) of the height of a titanium oxynitride particle fabricated using chlorine-based reactive ion etching using atomic force microscopy. The particle is larger than designed and not very uniform.
4.3. Fabrication and Characterisation of TiON Nanostructures

Figure 4.17: Scanning electron microscope image of a particle fabricated using a chlorine-based RIE recipe. The core is conductive suggesting it is the titanium oxynitride particle and it surrounding by a less conduction media likely to be re-deposited chloride residue. A much larger radius of 400 nm and height of 140 nm suggesting that either solidified resist was fixed to the particle and not removed by the developer or that residual TiCl$_4$ was redeposited during deposition due to the low substrate temperature (45 °C). This ring-like shape is also observed in scanning electron microscope (SEM) imaging shown in Figure 4.17. This presence of residue and inability to fabricate ideal particles limits the applicability of this recipe for plasmonic applications.

As an alternative RIE recipe, a F-based method was attempted using similar processing parameters to the Cl-based method. Following the 5 minute wafer cleaning and loading the sample into the chamber, etching is performed using a 10:30 sccm $F_2 : Ar$ mixture held at a fixed pressure of 8 mTorr for 6 minutes. The reactive plasma is directed to the substrate using an electric field between the two sides of the chamber with a power of 100 W. However, the temperature was increased to 80 °C, which is the maximum permissible temperature of

Figure 4.18: Cross-section (left) and 2D AFM scan (right) of the height of TiON particles fabricated using chlorine-based RIE. The pyramidal shape of the particles and additional height suggest redeposition of fluoride by-products produced during etching.
Chapter 4. Titanium Oxynitride for Plasmonic Applications

Figure 4.19: Scanning electron microscope image of a particle fabricated using a fluorine-based RIE recipe. The core is conductive suggesting it is the titanium oxynitride particle and it surrounding by a less conduction media likely to be re-deposited fluoride residue.

the system. Shown in Figure 4.18 is a 2D AFM image and corresponding cross-section of the F-based RIE processed particles designed disks with radii of 200 nm and height of 100 nm. The pyramidal shape with larger height (125 nm) and radius (300 nm at the base) than what was designed suggests again that some residue was redeposited around the particle. The in-homogeneity of the particle is visible in the scanning electron microscope image (Figure 4.19) with a bullseye-like structure. The visibly bright (conductive) edges of the particle surrounding nonmetallic residue (non-conductive) is indicative of this interpretation. The additional redeposited material and irregular shape restrict the use of such particles for plasmonic and other applications.

Cr-Liftoff

A chromium liftoff method was developed by Yi Li from Imperial Physics Department. A negative resit was spin-coated and EBL patterned prior to metal deposition. Following this, a thin chromium layer was deposited across the sample. By removing the remaining resist, an inverse mask of the pattern was formed over which a TiON layer was deposited. By then submerging the sample in Cr etchant, the Cr and any TiON sitting atop was lifted off leaving patterned TiON. The TiON directly in contact with the substrate was unaffected by the Cr etchant as the etch rate of TiON is very slow. This process was originally proposed by the Shalaev group [158] and adapted for use in this work.

A two-dimensional AFM scan of a single TiON nanoparticle is shown in Figure 4.20 along with a corresponding cross-sectional profile. The particle was designed to be 40 nm
4.3. Fabrication and Characterisation of TiON Nanostructures

Figure 4.20: Cross-section (left) and two-dimensional scan (right) of the height of a titanium oxynitride particle fabricated using the chromium mask liftoff procedure. The particle is slightly less than the designed height but has a clearly defined disk shape.

in height with a radius of 300 nm and the processed particle was very close to the designed particle with a radius of 280 nm and height of approximately 37 nm suggesting that the resist was completely etched away and etching continued for a short time afterwards. The shape appears disk-like with slight rounding at the top surface due to lateral etching. Figure 4.21 shows an SEM image of particles fabricated using Cr-liftoff with only minimal residue visible and reasonable uniformity between fabricated particles. As this method allows for the fabrication of uniform arrays of particles close to designed parameters, it remains the most viable method to fabricate particles for nanophotonic applications.

4.3.3 Optical characterisation

With a consistent method of fabricating TiON nanoparticles, we could experimentally verify that the material is sufficiently metallic to sustain localised plasmon resonances at high enough

Figure 4.21: Scanning electron microscope image of a particle fabricated using a chromium-mask liftoff procedure showing uniformity between particles and no non-conductive residue.
energies to be useful in plasmonic applications. To confirm the optical properties, two methods were used to measure the extinction spectra of various arrays depending on the spectral range. In the infrared ($\geq 1000$ nm), Fourier transform infrared spectroscopy (FTIR) was used with a quartz tungsten halogen (QTH) lamp. Extinction spectra in the visible ($\leq 1000$ nm) were measured using a supercontinuum laser, which generates white light.

Arrays of 50 nm thick, uniformly spaced ($1.5\mu m$ pitch) titanium oxynitride disks were fabricated on a thin (160 $\mu m$) fused quartz substrate with various radii from 65-225 nm using Cl-based reactive ion etching. Due to the large sizes the resonance was predicted to be in the infrared. As such, the FTIR method was used to measure the extinction spectra, which are shown in Figure 4.22. Substrate and background (no lamp) measurements were taken to account for ambient light and signals were normalised by the spectrum of the light source to account for any spectral artefacts. That is:

$$I = \frac{I_{\text{Sample}} - I_{\text{Substrate}}}{I_{\text{Lamp}} - I_{BG}} \quad (4.9)$$

The measured extinction is considerably weaker and red-shifted with respect to what was expected from the FDTD simulations. This is likely a result of the residues produced during fabrication and the irregular shape of the disk as seen in Figure 4.16. Nevertheless, plasmon...
resonances are observed for samples above 200 nm in diameter with a distinct redshift with increasing size consistent with LSPRs.

To compare, TiON strips (30 µm long and 100-300 nm wide) were fabricated on a thin (160 µm) fused quartz coverslip using the Cr-liftoff procedure. Here, extinction spectra were measured using the supercontinuum laser method as shown in Figure 4.22 for both perpendicular and parallel linearly polarised light with respect to the nanowires. For light linearly polarised along the length of the strip (parallel), no plasmon resonance is excited and the material has film like absorption. When polarised perpendicular to the strip, resonance-enhanced extinction is observed that red-shifts with increasing width. The 100 nm wide strips show a strong resonance in the visible range (740 nm) suggesting that the material maintains its metallic properties when patterned. For 200 nm wide strips, an even stronger plasmonics resonance is observable, extinguishing over 50% of 870 nm light. This is over an order of magnitude stronger resonance than the chemically etched disks. As such, the Cr-liftoff method was selected for all subsequent sample fabrication.

4.4 Summary

Unlike the conventional noble metals, titanium oxynitride has a tunable stoichiometry due to its three-atom unit cell. By balancing the relative concentration of oxygen and nitrogen, the free carrier concentration can be tuned over a wide range. This allows for engineered optical properties from highly metallic to entirely semiconducting. Using rigorous ellipsometry measurements, the structure and optical properties were related to the changes in deposition conditions. Taking one set of deposition conditions as an example, two nanofabrication techniques were compared: reactive ion etching an chromium mask liftoff. It was shown that both result in particles with sufficient free carrier concentration to sustain localised surface plasmon resonances. However, the uniformity and homogeneity of the Cr-liftoff procedure led to stronger and higher energy plasmon resonances and is now the preferred fabrication method in subsequent investigations. It should be noted that few groups have been able to pattern titanium nitride/titanium oxynitride consistently due to the uncertainty of its composition.
Chapter 5

Electron Dynamics at A Metal-Semiconductor Interface

In this chapter, the ultrafast electronic dynamics of titanium oxynitride are examined using transient pump-probe spectroscopy. Contrary to the extremely short lifetimes predicted by DFT calculations, long-lived excited electron states are observed lasting hundreds of picoseconds. As such, application of the two temperature model is not sufficient to describe the observed behaviour. Using the range of theoretical and experimental characterisations of the material system, it is deduced that this long-lived signal is produced by harvested electrons in the titanium dioxide surface oxide layer. A trap-mediated electron kinetic model is derived and applied to the pump-probe measurements to explain the unexpected behaviour of the TiON/TiO$_2$ film. This study is then extended to include TiON films with varying oxygen content to discern how both the film and interface properties dictate the electron dynamics. This shows how TiON can be optimised for hot-carrier applications.

5.1 Introduction

The recent developments in nanoscale fabrication and measurement techniques have allowed for more rigorous investigations of the charge transfer process at the interface of two materials [159, 91]. The results of these studies have spawned novel electronic and photonic applications in the past decade including infrared photodetection, [110, 28] higher efficiency photovoltaic cells, [160] photocatalytic systems [161, 162, 163] and fibre optic transmitters [164]. Such
applications, particularly photocatalysis, have the potential to greatly improve our quality of life by being able to decompose harmful pollutants [165, 166] or exploit the energy stored in the chemical bonds of water as an energy source [162]. As energetic carriers (excited electrons or holes) power many of these application, metals are typically used as a carrier source with a material or molecules in contact in order to extract carriers before they thermalise. As shown in Section 2.4, the electron harvesting mechanisms, and in turn the collection efficiency, will depend on the interface formed at the metal-semiconductor heterojunction.

5.2 Probing Electron Dynamics in Metals

In Section 2.3, the extended two-temperature model (TTM) was introduced to describe the response of a metal following optical excitation of the free carriers. The subsequent energy dissipation is modelled via electron-electron, electron-phonon, and phonon-phonon scattering as the system moves toward thermodynamic equilibrium. The associated scattering rates are determined by the thermal properties of the material [167]. In pump-probe experiments, the probe pulse (for positive delays) measures the degree of disturbance of the electron system, which is directly related to the change in electron temperature by the differential reflectivity [122, 129, 128]. Explicitly, the relationship between the differential reflectivity and change in electron temperature for small changes in temperature is [168]:

\[
\frac{\Delta R(\tau)}{\Delta R_{\text{Max}}} = \frac{\Delta T_e(\tau)}{(\Delta T_e)_{\text{Max}}} \tag{5.1}
\]

To model the experimental pump-probe data, a phenomenological solution of the extended two temperature model is used, where the only fitting parameters are the three relevant scattering lifetimes \((\tau_{Th}, \tau_{e-p}, \tau_{p-p})\) and the ratio of electron and phonon heat capacities, \(N = C_e/(C_e + C_l)\). The derivation of the phenomenological solution is shown in Appendix D. The fitting requires input of the maximum measured differential reflection signal \((M)\). The times can be observed as the exponential decay rates in the differential reflection measurements. The solution used to the fit the data is as follows:
\[
\frac{\Delta R}{R}(t) = M \left[ 1 - \frac{\tau_{ep} + \tau_{th}}{(N - 1)\tau_{th}} \right]^{-1} - N \left[ \frac{\tau_{ep} + \tau_{th}}{(N - 1)\tau_{th}} \right]^{-\frac{\tau_{Th}}{\tau_{ep}}} - \left[ \frac{\tau_{ep} + \tau_{th}}{(N - 1)\tau_{th}} \right]^{-1} \left[ (1 - e^{-\frac{t}{\tau_{ee}}}) e^{-\frac{t}{\tau_{ep}}} + N(1 - e^{-\frac{t}{\tau_{ee}}}) e^{-\frac{t}{\tau_{pp}}} \right]
\]

(5.2)

This model not only allows for the extraction of the thermalised electron population behaviour but also allows one to infer properties of the phonon and nonthermal electron population that is not directly observable in the optical measurements. Figure 5.1 shows the measured data and corresponding fit of pump probe reflectivity on a 60 nm gold film deposited on a fused quartz coverslip with a 2 nm Cr adhesion layer. An 850 nm, 5 mW pump pulse and 1150 nm, 150 µW probe are used to measure the response of the film over the first 20 ps following pump excitation. The fitted curve uses the Levenberg-Marquardt algorithm to minimise the mean squared error (MSE) by varying the four free-parameters of equation 5.2. The adjusted $R^2$ achieved is 0.979 suggesting a reliable fit and, as such, low associated uncertainties.

The excited electron-phonon lifetime was determined to be $\tau_{e-p} = 0.30 \pm 0.18$ ps and the phonon-phonon lifetime was determined to be $\tau_{p-p} = 1.70 \pm 0.05$ ps both agreeing reasonably well with previous measurements ($\tau_{e-p} = 0.5$ ps, $\tau_{p-p} = 1$ ps) [129]). The extracted nonthermal lifetime associated with the rise of the differential reflectivity signal (and heating of the thermal electron population) was $\tau_{Th} = 0.3 \pm 0.1$ ps. This is consistent with the fact that, although the individual electron-electron scattering events occur on the order of tens of femtoseconds, they are nearly totally elastic. As a result, many electron-electron collisions are required to fully distribute the absorbed energy throughout the entire electron population.

## 5.3 Probing Electron Dynamics in Semiconductors

The free carriers in a material can have a profound impact on the material’s interaction with light. The unique band structure of semiconductors allows for electrons to be optically excited into the conduction band with sufficiently energetic photons. In this excited state, the optical properties are altered until the electrons recombine with the holes remaining in the valence band. This change can be detected as a change in refractive index ($\Delta n$) and extinction coefficient ($\Delta k$). Through the Drude model, [169] these changes can be quantified in terms of the change in free
5.3. Probing Electron Dynamics in Semiconductors

![60 nm Gold on Glass](image)

Figure 5.1: Differential reflectivity measurement of a 60 nm gold film on glass using a 5 mW, 850 nm pump and 1150 nm, 150 µW probe. The system returns to equilibrium within 10 ps through electron-phonon and phonon-phonon scattering.

carrier concentration ($\Delta N_{FC}$):

$$\Delta n = -\frac{e^2 \lambda^2}{8\pi^2 c^2 \epsilon_0 n_0} \frac{\Delta N_{FC}}{m_e} \quad (5.3)$$

$$\Delta k = \frac{e^3 \lambda^3}{16\pi^3 c^3 \epsilon_0 n_0} \frac{\Delta N_{FC}}{\mu_e m_e^2} \quad (5.4)$$

where $e$ is the electron charge, $\lambda$ is the probe wavelength, $c$ is the speed of light, $n$ is the refractive index of the unexcited system, and $m_e$ is the mass of an electron. Through Frensel equations, both of these changes influence reflectivity. However, by comparing the magnitudes of the two parameters, it can be shown that the change in extinction coefficient is negligible for any excited carrier concentration. That is:

$$\frac{\Delta n}{\Delta k} = \frac{2\pi m_e c}{e\lambda} >> 1 \quad (5.5)$$

which is independent of $\Delta N_{FC}$ and only varies with probe wavelength ($\lambda$). At 1150 nm, $\Delta n/\Delta k \approx 9300$, which makes the corresponding change in $k$ nearly four orders of magnitude weaker than the change in $n$. 

Chapter 5. Electron Dynamics at A Metal-Semiconductor Interface

The differential reflectivity can then be defined explicitly in terms of the Fresnel reflection coefficients at the interface of the semiconductor. At normal incidence, the reflectivity from an interface between air and a material with refractive index $n_0$ is:

$$ R = \frac{(1 - n_0)^2}{(1 + n_0)^2} \quad (5.6) $$

Following pump excitation, the refractive index can be described using a new refractive index $n'_0 = n_0 + \Delta n$ where $|\Delta n| << |n_0|$ in pump-probe experiments using moderate pump power. Thus, the associated change in reflectivity ($\Delta R$) can be described as:

$$ \Delta R = R' - R = \left( \frac{(1 - n'_0)^2}{(1 + n'_0)^2} - \frac{(1 - n_0)^2}{(1 + n_0)^2} \right) = \frac{4(n_0 - n'_0)(1 - n_0n'_0)}{(1 + n'_0)^2(1 + n_0)^2} \quad (5.7) $$

The differential reflectivity is retrieved by normalising by the ground state reflectivity ($R$):

$$ \frac{\Delta R}{R} = \frac{4(n_0 - n'_0)(1 - n_0n'_0)}{(1 + n'_0)^2(1 + n_0)^2} \quad (5.8) $$

In the relevant experimental conditions $|\Delta n| << |n_0|$, which implies that $n'_0 \approx n_0$, allowing a simplification of equation 5.8:

$$ \frac{\Delta R}{R} \approx \frac{4\Delta n(1 - n_0^2)}{(1 + n_0)^2(1 - n_0)^2} = \frac{4\Delta n}{1 - n_0^2} \quad (5.9) $$

Combining equation 5.2 and 5.8 gives an explicit relationship between the measured differential reflectivity and the density of free carriers excited in the semiconductor’s conduction band.

$$ \left| \frac{\Delta R}{R} \right| \approx \frac{e^2\lambda^2}{2\pi^2c^2\epsilon_0n_0(1 - n_0^2)m_e} \Delta N_{FC} \quad (5.10) $$

In order to validate this description, Figure 5.2 shows the transient differential reflectivity of a bare silicon substrate for increasing pump power (5-20 mW at 850 nm) and fixed probe power (250 $\mu$W at 1150 nm). As the pump wavelength is above the bandgap of silicon (1100 nm), it excites free carriers ($N_{FC}$) from the valence band to the conduction band and, in turn, produces a nonzero differential reflectivity signal. The magnitude of the differential reflectivity increases monotonically with increasing laser power consistent with more carriers being excited.
5.4. Electron Dynamics at a Metal-Semiconductor Interface

The emergent behaviour at heterojunctions can provide unique properties not present in either of the composite materials. Exploitation of such behaviour has led to the development of lasers [171], transistors, [172] and effective photocatalytic devices [173]. Repeated layering of two or more materials can produce aggregate effects giving an effective bulk material that inherits properties from the interfacial behaviour [101]. Engineering the electronic behaviour

Figure 5.2: \textit{(Left)} Raw differential reflectivity measurements of a silicon film pumped above the bandgap (850 nm) at increasing power. The probe beam is held at 1150 nm and 150 $\mu$W to measure the conduction band occupation as a function of time. Following pump excitation the Kerr effect results in a ultrafast negative differential reflectivity before the rise of the signal. The decay traces the recombination of electrons and holes across the bandgap. The signal increases with increasing power associated with more electrons being excited across the bandgap. \textit{(Right)} Maximum differential reflectivity and corresponding harvested carrier density as a function of pump power. The linear increase follows the linear absorption of the increased photon density. The maximum measured value is plotted in Figure 5.2 along with the corresponding calculated harvested carrier concentration as calculated by 5.10. A near-linear trend is observed versus power, consistent with single photon absorption process (The ultrafast signal near the overlap $[\Delta\tau \approx 0]$ in the differential reflectivity measurements in Figure 5.2 has been reported in literature [170] and is attributed to the response of nonthermal carriers in the conduction band.) The relaxation follows a single exponential decay with the recombination of excited electrons and holes remaining in the valence band.
Chapter 5. Electron Dynamics at A Metal-Semiconductor Interface

Figure 5.3: (Left) Radiative recombination process in a direct bandgap semiconductor where an electron excited into the conduction band fills a hole remaining in the valence band resulting in the emission of a photon with energy equal to the semiconductor’s bandgap. (Right) Non-radiative recombination process in an indirect bandgap semiconductor where electron momentum change is provided by the phonons of the semiconductor.

at interfaces requires not only a thorough characterisation of each of the composite materials, but also their interfaces. Typically it is difficult to isolate the interfacial processes from the bulk ones. The following section serves as an example of the methodology used to understand the interface between titanium oxynitride and titanium dioxide.

5.4.1 Electron-hole recombination at a Metal-Semiconductor Interface

When electrons are excited from the valence to conduction band of a semiconductor, the carriers gradually return to their lowest energy state via photon generation (radiative decay) or phonon-assisted scattering processes (nonradiative decay), illustrated in Figure 5.3. The decay mechanism is largely determined by the alignment of the conduction and valence bands. Indirect bandgap semiconductors tend to recombine nonradiatively due to the need for phonons to compensate for the small photon momentum. This less efficient process is also associated with longer recombination lifetimes. For direct bandgap semiconductors, electrons may directly recombine with holes to generate photons, making them ideal light emitters [174].

Realistically semiconductors have trap states introduced by vacancies or dopants in the crystal lattice. This enables a third recombination channel via trap or impurity states within the bandgap, as shown in Figure 5.4. This process, termed Shockley-Read-Hall (SRH) recombination, results in two low-energy photons being emitted from each of the relaxation processes. The two-step process also makes it considerably slower than typical radiative recom-
5.4. Electron Dynamics at a Metal-Semiconductor Interface

Figure 5.4: (Left) Shockley Read Hall (SRH) recombination in a semiconductor where a trap state within the semiconductor bandgap facilitates the two-step recombination process resulting in the emission of two lower energy photons. (Right) SRH recombination at a metal-semiconductor interface where interfacial trap states act as the intermediate step for electron-hole recombination.

bination. Furthermore, the electron has the ability to detrap back into the conduction band, especially if the trap state is close to the band edge [175]. The finite lifetime of carrier separation at metal-semiconductor interfaces arises from the higher concentration of trap states at the interface due to defects and the mismatch of the lattice structure formed during deposition. Recombination via trap states suggests that electrons do not need to overcome the energetic barrier at the interface for recombination to proceed as is shown in Figure 5.4.

5.4.2 Distinguishing metal and semiconductor contributions

To characterise the electron harvesting process at metal-semiconductor interfaces, it is critical to delineate between the individual contributions of electrons in the metal and the semiconductor to the optical response. As the differential reflectivity of gold is well-characterised in the literature, [122, 129, 128] it is an ideal control for this investigation. Using a 5 mW, 850 nm pump pulse and 250 µW, 1150 nm probe, we measured the temporal evolution of the differential reflectivity of metal-insulator (50 nm gold film deposited on glass) and metal-semiconductor (30 nm TiO$_2$ deposited on top of a 50 nm gold film on glass) samples. Figure 5.5a shows the measured response on a semi-logarithmic plot to best distinguish the various decay timescales involved. The metal-insulator Au/SiO$_2$ sample exhibits a rapid decay, almost completely decaying within 10 ps. This can be fit to a two temperature model describing the heating ($\tau_{th} = 0.3 \pm 0.10$ ps) and rate of dissipation of electron energy via phonons ($\tau_{ep} = 0.77 \pm 0.18$ ps) and thermal
Figure 5.5: (a) Semi-logarithmic plot of the time-resolved differential reflectivity of Au/TiO$_2$ (metal-semiconductor) and Au/SiO$_2$ (metal-insulator). The Au response (blue shaded region) is clearly delineated from the TiO$_2$ response (red shaded region) confirmed by the Au/SiO$_2$ control sample, which only has the Au response. (b) Data from (a) over the first 10 ps following pump excitation. Using a combination of two-temperature and metal-semiconductor recombination models, the two contributions are separated showing long-lived electrons remaining in the TiO$_2$ conduction band. The inset shows the fitted Au contribution alongside the Au/SiO$_2$ sample (scaled by a factor of 0.4) showing very good agreement.

dissipation via phonon-phonon scattering ($\tau_{pp} = 1.70 \pm 0.05$ ps).

The Au/TiO$_2$ sample, however, exhibits a long-lived decay beyond 10 ps persisting for hundreds of picoseconds. It is well-known that upon contacting Au with TiO$_2$, a Schottky barrier is formed of approximately 0.9 eV [176]. Exciting the system with 850 nm (1.46 eV) light, a significant portion of the excited electrons have sufficient energy to cross the Schottky barrier into the TiO$_2$ where they recombine on the order of nanoseconds [177]. It is also known that absorption of the probe is primarily through free carrier absorption as strong trap-state absorption occurs for wavelengths below 1100 nm [178] suggesting that the probe is measuring the free carrier absorption in the TiO$_2$. The orders of magnitude difference between the decay rates in the metal (blue shaded region of Figure 5.5a) and that of the recombination time across the metal-semiconductor interface (red shaded region of Figure 5.5a) allows for easy separation of the two individual contributions. Using a two temperature model in addition to a nanosecond cooling model we can decompose our signal into the separate components shown in Figure 5.5. Employing the method from Section 5.3, the harvested electron population density is estimated to be $\approx 2.5 \times 10^{18} \text{cm}^{-3}$. The inset of Figure 5.5b shows the extracted Au contributions and the Au/SiO$_2$ response. A clear overlap across the entire temporal range is apparent.
5.5 Electron Dynamics in TiON Thin Films

To determine the viability of TiON as a platform for hot electron applications, it is imperative to benchmark its electron dynamics with that of gold, which is commonly used for such applications. Although TiON has favourable structural properties and strong absorption in the near infra-red, the DFT calculations from Section 4.2 cast doubt on its practicality in hot electron applications due to the strong electron-phonon coupling. However, experimental work using titanium nitride, which should have comparable electron-phonon coupling, shows enhanced hot electron behaviour [15, 16]. In this section, the electron dynamics are studied in more detail in order to develop an electron kinetic model to explain this discrepancy.

**Absorption Coefficient**

The absorption coefficient ($\alpha(\lambda)$) is used to describe interaction of a film with light. In terms of the measured refractive index $n$ and permittivity $\epsilon$ the absorption coefficient is described as:

$$\alpha(\omega) = \frac{4\pi Im\{\epsilon\}}{\lambda n}$$  \hspace{1cm} (5.11)

The results for TiON 10% (as examined in Section 4.2) are shown in Figure 5.6. The onset of the TiO$_2$ absorption is only present below 400 nm, as expected. It is clear that the absorption of light at wavelengths above 400 nm absorption is occurring strictly in the underlying titanium oxynitride film and not in the titanium dioxide. Below 500 nm, the TiON film behaves predominantly as a dielectric with absorption only occurring via interband transitions. At energies below the plasma frequency (wavelengths above 500 nm), the behaviour is predominantly metallic with light-absorption occurring via intraband transitions of the free electrons.

5.5.1 Transient Pump-Probe Spectroscopy Measurements

Identical pump probe measurements are performed on the TiON 10% film introduced in Section 4.2. The pump (850 nm) and probe (1150 nm) are shown on the absorption coefficient plot (Figure 5.6). At the pump wavelength, absorption occurs strictly within the TiON film. Knowing that electron-phonon scattering time is predicted to be on the order of 100 fs, similar
to the electron-electron scattering time, an ultrafast rise and decay (comparable to the laser pulse width) is also anticipated. However, as seen in the observed TiON response in Figure 5.7 a long-lived signal persists beyond 50 ps, decaying slower even than the Au/TiO$_2$ sample.

When looking at longer timescales (Figure 5.8), the differences between the two systems is even more striking. This is in direct contradiction to the extremely rapid theorised electron-phonon scattering time of 100 fs (shown in Figure 4.12 of Section 4.2). As such, the observed signal cannot be from energetic carriers in the TiON and applying the two temperature model would not be sufficient. Furthermore, knowing that the absorption takes place in the TiON it is forces the conclusion that electrons must be transferred from the TiON into TiO$_2$ following pump excitation. When comparing the two samples, TiON 10% experiences a bottleneck in the decay where the signal remains effectively constant over the measured range. As such, it does not fit the behaviour of a Schottky interface and further investigation is required.

Before discussing a theoretical model for this behaviour in the next section, consider first the measured response presented as a semi-logarithmic plot. This is shown in Figure 5.8 where the individual lifetimes are more clearly visible. Initially, there is a near resolution-limited rise over the first several hundred picoseconds characterised by a time-scale $\tau_0$. This is followed by a faster decay ($\tau_1$) on the order of tens of picoseconds then a slower decay ($\tau_2$) lasting a few hundred picoseconds. Beyond this, the decay progresses so slowly that it appears constant over the measured temporal range, which is considered a constant $b$. 

Figure 5.6: Absorption coefficients for Au, TiO$_2$ and TiON 10% calculated from complex refractive index measured by ellipsometry. Additionally, the fitted Drude contribution of TiON 10% is shown by the dotted line.
5.5. Electron Dynamics in TiON Thin Films

Figure 5.7: Comparison of the differential reflectivity for Au/TiO$_2$ and TiON, both normalised to the maximum value over the first 50 ps following pump excitation. A rapid decay of the electron-phonon population is not present in the TiON film, which exhibits a comparably slow decay over the first 25 ps.

5.5.2 Thermal Effects

This extremely slow decay can also be attributed to slow thermal dissipation in the metal instead of a long-lasting free electron population in the TiO$_2$. It is known that, when normalised to the maximum differential reflectivity, thermal effects in metals show a dependence on pump power [128], whereas the free electron populations in semiconductors do not exhibit this behaviour [175]. Shown in Figure 5.9 are the fitted $b$ values over the pump power range of 1-5 mW. Since no dependence on pump power was observed, thermal effects on the TiON response are assumed to be negligible in these measurements.

5.5.3 Trap-Assisted Recombination Kinetic Electron Model

As the penetration depth of this wavelength in TiON is approximately the thickness of the film, electrons are excited throughout the film. The high density of excited electrons at the surface of TiON allows for diffusion of electrons into the TiO$_2$ due to the negligible energy barrier formed between the two materials. This is facilitated by the rapid heating of phonons in TiON, which reach thermal equilibrium within the first 200 femtoseconds. This increases the quasi-Fermi
level in TiON, describing the transient high temperature electron distribution, which is long enough for diffusion to occur to vacant energy states in the titania conduction band. As this takes place within the time resolution of our laser system, these two processes (electron-phonon scattering and electron injection into TiO$_2$) are observed as the single exponential rise, $\tau_0$.

The recombination of injected carriers in the TiO$_2$ conduction band could be mediated by both shallow and deep traps, as illustrated in Figure 5.10. Shallow traps (formed in the bandgap at energies close to the valence band maximum (VBM) and conduction band minimum (CBM)) are a result of oxygen vacancies typically within fractions of an electron volt of the band edges. The traps formed deep within the bandgap are a result of interstitial Ti$^{3+}$ ions and are reported to be approximately 1 eV below the CBM.

Following excitation of an initial electron population into the conduction band, $N_{FC}(0)$, the free electron population ($N_{FC}(t)$) evolves with time as it decays into shallow trapped electrons ($N_{Sh}(t)$) and deep trapped electrons ($N_{De}(t)$). The evolution of the free electrons can then be described by the simple expression: $N_{FC}(t) = N_{FC}(0) - N_{Sh}(t) - N_{De}(t)$. To describe the bottleneck of the recombination dynamics, we posit that there is some steady state occupation density for the trap states denoted by $S$ and $D$ for shallow and deep traps, respectively. Assuming that the rates of proportionality are given by $k_{Sh}$ and $k_{De}$, the evolution of the two
5.5. Electron Dynamics in TiON Thin Films

Figure 5.9: Fitted values for the long-lived differential reflectivity normalised to the measured maximum differential reflectivity values. The value shows no pump-power dependence suggesting that it is not a thermal effect but, is instead produced by the free electrons that remain in the TiO$_2$ over much longer time-scales.

The trap populations are described by the following expressions:

$$\frac{d}{dt} N_{Sh}(t) = k_{Sh}(S - N_{Sh}(t))$$
$$\frac{d}{dt} N_{De}(t) = k_{De}(D - N_{De}(t))$$

(5.12)

The solutions to each of these are exponential functions, yielding the biexponential decay

Figure 5.10: Proposed trap-assisted recombination model at the TiON – TiO$_2$–$_x$ interface with the associated lifetimes observable in our measurements associated with shallow trap occupation ($\tau_{Sh}$), deep trap occupation ($\tau_{De}$) and recombination ($\tau_{Re}$).
observed in Figure 5.8:

\[
\frac{N_{FC}(t)}{N_{FC}(0)} = (1 - s - d) + se^{-t/\tau_{Sh}} + de^{-t/\tau_{De}}
\]  

(5.13)

where \(s = S/N_{FC}(0)\) and \(d = D/N_{FC}(0)\). To remain consistent with the temporal units and nomenclature described thus far we use the timescales \(\tau_{Sh} = k_{Sh}^{-1}\) and \(\tau_{De} = k_{De}^{-1}\). The energy remaining in the free electrons after the trap states reach their steady-state occupation is denoted by \(\delta = 1 - s - d\). It is assumed that once the electrons are trapped, they no longer contribute to the free electron response and thus the magnitude of the differential reflectivity decreases. These newly proposed parameters are summarised on the semi-logarithmic plot below (Figure 5.11).

Figure 5.11: Experimental data with the trap-mediated recombination model parameters superimposed. This includes shallow and deep trap occupation lifetimes along with the exponential rise time of the signal \((\tau_0)\) and the amount of energy lost to occupying traps \((s + d)\) and the amount remaining in the free carriers \((\delta)\).
5.6 Controlling Relaxation Dynamics with Oxygen Composition

The electron kinetic model now gives a physical basis for interpreting the pump probe differential reflectivity measurements. This section looks to investigate the role of various deposition conditions on the electron behaviour of TiON/TiO$_2$ films. The parameter that distinguished each film is the amount of oxygen present in the bulk of the film as determined by time-of-flight spectral interferometric spectroscopy (ToF SIMS) as described in Section 3.3. The role of oxygen in both the harvesting and recombination dynamics is quantified using four films between 10% and 40% atomic ratios covering metallic and semiconducting films.

5.6.1 Deposition in various oxygen environments

As shown in Section 4.2, the properties of titanium oxynitride can be widely tuned through careful control of the deposition conditions. The oxygen content throughout the film was controlled by varying the titanium target pre-sputtering time, with longer times decreasing the residual oxygen in the chamber. 50 nm of each film was deposited by RF magnetron sputtering in a N$_2$/Ar = 3 : 7 (30% N$_2$) environment onto a fused quartz coverslip substrate. The atomic composition (as measured by ToF SIMS) as well as the real and imaginary parts of the permittivity are shown for each film in Figure 5.12.

The first film, which was the subject of investigation in the previous section (TiON 10%), was deposited at high temperature (600 °C) after a one hour titanium pre-sputter resulting in residual oxygen pressure below 5 nTorr (Figure 5.12). A second film was deposited at 600 °C using a 30 minute pre-sputter giving an intermediate residual oxygen pressure and was determined to be TiO$_{0.3}N_{0.7}$ (TiON 15%) shown in Figure 5.12. There is a clear increase in oxygen throughout the film with a pronounced diffusion layer below the surface oxide layer. The third film was deposited at high oxygen pressure, with no pre-sputter with oxygen partial pressure of 20 nTorr. This gave a balanced composition with a nearly 1:1 ratio between oxygen and nitrogen (TiO$_{0.25}N_{0.25}$, TiON 25%) but with still slightly more nitrogen than oxygen. Surprisingly, this film has no observable oxygen diffusion layer suggesting a uniform distribution of oxygen throughout. The final film is deposited at room temperature high oxygen partial
pressure (20 nTorr) and has a very high non-stoichiometric oxygen content (TiO$_{0.9}$N$_{0.45}$, TiON 40%) shown in Figure 5.12. This film has no observable diffusion layer immediately below the surface oxide layer.

With an explicit characterisation of the oxygen profile as a function of depth, it is now possible to directly relate the oxygen content to the optical and electronic properties. Using variable-angle spectroscopic ellipsometry and fitting to a Drude-Lorentz model incorporating substrate and surface oxide reflections, the real and imaginary components of the permittivity are extracted. As seen qualitatively in Figure 5.12e, there is a monotonic increase of the magnitude of the real component of the permittivity with increasing oxygen as well as a red-shifting of the crossover wavelength to the point where it remains positive over the entire measured spectral range for the semiconducting TiON 40%. The influence of more oxygen on the imaginary component is much more complicated. There is an initial increase associated with the decrease in conductivity and subsequently more loss. Beyond this, there is a decrease due to the carrier concentration decreasing to a point where interaction with incident light is diminished. The fitted parameters to a Drude-Lorentz model are summarised in Figure 5.13. There is a monotonic increase of the background permittivity associated with the less metallic behaviour and in turn weaker polarisability. This is also reflected in the Drude loss term with the faster scattering time associated with the tighter binding between the electrons and the lattice atoms.

5.6.2 Role of oxygen in electron dynamics

With the physical and optical properties of the four films well characterised, they can now serve as an effective platform to investigate the role of oxygen on the relaxation dynamics in the titanium dioxide surface layer. In the trap-assisted recombination model (Section 5.5) it was proposed that the observed lifetimes are related to the density of trap states in the titanium dioxide surface layer. It was shown that increasing the amount of oxygen in the underlying titanium oxynitride film decreases the presence of oxygen vacancies in the surface oxide layer formed [179]. It follows that this can influence the observed electron dynamics in the titania surface oxide.

Using transient pump-probe spectroscopy (Section 3.1), the picosecond behaviour of
Figure 5.12: (a-d) Time-of-flight secondary ion mass spectroscopy (ToF-SIMS) analysis of the elemental composition along the depth from surface (t=0) to substrate. (a), TiO$_{0.2}$N$_{0.8}$ (TiON 10%) shows the lowest oxygen content throughout the film whereas (b) TiO$_{0.3}$N$_{0.7}$ (TiON 15%), exhibits more notable variation of oxygen along its depth. (c) TiO$_{0.5}$N$_{0.5}$ (TiON 25%), shows uniform oxidation throughout the film (nearly 1:1 ratio between oxygen and nitrogen). The further oxidised (d) TiO$_{0.9}$N$_{0.35}$ (TiON 40%) shows a much higher oxygen content than nitrogen and is expected to have limited metallic behaviour. The real (e) and imaginary (f) parts of the dielectric permittivity described by the Drude-Lorentz fitting parameters above. With increasing oxygen there is a monotonic increase in the real component and red-shifting of the crossover wavelength due to the decrease in free carrier concentration.
## Figure 5.13: The fitted parameters of the spectroscopic ellipsometry measurements to a Drude Lorentz model with two Lorentz oscillators fitted using a Levenberg-Marquardt algorithm to minimise the mean squared error (MSE).

<table>
<thead>
<tr>
<th>TiON</th>
<th>TiO₂ Thickness (nm)</th>
<th>ENZ (nm)</th>
<th>Interband 1 (eV)</th>
<th>Interband 2 (eV)</th>
<th>(\epsilon_\infty)</th>
<th>(E_{\text{loss}}) (eV)</th>
<th>Drude Loss Term (fs)</th>
<th>MSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%</td>
<td>6.4</td>
<td>495</td>
<td>5.61</td>
<td>3.96</td>
<td>1.82</td>
<td>5.7</td>
<td>9.4</td>
<td>3.3</td>
</tr>
<tr>
<td>15%</td>
<td>6.8</td>
<td>565</td>
<td>5.60</td>
<td>4.07</td>
<td>2.14</td>
<td>5.3</td>
<td>4.0</td>
<td>6.8</td>
</tr>
<tr>
<td>25%</td>
<td>10.2</td>
<td>625</td>
<td>5.62</td>
<td>3.75</td>
<td>2.36</td>
<td>5.0</td>
<td>2.7</td>
<td>2.9</td>
</tr>
<tr>
<td>40%</td>
<td>4.9</td>
<td>N/A</td>
<td>4.34</td>
<td>1.17</td>
<td>3.02</td>
<td>N/A</td>
<td>2.6</td>
<td>9.8</td>
</tr>
</tbody>
</table>

hot carriers and free electrons are measured using an 850 nm, 5 mW average power pump beam and 1150 nm, 250 \(\mu\)W average power probe beam. Figure 5.14 shows the differential reflectivity for the three newly-introduced films (TiON 15%, TiON 25% and TiON 40%) with the corresponding fits to the trap-mediated relaxation model from Section 5.5.2 with the shallow \(\tau_{\text{Sh}}\) and deep \(\tau_{\text{De}}\) trap lifetimes. Alongside each plot is the fitted curves for the Au/TiO₂ and TiON 10% to serve as a reference for comparison. Additionally, on the right-hand side of the differential reflectivity curve is the oxygen profile of each film as measured by ToF SIMS.

In Figure 5.14a, the difference in oxygen of TiON 15% compared to TiON 10% does not have a substantial impact on the relaxation dynamics. A slight increase in differential reflectivity signal across the entire measured range suggests oxygen increases hot carrier generation and injection into TiO₂. This can also be attributed to the increased absorption of the TiON layer as predicted by the higher imaginary component of the permittivity at the pump wavelength (850 nm) as observed in Figure 5.12f. Indeed the distribution of oxygen throughout the film is almost identical to TiON 10% with the presence of an intermixed oxygen layer below the surface oxide layer. However, this oxygen diffusion layer is not present in TiON 25% (Figure 5.14b) and, indeed, a more substantial change to the magnitude despite a similar \(\text{Im}\{\epsilon\}\) compared to the TiON 15% film. In addition, an ultrafast peak emerges immediately following pump excitation that is not present in any other film. This peak will be discussed in Section 5.7.

The TiON 40% sample shows a decrease in differential reflectivity, suggesting that the TiON 25% is the optimal film. The fitted lifetimes for TiON 25% are much slower than those
Figure 5.14: Differential reflectivity following a 5 mW pump pulse (left) and oxygen composition (right) measured with ToF-SIMS for films with increasing oxygen content: TiON 15% (a), TiON 25% (b), and TiON 40% (c). Each film exhibits a higher differential reflectivity than both the Au/TiO2 and TiON 10% films over the entire temporal range.
observed in the TiON 10% and 15% films with a shallow trapping lifetime of $\tau_{Sh} = 16.7$ ps and a deep trapping lifetime of $\tau_{De} = 324$ ps. These trapping lifetimes approach those observed in the relaxation after direct bandgap excitation of TiO$_2$ [180]. Finally, the TiON 40% film (Figure 5.14c) shows similar dynamics to TiO 25% with only slightly faster fitted lifetimes ($\tau_{Sh} = 12.3$ ps, $\tau_{De} = 237$ ps) for the trapping processes but with a much lower measured differential reflectivity than the TiON 25% film. Additionally, there is no oxygen diffusion layer observed at the interface. There appears to be a threshold level of oxygen, which enables the formation of a uniform surface oxide layer that reduces subsequent diffusion of oxygen into the film.

5.6.3 Role of pump power on electron relaxation dynamics

The initial excited electron distribution can be controlled by varying the pump power. Since this translates to a proportionate increase in harvested electrons, the decay and recombination dynamics can be studied as a function of the excited carrier concentration. The extracted lifetimes of the transient pump-probe spectroscopy measurements with pump powers between 1 and 5 mW are shown in Figure 5.15. The dotted line for each film displays the arithmetic average of the five measurements. Notably, there is no observable dependence on pump power over the measured range with near-constant behaviour observed for both the shallow and deep trap lifetime. This suggests that the extracted lifetimes are intrinsic material properties and not dependent on absorption. It is, however, well-known that the lifetimes associated with the thermodynamic interaction of electrons and phonons shows a distinctive power-dependence due to the temperature-dependent electron-phonon coupling constant and electron heat capacity (Section 4.2). This supports that the observed lifetimes are a probing decays occurring the titania surface oxide layer.

5.6.4 Role of oxygen on carrier extraction efficiency

In addition to oxygen influencing the relaxation dynamics, it can also control the injection dynamics at the interface. A pristine interface is critical to efficiently collect electrons as a high-defect layer, such as the oxygen diffusion layer seen in TiON 10% and TiON 15%, can
5.6. Controlling Relaxation Dynamics with Oxygen Composition

Figure 5.15: The fitted decay times for shallow (left) and deep traps (right) are shown with no significant dependence on pump power. Dotted lines show the average of the 5 displayed measurements. Almost no variation of shallow trapping lifetime is observed between TiON 10% and TiON 15% whereas TiON 25% shows a much slower relaxation time. The deep trapping time, however, is observed to slow with increasing oxygen content.

trap electrons or result in high energy electrons losing their excess energy before reaching the surface. Shown in Figure 5.16 is the calculated harvested electron density (as calculated from the maximum measured differential reflectivity) for the four titanium oxynitride films as well as the gold-titanium dioxide sample as a reference.

Alongside, in Figure 5.16, is the absorption coefficient at 850 nm for each of the films, calculated from the fitted spectroscopic ellipsometry data. It is clear that each titanium oxynitride film provides a clear advantage over an equivalent Au/TiO$_2$ system with even the least efficient film (TiON 10%) proving a four-fold increase. However, when comparing between the TiON films, there is unexpectedly high harvested carrier density in the TiON 25% film, which is attributed to the density of defects at the interface.

If the defect density at the TiON/TiO$_2$ interface did not influence the electron harvesting, it would be expected that the harvested electron density is directly proportional to the absorption coefficient. That is, an electron excited in any of the TiON films has equal probability of injection implying that an increase in absorption would have a proportionate increase in the harvested electron density. However, as shown in Figure 5.16 a disproportionate increase in the harvested electron density is observed for the TiON 25% and 40% films when comparing their absorption coefficients.
5.7 Hot Carrier Dynamics at the TiON/TiO₂ Interface

Consider now the fast relaxation peak observed in the TiON 25 % film (Figure 5.14). In order to be able to initiate a chemical reaction, the electrons reaching the surface must maintain sufficient energy during the injection process. The ultrafast peak is interesting, since the signature of hot electron population is sub-picosecond decay dynamics. To investigate this possibility, the power-dependent dynamics are explored as the heat capacity, which determines the lifetimes, has a temperature-dependence.

It is posited that the oxygen diffusion layer observed in ToF SIMS measurements of TiON 10% and 15% likely has a large degree of disorder and concentration of defects due to the intrinsic randomness of the diffusion process. When electrons are traversing this portion of the film, much of the initially excited electrons are trapped or scattered to lower energy states reducing the harvesting efficiency. In contrast, the more uniform interface of TiON 25% and TiON 40% allows for the passage of electrons without significant scattering. This results in more electrons reaching the TiO₂ surface layer.

**Figure 5.16:** *(Left)* Maximum free carrier concentration in the TiO₂−ₓ determined from the peak of differential reflectivity measurements. *(Right)* Absorption coefficient at the pump wavelength (850 nm) for each film. The strong enhancement in electron harvesting observed in TiON 25% cannot be explained by a larger absorption.
Figure 5.17: Differential reflectivity measurements of Au/TiO\textsubscript{2}, TiON 10\% and TiON 25\% over the first 1.75 picoseconds. TiON 25\% exhibits an additional ultrafast peak (shaded region) in addition to the rise observed in TiON 10\%.

### 5.7.1 Detection of hot carriers

Figure 5.17, compares three films from Figure 5.14b but over a much shorter range of probe delays (-0.5 ps to 1.5 ps) to expose the ultrafast peak present in the measurement of the TiON 25\% film. The additional peak is fit to a Gaussian in addition to the electron kinetic model derived in Section 5.5. The fit to the electron kinetic model is shown by the dotted line in Figure 5.17 whereas the additional Gaussian response is shown as the blue shaded region. This reproduces the measured behaviour well with an adjusted \( R^2 \) value of 0.982. As this behaviour is not observed in TiON 10\%, it cannot originate from the electron-phonon scattering in titanium oxynitride as density functional theory predicts this should occur within the pulse width of the pump (150 fs). As such, the peak is attributed to hot electrons reaching states above the conduction band minimum in the TiO\textsubscript{2} surface layer and subsequently relaxing to the conduction band minimum. This could suggest that the higher oxygen content of TiON 25\% fills oxygen vacancies leaving less defects near the TiON/TiO\textsubscript{2} interface layer to trap carriers.

This model allows for the decomposition of the signal to separately analyse the fast response peak. The metric used to characterise the fast component is the full-width half-maximum (FWHM) of the fitted Gaussian component. This decomposition is shown in 5.18 where the red-dotted line shows the temporal evolution extracted from the fitted equations. The entire process persists for approximately 700 fs, which is above the resolution limit of the
Figure 5.18: (Left) Decomposition of the TiON 25% signal into conduction band electron occupation (blue dashed line) and hot electron population (red-dashed line). The lifetime of the hot electron distribution ($\tau_{CB}$) describes the electron-phonon scattering time in the TiO$_{2-x}$. It is described by the fitted full-width half-maximum (FWHM) of the signal showed by the red arrow. (Right) Power-dependence of $\tau_{CB}$, showing a slower relaxation with increasing power (and thus increased electron temperature) characteristic of a hot electron population.

pump-probe system. Similar behaviour has been observed in dye-sensitised semiconductors with a hot electron injection channel [181].

Shown in Figure 5.18 is also the pump power dependence of the fitted conduction band relaxation lifetime ($\tau_{CB}$) between 1 and 5 mW. Unlike the shallow and deep trap lifetime, there is an increase in lifetime with increasing pump power, which is a signature of a hot electron process. As more energy is coupled into the initial electron distribution, it takes an increasing number of electron-electron and electron-phonon scattering events to fully dissipate the energy. This was previously observed to be on the order hundreds of femtoseconds in semiconductors [170], which compares well with our observed conduction band relaxation lifetime. As such, the process can be attributed to hot electrons reaching the titania surface oxide layer and relaxing to the conduction band edge of the TiO$_2$.

5.8 Extension to Other Material Systems

Titanium nitride and titanium oxynitride are not unique in having semiconducting surface oxide layers. Many transition metal oxides are known to exhibit semiconducting behaviour [182, 183] due to the high conductivity of metallic bonds being offset with stronger covalent bonds due to the high electronegativity of oxygen. The strong pull of electrons toward oxygen restricts
the free conduction of electrons through the material. The oxide formed on other transition metal nitrides via nitrogen-oxygen substitution would also exhibit similar properties to the titanium oxynitride investigated above resulting in similar crystal structure and comparable or even larger band gaps than titanium dioxide.

The oxidation of zirconium nitride (ZrN) forms zirconium dioxide (ZrO$_2$) with a measured band gap between 5 and 7 eV [184]. Similarly, hafnium dioxide formed from HfN (HfO$_2$) has a band gap energy of approximately 5.5 eV [185] and niobium pentoxide, formed from NbN (Nb$_2$O$_5$) has a bandgap of 3.4 eV [186]. Monoatomic transition metals are also capable of forming such semiconducting metal oxide semiconductors with PdO having a band gap between 2.1 and 2.7 eV [187] and platinum dioxide (PtO$_2$) shown to have a smaller band gap of approximately 1.5 eV [188]. Both PdO and PtO$_2$ are known to be efficient catalysts and are routinely used in organic synthesis reactions [189, 190, 191, 192].

5.8.1 Film Deposition

To compare to the previous titanium oxynitride results, an additional transition metal nitride, niobium nitride (NbN), and a transition metal, palladium (Pd), are chosen due to accessibility and the relevance to photocatalytic applications [42].

A 50 nm Pd film is deposited by sputtering of a palladium target at room temperature in a vacuum ($5 \times 10^{-5}$ mbar) while flowing Ar using a Quorum Q150T Modular Coating system. To deposit the niobium nitride films, a niobium target was RF Magnetron sputtered in a 3:7 N$_2$ : Ar plasma and accelerated toward a Si (100) substrate. This results in a continuous 50 nm NbN thin film, which was deposited directly on the Si substrate with the native SiO$_2$ layer remaining between the film and substrate.

These two films were then removed from the deposition chambers and left exposed to air prior to any measurements being performed. Sufficient time was allowed for the self-limiting oxide layers to form, which should only take minutes to hours [193, 194].
Figure 5.19: Ellipsometry measurements of palladium (top-left) and niobium nitride (bottom-left) fitted to a Drude-Lorentz model to estimate the real and imaginary components of the permittivity. The extracted permittivity of the respective surface oxides are also displayed: PdO (top-right) and Nb$_2$O$_5$ (bottom-right). Each shows typical semiconductor behaviour with approximate bandgaps of 2.25 eV and 3.1 eV for PdO and Nb$_2$O$_5$, respectively.

5.8.2 Optical Characterisation

To determine the optical properties of the NbN and Pd thin films, variable angle spectroscopic ellipsometry was performed on each of the films. A three layer model was used to describe the collected reflections consisting of a few nanometer surface oxide layer, a Drude-Lorentz layer, and substrate layer. The substrates were measured and analysed independently to extract the refractive index over the measured spectral region (300-1600 nm). These values are held constant in subsequent multi-layer fitting procedures. As the surface oxide layers are known to be semiconducting, the model is initiated as a 2 nm titanium dioxide layer with refractive index (with both real and imaginary components) and layer thickness as adjustable parameters. Finally, the Drude-Lorentz metallic layer is initialised using a Drude-Lorentz layer with a single Lorentz oscillator and the number of oscillators is increased following the procedure outlined
Figure 5.20: Calculated absorption coefficient of Pd, PdO, NbN, and NbON thin films from measured ellipsometry data. At the pump wavelength (850 nm), absorption takes place in the metal film.

in Sections 3.2 and 4.2.

The extracted real and imaginary components of the material permittivities for the Pd and NbN films as well as the associated oxide layers (PdO and Nb$_2$O$_5$) are plotted in Figure 5.19. Palladium (Figure 5.19) exhibits a conventional metallic dielectric function heavily dominated by the Drude (free carrier) concentration. The crossover wavelength ($Re\{\epsilon\} = 0$) is in the UV, at wavelengths below the measured region meaning it has metallic behaviour at all wavelengths considered. It was also shown to have two transitions at 0.83 eV and 5.19 eV and a background permittivity of $\epsilon_\infty = 1.6$. The two-Lorentz oscillator model fit has a corresponding MSE of 1.7, which is considered to be very good.

The permittivity of PdO (Figure 5.19) shows semiconducting behaviour with nearly no absorption below the optical band gap and a sharp increase in absorption ($Im\{\epsilon\}$) and corresponding change in the real part at photon energies above (wavelengths below) the optical band gap. This can be used to estimate the band gap energy using the onset of the absorption, which in this case occurs at 550 nm or 2.25 eV. This lies in the range reported in literature (2.1-2.7 eV [187]), supporting the reliability of the proposed three-layer system with the given optical data.

Unlike the conventional behaviour of Pd, the extracted permittivity of NbN exhibits a much more interesting behaviour with the emergence of two crossover ($Re\{\epsilon\} = 0$) wavelengths. The first lies in the visible at approximately 400 nm whereas the second crossing of the $Re\{\epsilon\}=0$
lies in the infrared closer to 1300 nm. Beyond 1300 nm, the behaviour is dielectric-like with a positive real component and large imaginary component. Similar behaviour was observed in titanium oxynitride films with sufficiently high oxygen concentrations [43] suggesting the film is actually niobium oxynitride. The anomalous infrared behaviour is described as a broad Lorentz oscillator centred 0.93 eV (1333 nm) in addition to the two additional interband transitions at 4.87 eV and 6.01 eV and a background permittivity of $\epsilon_\infty = 1.5$. This fit yields an incredibly low MSE of 0.7 suggesting very reliable extraction of the optical parameters.

Semiconducting behaviour is observed with the extracted permittivity of $Nb_2O_5$ (Figure 5.19c) with an absorption onset estimated to be at 400 nm (3.1 eV). Although this is slightly lower than the literature value (3.4 eV [186]), the reduction may be a result of oxygen vacancy states within the band gap. This would provide channels for valence to conduction band excitation at lower energies as observed in titanium dioxide thin films [195]. Additionally, the absorption cross-sections for each material is presented in Figure 5.20.

### 5.8.3 Pump-Probe Investigation

With the optical properties of the two additional metal-semiconductor systems well-characterised and some electron properties inferred from the fitted models, it follows naturally to consider pump-probe spectroscopy. To compare new data to the TiON ones, identical transient pump-probe spectroscopy measurements were performed to resolve both the ultrafast (hundreds of femtoseconds) and slower (hundreds of picoseconds) responses (Figure 5.21).

Each film exhibits the same long lifetime observed in the titanium oxynitride films, which is attributed to a similar interplay of states between the metal and semiconductor (Figure 5.21). This further supports the interpretation of the injection and subsequent trap-mediated relaxation in the semiconducting oxide layer. The magnitude of the differential reflectivity, however, is over a factor of two smaller than the response of TiON 10%. This could be a result of the band alignment at the metal-semiconductor may not be preferential for electron harvesting into the semiconducting layer. This is consistent with the larger work functions for NbN and Pd resulting in energy barriers at the interface.

The bi-exponential (shallow and deep trap) model was used to explain the dynamics of excited electron populations. With the presence of the ultrafast peak in the NbN signal,
the bi-exponential decay model was adapted to include an additional Gaussian response as was done with TiON 25% and TiON 40% previously. Shown in Table 5.1 are the extracted lifetimes from fitting the measured differential reflectivity to the trap-assisted decay model alongside that of TiON 10% and TiON 25% for reference. The rise time ($\tau_0$) is the slowest in NbN (650 fs) with Pd also exhibiting a much longer lifetime than TiON (530 fs). Although NbN shows the ultrafast peak, its temporal width is almost half that of TiON 25% (340 fs and 190 fs for TiON 25% and NbN, respectively). The shallow trapping lifetimes are within the same range as both TiON samples but NbN loses considerably more energy to shallow traps (44%), which is observed as a rapid decrease in differential reflectivity over the first 50 ps. The deep trap lifetimes are comparable except for palladium where the deep trap lifetime is much slower (1450
Table 5.1: Fitting parameters of NbN and Pd pump probe measurements to the trap-mediated recombination model along with that of TiON 10% and TiON 25% for comparison.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\tau_0$ (fs)</th>
<th>$\tau_{NT}$ (fs)</th>
<th>$\tau_{Sh}$ (ps)</th>
<th>S (%)</th>
<th>$\tau_{De}$ (ps)</th>
<th>D (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbN</td>
<td>650</td>
<td>190</td>
<td>19.4</td>
<td>44</td>
<td>223.3</td>
<td>26</td>
</tr>
<tr>
<td>Pd</td>
<td>530</td>
<td>-</td>
<td>8.9</td>
<td>28</td>
<td>1450.4</td>
<td>46</td>
</tr>
<tr>
<td>TiON 10 %</td>
<td>270</td>
<td>-</td>
<td>7.6</td>
<td>27</td>
<td>99</td>
<td>18</td>
</tr>
<tr>
<td>TiON 25 %</td>
<td>240</td>
<td>340</td>
<td>16.7</td>
<td>14</td>
<td>324</td>
<td>26</td>
</tr>
</tbody>
</table>

5.9 Summary

Although transition metals and transition metal nitrides have been prevalent in the literature, their potential as optical materials has only recently been realised. The novelty of these materials for use in photo-driven applications means there is a lack of theoretical work and widespread misunderstanding of the materials. Due to their metallic properties it is instinctual to apply models derived for noble metals to describe these systems. However, as shown with three distinct materials (TiON, Pd, and NbN), this is not sufficient to explain the rich physics observed in ultrafast optical measurements.

To assist in exploring the complexity of these systems, an electron kinetic model was introduced describing the observed ultrafast electron dynamics. This model can serve as a framework for describing the interplay between the strongly absorptive metallic layer and the omnipresent semiconducting surface oxide layer. An exemplary investigation using four TiON films with varying oxygen content to optimise the material for use in photocatalytic applications. Not only did this characterise material and interfacial properties but it also uncovered the presence of hot electrons in the titania and the physical processes that facilitates this. It is now necessary to apply these models to nanoscale particles to elucidate the role that surface plasmons can play in the excitation and harvesting of hot electrons.
Chapter 6

Plasmon-Excited Electron Dynamics and Thermal Effects

This chapter explores the electron dynamics in titanium oxynitride nanostructures building on the insight gained from the thin film study in the previous chapter. Through a series of ultrafast optical studies, the viability of titanium oxynitride as a plasmonic hot electron platform is investigated. As surface plasmons are very sensitive to properties of the surrounding medium, emphasis is placed on clarifying how the surface oxide influences both the excitation and decay of the plasmon resonances as well as electron harvesting from the metal. With the deeper understanding of the constituent materials, it is possible to quantify the degree of plasmonic enhancement and attribute it to specific physical processes. It is shown that the interfacial states damp the surface plasmon and increase absorption beyond what is expected from the plasmonic mode alone. Although strong plasmon damping is seen as deleterious in many applications, it is favourable in hot electron devices. The results are a culmination of the insight gained from the theoretical modelling, material characterisation and experimental investigations presented thus far.

6.1 Introduction

The increase in visible and infrared absorption and generation of high energy electrons has made plasmonic nanoparticles a staple in many photocatalytic applications. The benefits have been demonstrated in countless experimental works including solar water splitting [162, 196]
and reduction of air pollutants [166]. In this work, plasmonic modes in titanium oxynitride nanowires are exploited to enhance electron harvesting compared to a thin film counterpart. The plasmonic properties of TiON particles are demonstrated along with the associated electron dynamics. Using the established model in the previous section, the harvesting efficiency as well as thermal resilience is investigated. Surprisingly, TiON shows improved carrier harvesting after being exposed to high temperatures. This phenomenon is associated with crystal structure and defect changes implied by the pump-probe experiments.

6.2 Plasmonic Properties of TiON Nanostructures

In Section 4.3, excitation of surface plasmon resonances was demonstrated in titanium oxynitride nanoparticles fabricated using two techniques. The strong broadband absorption and weak scattering of titanium oxynitride particles makes them ideal for hot electron applications as most of the energy concentrates inside the particle. This provides a higher probability of exciting high energy electrons in the metal through intraband transitions. Using transmission measurements, the tunability of the plasmon resonance and the influence of the encapsulating surface oxide is analysed.

6.2.1 Influence of oxide layer on plasmon resonance

In the previous chapter, the surface oxide and the defect density played key roles in mediating the electron harvesting efficiency. In patterned TiON, the freshly exposed sidewalls of the structure are now susceptible to oxidation as well. Upon exposure to air, this leads to a fully-encapsulating surface oxide layer as shown in Figure 6.1. This can have a profound impact on the plasmonic resonance frequency and damping as the dielectric environment of the excited
Figure 6.2: Mie theory calculations of the absorption cross-section of a single spherical titanium oxynitride particle embedded in air (left) and titanium dioxide (right). The surface oxide will have a significant impact on the plasmon resonance frequency of a titanium oxynitride particle. The damping of the high-refractive index titanium dioxide is evident with the broadening and red-shift of the absorption cross-section resonance peak.

LSPR is much higher refractive index than air ($n \approx 2.5$ [197]).

To illustrate this effect, the absorption cross-section of spherical TiON particles embedded in a uniform homogeneous media are calculated using Mie theory (Figure 6.2). At visible wavelengths, the refractive index of titanium oxynitride is smaller than that of titanium dioxide resulting in stronger field confinement inside the particle, increasing the absorption over this range. The change in the surrounding refractive index also produces a significant red-shift observed in the plasmon resonance peak wavelength.

### 6.2.2 Tunable Plasmon Resonance

In addition to controlling the optical properties by tailoring the free carrier concentration as was done in Chapters 4 and 5, it is possible to shift the resonance peak to lower energies (red-shift) by increasing the size of the particle. This size dependence of the plasmon resonance is a result of the increased influence of retardation (change of electric field phase) in larger particles [198]. This then allows for a fine-tuning of the resonance using a single set of deposition parameters.

To investigate the role of surface plasmon resonances on the electronic behaviour while precluding any minor variations of carrier concentrations, a strip geometry is fabricated on fused quartz coverslip using the chromium lift-off procedure performed by Yi Li. The material was
Figure 6.3: Scanning electron microscope (SEM) image of the patterned titanium nitride strips on fused quartz coverslip using the Cr-liftoff procedure (Section 4.3). The geometry of the strips (200 nm wide, 30 µm long) allows for polarisation-selective excitation of the localised surface plasmon resonance (LSPR) resulting from the 2D confinement of the metal.

deposited by Andrei Mihai using the Cr-backside thermal contact, at 600°C, 30% nitrogen to argon following a 1h pre-sputter of titanium to reduce the residual oxygen in the chamber. These are identical conditions to what produced the TiON 10% thin film in the previous chapter. The strips were made to be 30 µm in length but with variable, sub-wavelength width (100nm, 150nm, and 200 nm) and a pitch of 600 nm. Figure 6.3 shows a scanning electron microscope image of the titanium oxynitride strips.

The lateral confinement in one direction allows for polarisation-selective excitation of the localised surface plasmon resonance. That is, a surface plasmon is only generated when exciting with a polarisation perpendicular to the length of the strip. Using transmission measurements of a white light source generated by a SuperK compact supercontinuum laser dispersed on a CCD camera, the extinction spectra of the fabricated strips using a focused spot on the structure surface (Figure 6.4). Due to the packing density of the strips, the hybridisation of the plasmon modes between adjacent strips results in a blue-shift of the plasmon resonance into the visible range not observed with the isolated disks in Section 4.3. Indeed, the size-dependent
resonance shift characteristic of LSPRs is observed with the resonance peak tunable from below 750 nm to above 900 nm using only this small range of sizes. The peak in extinction reaches almost 60% for the largest strips due to the efficient excitation of the plasmon resonance and the increased filling factor.

6.3 Pump Probe Differential Reflectivity Measurements

In this section, transient pump-probe spectroscopy is used to determine the specific role of surface plasmon excitation on the electron harvesting dynamics across the metal-semiconductor interface formed at the surface of TiON. Beyond the straightforward absorption enhancement brought about by the plasmonic mode, the changes in dielectric environment and presence of interfacial states allows for even further enhanced electron harvesting.

6.3.1 Experimental procedure

To investigate the electron dynamics, time-resolved pump-probe spectroscopy is used as described in Chapter 5. However, the pump pulse is varied over a wider power range (0.5-20 mW) and across the wavelength range 790-860 nm. The time-delayed probe pulse is fixed at 1150 nm with a power of 150 µW and the differential reflection is detected using an InGaAs
photodetector. The strips of width 150 nm are selected for pump probe studies due to the overlap of the resonance peak with pump wavelength range. The plasmon resonance is selectively excited by switching the polarisation of the pump beam using a half-wave plate. When the polarisation is aligned to the length of the strip, it is assumed that no plasmon resonance is excited whereas when the polarisation is aligned perpendicular to the length of the strip, a localised plasmon resonance is generated due to the sub-wavelength confinement of the electrons. The probe beam is kept parallel to the strips to exclude the influence of subsequent plasmonic effects.

6.3.2 Comparison of resonant and non-resonant excitation

For the 150 nm wide strips selected, the plasmon resonance peak is determined to be approximately 850 nm (Figure 6.4). The corresponding transient differential reflectivity for both pump polarisations at 850 nm is shown in Figure 6.5. Notably, the differential reflectivity of the resonant excitation is much higher than that of the non-resonant excitation over the entire measured range. Immediately following pump excitation, the maximum differential reflectivity is nearly four times as large as that of the non-resonant excitation. With the relationship between differential reflectivity and free carrier concentration (Section 5.3), the plasmon enhancement to the electron harvesting is clearly discernible.
Following this, the spectral dependence of the electronic response of the particles was examined by varying the pump wavelength to more thoroughly explore the underlying physical processes associated with resonant enhancement. Shown in Figure 6.6 are the corresponding differential reflectivity traces of the titanium oxynitride strips measured at various wavelengths between 790 nm and 860 nm for both polarisations at a fixed pump power (5 mW). The magnitude of the differential reflectivity shows a clear pump wavelength dependence in the perpendicular-pump configuration whereas the parallel configuration shows little variation between measurements. This wavelength-sensitivity is expected for plasmon-like absorption shown explicitly by the maximum differential reflectivity in Figure 6.7. Although this is indicative of simply plasmon-enhanced absorption, the interfacial properties can still play a determining role in the extracted carrier concentration.

To separate the absorption and interfacial enhancements, the measured signals can be normalised by the measured absorption cross-section (Figure 6.8). This is valid with the assumption that there is a linear relationship between the measured signal and carrier concentration (Section 5.3) and that the electron transfer probability is linear with increasing carrier concentration (Fowler theory [199, 200]). The increased absorption alone does not explain the more dramatic enhancement of the differential reflectivity. There is still a three-fold enhancement attributed to interfacial effects. This has been observed previously with the inconsistency between the catalytic enhancements and the predicted hot electron generation enhancement.
Figure 6.7: Maximum differential reflectivity of the TiN strips measured with the two different pump polarisations. The resonant enhancement of the differential reflectivity, and in turn the harvested electron density, is clearly visible with the peak corresponding to the extinction peak in Figure 6.4 [159, 201]. The discrepancy was attributed to the increase in the plasmon decay pathways due to presence of interfacial states. In this case, the interfacial states are those formed between the titanium oxynitride strips and the surface oxide layer.

As shown in Figure 6.2, the plasmonic behaviour of a particle is strongly influenced by its dielectric environment. The resonance behaviour with and without the oxide layer cannot be shown experimentally due to the rapid oxidation of the titanium oxynitride surface. As such, finite-difference time-domain (FDTD) simulations are performed using the commercial software, Lumerical. An array of 30 µm x 150 nm strips with 600 nm pitch were modelled. Using a total-field scattered-field (TFSF) method (Section 4.3) and an absorption monitor, the absorption cross-sections of the perpendicular excitation of the TiON strips with and without an encapsulating 5 nm TiO$_2$ coating. As predicted in the Mie theory calculations (Figure 6.2), the simulated absorption is stronger (larger absorption cross-section) and broader due to the increase in damping of the plasmon resonance by the titania layer.

To explicitly calculate the plasmon decay in the FDTD simulations, a field monitor is placed at the sidewall of the structure. The electric field magnitude is calculated, which is expected to have the form of an exponentially decaying $sin^2$ function for a surface plasmon
6.4 Power-Varied Measurements of TiON Strips

One of the initial motivations to adopt titanium nitride as a plasmonic material is its high melting temperature resulting from the strong bonds between titanium and nitrogen. The high melting temperature compared to conventional plasmonic materials (Au, Cu, Ag) suggests that it would be able to maintain nanoparticle structure at higher laser powers. In this section, the

resonance decaying on the order of femtoseconds. Shown in Figure 6.9 are the corresponding electric field intensity of the bare TiN strips compared to TiN strips with a 5 nm TiO$_2$ surface oxide layer. The damping of the resonance is clearly observed in the smaller magnitude and more rapid decay. Although deleterious for many plasmonic applications, behaviour such as this enhances the generation of hot electrons. Combined with the availability of surface states the decaying plasmon can excite electrons into the conduction band of the semiconducting surface. Such a process is termed chemical interface damping (CID) and is common when there are adsorbed molecules at the surface of a plasmonic particle [90, 201, 91, 131, 159].

Figure 6.8: Time-resolved differential reflectivity measurements for resonant (black) and non-resonant (red) excitation of the titanium nitride strips at 850 nm normalised by the measured absorption of the strips. Even beyond the stronger absorption of the LSPR, there is more efficient electron harvesting upon resonant excitation. In addition to the interface being perpendicular to the initial momentum of the electrons, the presence of the surface oxide damps the plasmon resonance providing additional loss channels.
resilience of the titanium oxynitride strips to laser power exposure is examined. As electron harvesting was shown to depend on maintaining a low-defect interface between the titanium oxynitride and surface oxide, particular attention is paid to the interfacial conditions.

### 6.4.1 Reversible power-sweep resonant measurements

When looking at the power-dependence of the recombination dynamics of titanium oxynitride films in Section 5.6, no variation was observed at low powers (1-5 mW) for either the shallow or deep trapping lifetimes (Figure 5.15). With the understanding gained from those measurements in mind, identical measurements are performed to analyse the behaviour of plasmon-enhanced carrier harvesting in titanium oxynitride strips. Resonant excitation (pump polarised perpendicular to the length of the strip) at increasing power (1-15 mW) is performed. Following this, the power is reduced back to 1 mW.

Some exemplary transient differential reflectivity measurements are shown in Figure 6.10 normalised by the maximum measured value to be able to compare the electron dynamics independently of the absolute number of carriers excited by the pump. The behaviour over this range of powers is identical, consistent with the previous investigation of thin films. To quantify this behaviour, the measurements are fitted to the bi-exponential trap-mediated recombination model. In Figure 6.10, the extracted shallow trap lifetime is plotted for increasing (red) and decreasing (blue) measurements. There is a slightly larger uncertainty on the extracted values
6.4. Power-Variated Measurements of TiON Strips

Figure 6.10: *(Left)* Normalised differential reflectivity measurements for increasing pump power from 1 mW to 12 mW. There is no significant change in behaviour over the entire measured range. *(Right)* Shallow trap lifetime as a function of increasing pump power up to 15 mW (red) and decreasing pump power back to 1 mW (blue). There no distinct dependence on power beyond the uncertainty of the extracted parameters.

compared to the films attributed to the acousto-optical vibrations. Regardless, there is no clear change in the shallow lifetime across this power range and, as such, it is assumed that there is no change in the physical or electronic properties of the structure.

6.4.2 Irreversible modification of TiON interfacial states

The high temperature effects on the electron harvesting is now studied by increasing the pump powers until a change is observed in the decay dynamics. Shown in Figure 6.11 are the transient differential reflectivity at increasing pump power excitation on resonance at 850 nm. As pump powers are increased to 16 mW, the signal across the entire measured range of probe delays. This increase is attributed to additional carriers excited in the TiON and a proportionate increase in harvested carriers. However, at a pump power of 16 mW, the slow decay appears to happen faster. When exciting with powers beyond 16 mW (bold blue and purple curves in Figure 6.11) this increase is significantly more pronounced and the maximum differential reflectivity appears to saturate.

The more rapid decay of the differential signature could suggest a change in the trap density of the TiO$_2$ or in the ability to maintain electron separation, which could be affected by the interfacial condition. The cause of the observed change is examined in more detail in the next section. However, as an initial investigation, the laser power is decreased following 15
minutes of laser exposure at 20 mW. The response of the titanium oxynitride strips to a 5 mW pump pulse before and after laser annealing at 20 mW is shown in Figure 6.12. The changes to the system are maintained suggesting a permanent reconfiguration of the material. It should be noted that after annealing there is a significant increase in the maximum differential reflectivity, which may suggest increased photocatalytic abilities due to the larger electron density at the surface.

6.5 Laser-Induced Material Changes

Due to the incredibly small sizes of oxygen vacancies and dopant ions, it is not feasible to observe the material and interface conditions directly. However, using a wide range of indirect probes of the materials, an informative picture can be constructed. The experimental techniques used in this section include scanning electron microscopy, Raman vibrational spectroscopy, and lifetime analysis using curve fitting to the tap-mediated recombination model. As the system involves two distinct materials, emphasis will be placed on resolving the individual contributions and
6.5. Laser-Induced Material Changes

Figure 6.12: **Differential reflectivity signal before and after the laser annealing process, where irreversible changes to sample are made.**

how it results in the observed behaviour in the pump-probe measurements in the previous section.

### 6.5.1 Optical and vibrational spectroscopy investigations

Initial intuition would suggest that the elevated laser power increased the lattice temperature to the melting temperature of the particle (known to be be much less than the bulk melting temperature [202]) resulting in deformation and changes to the plasmonic properties. As such, the first material characterisation measurement involves examining the heated area with a scanning electron microscope to observe any structural or conformational changes. Figure 6.13 shows the captured SEM image with 6740x magnification. There is no evidence of melting or deformation in either exposed region shown by the dashed circles on the image. There is, however, a change in colour observed in the SEM image suggesting a change in surface conductivity after laser exposure. Lighter areas SEM image are indicative of charging suggesting a lower conductivity as accumulating charges result in a brighter spot in the SEM image. This could be due to either less conductive metal or modified TiO$_2$ surface layer.
To understand the material differences following laser annealing, Raman vibrational spectroscopy was used to understand the nature of the bonds within the material. In Raman spectroscopy, light is scattered by phonons to reveal information about the material structure. Shown in Figure 6.14 are two Raman spectrum of TiON taken using a focused green (532 nm) laser before and after exposure to the high-power laser. The as-deposited sample has a series of peaks characteristic of TiON [203], at approximately 220 cm$^{-1}$, 310 cm$^{-1}$, and 500 cm$^{-1}$. The naturally forming surface oxide layer is likely to be amorphous having no distinguishable peaks [204]. Following annealing, a new strong peak appears at 145 cm$^{-1}$ followed by a very small peak at slightly larger shift-values known to be characteristic of anatase titanium dioxide [204]. From the literature, the transformation from amorphous to anatase titanium dioxide is known to occur at relatively low temperatures ($\leq 400{^\circ}C$) compared to the bulk melting temperature of titanium nitride (2930 °C) and the threshold is likely even lower for such a thin layer of titanium dioxide. Therefore, the proposed explanation of the observed change above 16 mW is the annealing of the surface oxide layer from amorphous to anatase titanium dioxide. This
Figure 6.14: Raman vibrational spectra of TiON before (black) and after laser annealing (red). Before annealing, there are no sharp TiO$_2$ peaks suggesting an amorphous oxide layer, which is also the most likely to form by oxidation at room temperature. Meanwhile, the annealed sample shows peaks distinctive of anatase TiO$_2$.

Annealing would influence both the trap density and interfacial properties, which in turn would influence the hot electron generation and separation.

### 6.5.2 Irreversible changes to trapping lifetimes

With the set of experimental power-dependent pump-probe measurements, it is straightforward to estimate the shallow and deep trapping behaviour by fitting each to the trap-mediated recombination model (Section 5.5). Figure 6.15 shows the shallow trapping lifetime and amplitude while heating up to 20 mW (red) and cooling back down to 1 mW (blue). There is a distinct slowing (increase) of the shallow trapping lifetime observed at 18 mW but at higher powers, the extracted shallow trap lifetime seems to stabilise to just below 11 ps. There is no corresponding change to the shallow trapping amplitude, suggesting a comparable percentage of the initially harvested free carriers is lost to shallow trapping but at a slower rate. This is consistent with lower electron conductivity as observed in the SEM image.

Figure 6.16 shows the deep trapping lifetime and amplitude while heating at powers up to 20 mW (red) and cooling for powers down to 1 mW (blue). Above 15 mW, the deep trap lifetime also experiences a drastic slowing (increase) from 50 ps at 14 mW to almost 150 ps.
Figure 6.15: **(Left)** Shallow trap lifetime fits according to the fit of an electron kinetic model showing the permanent slowing of shallow trapping. **(Right)** Magnitude of the fitted exponential ($S$) associated with the shallow trapping of the electrons, related to the percent of the initial energy lost through this channel. No change in this channel is observed suggesting that the less frequent shallow trapping is attributed to the decreased conductivity of the surface oxide layer.

and then stabilising around 100 ps. When the power is decreased following the heating at 20 mW for 15 minutes, the deep trap lifetime remains at 100 ps. This slowing is also consistent with the lower conductivity of TiO$_2$ and, in turn, less frequent electron trapping events. This also demonstrates the permanent material change as the properties are maintained even in the absence of the high powers. However, unlike the shallow trapping process, the percentage of the initial energy lost in this process (quantified by the amplitude of the exponential) increases by nearly a factor of two after laser annealing. This is the source of the seemingly faster decay observed in the pump probe measurements (Figure 6.12). Although the trapping process are occurring less frequently (lower rate), the amount of electrons lost per unit time is higher, limiting the number of electrons accessible for use in applications. This change in behaviour is indicative of a change to the lattice structure as hypothesised in previous sections.

### 6.5.3 Influence on electron harvesting abilities

For plasmon-enhanced photocatalytic reactions, only the high energy electrons initially collected are capable of initiating chemical reactions. We cannot calculate this, so instead we consider the harvested free carrier density, calculated from the maximum measured differential reflectivity value and theory defined in Section 5.3. The calculated carrier concentration of i-
6.6. Acousto-Optical Oscillations of TiON Strips

Figure 6.16: (Left) Deep trap lifetime fits to the electron kinetic model showing the permanent slowing of deep trapping. (Right) Magnitude of the fitted exponential (D) associated with the deep trapping of the electrons indicating the percent of the energy lost through to deep traps.

jected carriers is a proportional estimate of carrier that could contribute to a chemical reaction. Figure 6.17 shows the calculated harvested carrier density in response to a 5 mW, 850 nm pump pulse for the TiON film (Section 5.6), non-resonant (parallel pump) strip excitation, as well as resonant (perpendicular pump) strip excitation of both the as-deposited and annealed material. Both the film and non-resonant excitation have comparably small absorption as excitation only occurs through the intraband transitions in titanium oxynitride. The ability to excite the plasmonic TiON structure dramatically increases photocatalytic ability, especially in the annealed material, which reaches a harvested carrier concentration of over $5 \times 10^{20} \text{ m}^{-3}$. Although advantageous for photocatalysis, the as-deposited material might be advantageous for applications requiring electron conduction toward a contact such as in sub-bandgap photodetection or photovoltaics.

6.6 Acousto-Optical Oscillations of TiON Strips

A material’s temperature is a macroscopic quantity that estimates the energy stored in the electrons and phonons of a crystal lattice. An increase in energy is reflected in more vibrations of lattice ions, which propagate through the lattice as waves called phonons. A well-known physical property of materials is the thermal expansion due to heating. That is, an increase in lattice temperature results in atoms moving apart leading to a net expansion of the unit cell.
Figure 6.17: Estimates of the electron harvesting efficiency of a titanium nitride film and the titanium nitride strips measured at a pump power of 2 mW. Shown are the maximum harvested carrier concentration (red). As expected, the non-resonant excitation of the strips is similar to what is observed for the titanium nitride film. The role plasmon-enhanced electron harvesting is clear reaching well-over an order of magnitude higher concentrations in the annealed sample.

and thus a measurable volumetric change of the material. As plasmon resonances are extremely sensitive to the lateral extent of the particle, these changes in size can have notable influence on the absorption, which in turn may alter the temperature potentially causing a subsequent decrease in lattice size. As the lattice size decreases, absorption increases and the process repeats. On time-resolved measurements this behaviour results in observable oscillations in the signal [205].

6.6.1 Temperature-dependence of plasmon resonances

The volumetric thermal expansion of titanium nitride is $9.35 \times 10^{-6} K^{-1}$, which suggests a temperature change of 200 K can result in a lateral expansion of almost 12%, which would have a dramatic influence on a nanometer-scale particle. Using a SuperK Compact supercontinuum laser, the temperature dependence of the plasmon resonance is examined in the 200 nm wide TiN strips by varying the repetition rate of the laser between 1 kHz and 8 kHz. With a higher repetition rate, pulses arrive at the sample more frequently allowing less cooling between pulses and a higher average temperature. Shown in Figure 6.18 are the extinction factors of both
6.6. Acousto-Optical Oscillations of TiON Strips

Figure 6.18: Measured extinction of a TiON strip pumped on (left) and off (right) resonance at increasing laser repetition rates to measure at different temperatures. The plasmon resonance shows a distinct temperature-dependence whereas parallel excitation shows little to no variation with temperature.

perpendicular and parallel polarisation using the dispersion of the transmitted supercontinuum pulse on a CCD camera. For resonant (perpendicular) excitation there is a clear dependence on repetition rate with an broadening and red-shift occurring at higher repetition rates. If looking at one wavelength, say with a fixed-wavelength probe pulse, temperature fluctuations can lead to a several-percent change in absorption. Shown as well is the extinction measurements for non-resonant (parallel) excitation showing no clear trend with temperature.

6.6.2 Oscillation modes and frequency extraction

To extract quantitative parameters to provide insight into the oscillation behaviour of the strips, an extension of the trap-mediated recombination model is required. Shown in Figure 6.19 is an exemplary pump probe measurement of an annealed strip excited with a 5 mW perpendicular-polarised 850 nm pump pulse. Imposed over the experimental data is the fitted curve with the standard trap-mediated recombination model. It does not fit the observed response, however, when looking at the residue of the fit (Figure 6.19), only the oscillatory component remains. To extract an oscillation frequency, a decaying sinusoidal function is used to fit the residue. The equation used is as follows:

\[ y = y_0 + A \sin\left(\frac{\pi(t - x_0)}{w}\right) \exp\left(-\frac{t}{t_0}\right) \]  

(6.1)
where $y_0$ is an arbitrary vertical shift to account for small errors in the initial fitting, $A$ is the amplitude, $x_0$ is the phase shift of the sine function, and $t_0$ is the decay rate of the signal. The $w$ parameter quantifies the period of the sine function (the acoustic oscillations) and can be directly converted to a frequency by taking the reciprocal of the period. In this exemplary measurement, the estimated frequency is $4.73 \pm 0.06$ GHz, which is much lower than what has been reported for gold [132]. This frequency coincides with a standard WiFi band [206] suggesting there are commercially available detectors for easy photoacoustic imaging using titanium nitride particles [207].

![Figure 6.19: (Left) An exemplary pump probe measurement of a titanium oxynitride strip along with the corresponding fit to the trap-assisted recombination model. The acoustic oscillations are clearly visible and not accounted for in the model. (Right) The residue of the previous fit isolates the resonance and can be fit to a decaying sinusoidal function to estimate its frequency.](image)

6.6.3 Wavelength Dependence

To probe the dependence of the nanoscale temperature on the excitation conditions, in particular the excitation of the plasmon resonance, the pump-wavelength dependence can be analysed. In a bulk material, higher energy photons (lower wavelength) excite higher energy electronic transitions. The resulting phonons will have a correspondingly higher temperature due to this energy being dissipated through electron-electron and electron-photon scattering events. However, in nanostructures, the additional absorption brought about by the excitation of a plasmonic mode can also bring about a rise in temperature. The increased number of electrons excited also increases the net energy transferred to the system and once dissipated, results in a higher lattice temperature. This phenomenon is exploited in so-called thermoplasmonic ap-
6.7 Summary

The work presented in this chapter employed ultrafast optical measurements of titanium oxynitride nanostructures to delineate two factors for plasmon-enhanced electron harvesting. Beyond the plasmon-enhanced absorption generating a larger number of carriers within the titanium oxynitride, it was shown that the presence of the surface oxide layer damps the plasmon resonance increasing the non-radiative decay. When this is combined with the presence of interfacial electron states, the synergistic enhancement of chemical interface damping emerges. This resulted in a nearly four-fold enhancement in the generated carriers, well beyond what was expected from the enhanced absorption alone.

This effect likely gives rise to the enhanced catalytic abilities of titanium nitride and titanium oxynitride observed in literature. As such, titanium oxynitride will continue to play
a vital role in plasmonic hot electron applications. As such applications still generate large amounts of heat, the temperature-stability was also analysed to examine the practical implementation of the material into devices. Although heating was shown to change the properties of the material at moderate laser powers, it was also shown to enhance the generated free-carrier density during the first few picoseconds following excitation. This has the potential to even enhance the catalytic ability of the structure of TiON based device, post-fabrication, potentially independent of the initial quality/purity of TiON.
Chapter 7

Conclusion

The work in this thesis provides a holistic investigation of a complex material system to provide guidelines for the design of practical plasmonic devices. The material is first systematically characterised to discover the fundamental strengths and limitations. The understanding of this is imperative for the development of use cases where plasmonics can be best integrated. This step is often neglected in experimental work where the goal is incremental improvements on existing technology. Using straightforward physical models derived from fundamental physics, the optical measurements in this work were used to consolidate the structural, optical, electronic and thermal properties of several materials. Although titanium oxyntiride was the focus of this work, supporting experiments on other materials demonstrated that parts of this approach can be generalised. By unifying tools from theoretical physics, experimental physics, materials science, and engineering it was possible to provide physical insight into both microscopic and macroscopic properties critical for overall efficiency. Reaping the benefits of these novel materials is not as straightforward as substituting one material for another, they must be evaluated objectively for their potential benefits.

7.1 Key Contributions

7.1.1 Deposition-Controlled Optical Properties of TiON

It is widely known that the properties of TiN and TiON are sensitive to deposition conditions including temperature, nitrogen concentrations and substrate material. However, the few op-
tical studies that have been done on these systems use a homogeneous model, discounting the surface oxide layer. As ellipsometry and other reflection-based measurements probe the surface properties, the oxide layer should not be ignored. By optimising a multi-layer Drude-Lorentz ellipsometry, it was possible to isolate the effects of various deposition parameters on the optical properties of titanium oxynitride alone. The parameters investigated included the deposition temperature, relative nitrogen concentration, and residual oxygen removal using a titanium pre-sputtering processes. Although the deposited films always contained some degree of oxygen throughout the lattice, a highly metallic film for use in plasmonic studies was produced. Through correlation with mass spectroscopy measurements, the crossover wavelength for pure titanium nitride was estimated ($\Re\{\epsilon\} = 0$ point, related to $\omega_p$) to be 352 nm. As this is much lower than any value reported for of titanium nitride to date, it suggests that TiN reported in literature is most likely TiON.

7.1.2 Differential Reflectivity Models

In order to analyse the differential reflectivity measurements of metal-semiconductor heterojunctions, it was imperative to analyse metals and semiconductors alone to be able to exclude the individual responses from the measured signal. To describe the ultrafast response of metals the two temperature model is extended to incorporate nonthermal (hot) electrons. A phenomenological solution was derived which minimised the number of free parameters thus increasing the reliability of fitting to data. For the analysis of free carriers in semiconductors, the differential reflectivity was related to the free carrier concentration in the conduction band via the Drude model. In the case of Schottky interfaces formed between a metal and semiconductor, it was straightforward to resolve the two individual responses and recombination is described by a single exponential decay process. In the TiON system, however, it was necessary to introduce a trap-mediated electron kinetic model to describe the observed behaviour. The unique thermal properties of TiON allow for nanosecond separation of electrons across the interface which also relax through trap-mediated processes. These models were also applied to other materials including transition metals and their semiconducting oxides to determine the electron dynamics of a wider range of materials using only optical measurements.
7.1.3 Engineering Electron Dynamics at Metal-Semiconductor Interfaces

Oxygen vacancies played an operative role in the electron dynamics of $TiON/TiO_2$. As oxygen vacancies form trap states immediately below the conduction band, it is more likely for electrons in the conduction band to interact with these rather than the deep traps resulting from interstitial titanium ion implantation. Four films with oxygen ratios from 10-40% were deposited to determine the effect on the harvesting efficiency relaxation dynamics. Increasing the oxygen during deposition appears to decrease oxygen vacancies at the surface of TiON, effectively reducing scattering centres. This also allows more electrons excited in TiON to reach the titanium dioxide surface layer. Furthermore, the decrease in trap states slows the decay of carriers as they are trapped less frequently. However, when oxygen exceeds a threshold, the TiON film is no longer metallic and the harvested electron density reduces due to the decrease in absorption of the underlying film. Finally, for low-defect interfaces formed with higher oxygen films (greater than 20%), a hot electron response is observed at the surface.

7.1.4 Physical Origins of Plasmon-Enhanced Electron Harvesting

Metallic nanoparticles are widely used for their enhanced interaction with incident electromagnetic fields. Historically, the enhanced absorption was seen as deleterious to devices that primarily focused on the far-field scattering or near-field confinement of light using plasmonic particles. However, there has been a surge in interest in harnessing the absorbed energy from the light before it is converted into heat in so-called hot electron applications. In order to utilise these electrons before they thermalise, they need to be harvested on ultrafast timescales. Considering this occurs naturally in TiON it was logical to use it as a platform to investigate plasmon-enhanced harvesting. Unlike a gold system, the encapsulating surface oxide layer damps the plasmon resonance increasing absorptive loss, which in this case is preferential. The concentration of damping at the surface provides a synergistic effect with interfacial states that facilitate direct decay of electrons into the conduction band of the titanium dioxide. This effect, termed chemical interface damping, is widely observed in adsorbed molecules enhancing photocatalytic abilities of absorbers.
7.1.5 Thermal Resilience of TiON Nanostructures

An initial promise of adopting TiN, and similarly TiON, over other metals was for use in high-power plasmonic applications such as second- and third-harmonic generation. The ionic-like bonds formed between Ti and N give the material its physical strength and high melting temperature. It was not clear, however, the degree to which substituted oxygen weakens the lattice. Additionally, as many of the observed behaviours arise from the titanium dioxide surface oxide layer (with a lower melting temperature), it was not clear how resilient TiON nanostructures are to laser-induced heating. Using variable-power pump-probe spectroscopy the electron dynamics were observed at increasing material temperature. The high-temperature exposure was shown to anneal the surface oxide layer (changing from amorphous to anatase $TiO_2$), which slowed the trapping of electrons in oxygen vacancies and permanently increased the harvested electron efficiency. This is attributed to the improved interfacial conditions formed after annealing.

7.2 Outlook

Due to its prevalence in existing literature, gold is the standard in plasmonic devices and serves as a benchmark for novel geometries or materials. Following the characterisation performed in this work, titanium oxynitride can now be strategically incorporated into a range of hot electron applications. In place of the rigorous physical characterisations performed here, the relationship between oxygen content and crossover wavelength can be used during optimisation of deposition conditions. With the electron transfer and trapping processes elucidated, it should be more straightforward for those continuing this work. As an example, the electron transfer process between the titanium dioxide and an adsorbed material is yet to be studied. With the significant amount of hot electrons reaching the surface of optimised films the electrons should be able to participate in reduction reactions. The presence of high-energy electrons should result in an observable difference compared to low-oxygen TiON samples with less hot electrons present. Furthermore, there should also be an observable photocatalytic enhancement when the surface oxide is annealed as was observed.

An exploratory measurement of the photocatalytic ability of TiON was performed by
collaborators Ludwig Huettenhofer and Yi Li at Lugwig Maximilian University of Munich. A TiON film (TiON 10%) and a sputtered TiO\textsubscript{2} sample were immersed in a 1 mol/litre solution of AgNO\textsubscript{3} in DI water where the presence of hot electrons at the surface will be able to reduce the AgNO\textsubscript{3} to silver atoms, which can scatter light in dark field illumination. The TiO\textsubscript{2} control sample was illuminated at 7 mW with a 785 nm CW laser for over 1 minute with no Ag deposition observed. However, on the TiON film, exposure for less than 20 seconds per point at 6 mW was sufficient to deposit Ag in the illuminated area. Figure 7.1 shows the writing of ICL on the TiON surface using the reduction of silver using the harvested electrons in TiO\textsubscript{2} surface. However, as this is not quantitative, a more thorough study is required to compare between TiON films.

![Figure 7.1: Before (Left) and after (right) CW laser exposure to a TiON thin film in a AgNO\textsubscript{3} solution. The laser excites electrons in the TiON, which transfers to the TiO\textsubscript{2} that remain sufficiently energetic to reduce the AgNO\textsubscript{3} and deposit silver on the film’s surface.](image)

The initial excitement of plasmonics brought with it many enthusiastic claims that could not be realised due to the intrinsic losses in metals. As many plasmonic systems could not compete with their photonic counterparts, many researchers disregarded plasmonics devices. Those who remained devoted, worked to mitigate the loss issues in plasmonics using creative device design, gain materials or looking at novel materials. However, if plasmonics is to play a role in the future, these “losses” must be embraced and applications built that harness that energy. Fundamentally, plasmonic particles are efficient light to electron energy (hot electron) or light to heat (photothermal) converters. Instead of having a device or application in mind and working to accomplish incremental improvements, it is more fruitful to investigate a material’s strengths and weaknesses and develop applications within these constraints. The methodology
and tools developed in this work can now serve as a starting point for those in the broader photonics community.
Appendix A

Mie Theory Formalism

By expanding the scattered ($\vec{E}_{\text{Sca}}(\vec{r})$), incident ($\vec{E}_{\text{Inc}}(\vec{r})$), and internal ($\vec{E}_{\text{In}}(\vec{r})$) fields using orthonormal vector spherical harmonic functions (VSH) ($\vec{M}_{nm}(k_M, \vec{r})$, $\vec{N}_{nm}(k_M, \vec{r})$). These functions relate to the multipole electric and magnetic fields of order $n$ (with $m < |n|$ and are functions of $r$, $\theta$, $\phi$. They are defined as:

$$\vec{M}_{nm}(k, \vec{r}) = \nabla \times \left[ \frac{1}{\sqrt{n(n+1)}} j_n(kr) Y_{nm}(\theta, \phi) \right] \quad (A.1)$$

$$\vec{N}_{nm}(k, \vec{r}) = \frac{1}{k} \vec{\nabla} \times \vec{M}_{nm}(k, \vec{r}) \quad (A.2)$$

where, $k = \sqrt{\epsilon \omega/c}$ are the permissible wave vectors, $j_n(kr)$ is n-th order spherical Bessel function and $Y_{nm}(\theta, \phi)$ is the standard spherical harmonic function defined by [208]:

$$Y_{nm}(\theta, \phi) = \sqrt{\frac{2n+1}{4\pi} \frac{(n-m)!}{(n+m)!}} P_n^m(\cos(\theta)) e^{im\phi} \quad (A.3)$$

in terms of the associated Legendre polynomial $P_n^m(\cos(\theta))$. The orthogonality of the VSH functions is critical in evaluating the coefficients used in subsequent calculations of field enhancements. They are summarised as follows [208]:

$$\int \int \vec{M}_{nm}(k, r, \theta, \phi) \cdot \vec{N}_{nm'}^*(k, r, \theta, \phi) d\theta d\phi = 0 \quad (A.4)$$

$$\int \int \vec{M}_{nm}(k, r, \theta, \phi) \cdot \vec{M}_{nm'}^*(k, r, \theta, \phi) d\theta d\phi = \delta_{n,n'} \delta_{m,m'} |j_n(kr)|^2 \quad (A.5)$$
\[ 
\int \int \hat{N}_{nm}(k, r, \theta, \phi) \cdot \hat{N}_{n'm'}^*(k, r, \theta, \phi) d\theta d\phi = \delta_{n,n'} \delta_{m,m'} [n(n + 1) |j_n(kr)|^2 + |j_n(kr) + krj'_n(kr)|^2]
\]

(A.6)

For an incident electric field magnitude of \( E_0 \) the expansions are as follows:

\[ 
\vec{E}_{\text{Sc}} = E_0 \sum_{n,m} \Gamma_n a_{nm} \vec{M}_{nm}(k_M, \vec{r}) + \Delta_n b_{nm} \vec{N}_{nm}(k_M, \vec{r})
\]

(A.7)

\[ 
\vec{E}_{\text{Inc}} = E_0 \sum_{n,m} a_{nm} \vec{M}_{nm}(k_M, \vec{r}) + b_{nm} \vec{N}_{nm}(k_M, \vec{r})
\]

(A.8)

\[ 
\vec{E}_{\text{Sc}} = E_0 \sum_{n,m} A_n a_{nm} \vec{M}_{nm}(k_I, \vec{r}) + B_n b_{nm} \vec{N}_{nm}(k_I, \vec{r})
\]

(A.9)

Here, \( k_M \) describes the wave vector inside the surrounding medium and \( k_I \) the wave vector inside the material. For a planar wave, at normal incidence, the above expansions can be simplified using the following expressions:

\[ 
\begin{aligned}
  a_{nm} &= b_{nm} = 0 \quad \forall |m| \neq 1 \\
  a_{n,1} &= a_{n,-1} = i^{n+1} \sqrt{\pi (2n + 1)} \\
  b_{n,-1} &= -b_{n,1}
\end{aligned}
\]

To simplify the remaining expansion factors further, it is convenient to define two parameters \( x = k_M a \) and \( N = n_I / n_M \). It is now possible to write the expressions as follows [208]:

\[ 
\Gamma_n = \frac{Nj_n(x)[xj_n(Nx)]' - j_n(Nx)[xj_n(x)]'}{j_n(Nx)[xh_n^{(1)}(x)]' - Nh_n^{(1)}(x)[xj_n(Nx)]'}
\]

(A.10)

\[ 
\Delta_n = \frac{j_n(x)[xj_n(Nx)]' - Nj_n(nx)[xj_n(x)]'}{Nj_n(Nx)[xh_n^{(1)}(x) - h_n^{(1)}(x)[xj_n(Nx)]'}
\]

(A.11)

\[ 
A_n = \frac{j_n(x)[xh_n^{(1)}(x) - h_n^{(1)}(x)[xj_n(x)]'}{j_n(Nx)[xh_n^{(1)}(x) - h_n^{(1)}(x)[xj_n(Nx)]'}
\]

(A.12)

\[ 
B_n = \frac{j_n(x)[xh_n^{(1)}(x) - h_n^{(1)}(x)[xj_n(x)]'}{Nj_n(Nx)[xh_n^{(1)}(x) - h_n^{(1)}(x)[xj_n(Nx)]'}
\]

(A.13)

As shown in Section 2.2.3, the normalised cross-section \( (Q_i) \) used to quantify plasmonic performance is the ratio of either scattered, absorbed or extinguished power to the incident power. Using the orthonormality between the vector spherical harmonics and the intensity \( I = |E|^2 \) can be calculated, which is identical to the normalised cross-section. This gives explicit expressions
for the desired cross-sections in terms of the analytical forms of the expansion coefficients:

\[ Q_{\text{Sca}} = \frac{2}{\lambda^2} \sum_{n=1}^{\infty} (2n + 1)(|\Gamma_n|^2 + |\Delta_n|^2) \]  
(A.14)

\[ Q_{\text{Ext}} = -\frac{2}{\lambda^2} \sum_{n=1}^{\infty} (2n + 1)(\text{Re}\{\Gamma_n\} + \text{Re}\{\Delta_n\}) \]  
(A.15)

\[ Q_{\text{Abs}} = Q_{\text{Ext}} - Q_{\text{Sca}} \]  
(A.16)

This is the key result of Mie theory, and allows for the evaluation of materials for use in plasmonic applications as presented in subsequent appendices.
Appendix B

Plasmonic Material Characterisation

To measure the optical response of the thin films in the visible and near-infrared regions (300-1600 nm), a variable-angle spectroscopic ellipsometer was used. This is performed using the Drude-Lorentz modelling and fitting process as laid out in Section 3.2.4. Figure B.2 shows the fitted permittivites of all materials considered in this work separated into real and imaginary contributions which characterise the induced polarisation (conduction) and absorption (loss), respectively. Upon inspection it is clear that, among the materials investigated, there is high variability between the degree of losses (characterised by the magnitude of the imaginary part of the permittivity) and the regions where metallic behaviour onset occurs (characterised by the point where the real part of the permittivity changes from positive to negative).

As a result of the variability, it is not straightforward to understand how to efficiently implement these materials in specific applications. The fitting parameters are shown in Figure B.1 which organises the relevant fitted and measured parameters of the films for a direct comparison. The operation range of a plasmonic device in air is determined roughly by the point at which is satisfies the Fröhlich condition \((Re\{\epsilon\} = -2)\), explained in detail in the subsequent section. The library of materials allows for operation from the ultraviolet (Al, Cu, Pd, Rh, Ni) through the visible (Ag, Au, NbN, TiN, CuxOy) and into the infrared (Mo, W, Ti, TiON, SMO, SNO, SRO). The Drude loss term (in femtoseconds) is also shown, which describes the mean time between electron collisions due to electron-electron and electron-phonon scattering, as well as with impurities and defects as defined by Matthiessens Rule. [17] The fitted background permittivity \((\epsilon_\infty)\) and interband transition properties are also presented, which are relevant to the design of experimental procedures including hot-carrier generation and local heating.
Figure B.1: Included are the wavelengths for the epsilon-near-zero (ENZ) point and Frohlich condition ($\text{Re}\{\epsilon\} = -2$) relevant for several plasmonic applications. For the noble metals, Ni, and Cu$_2$O they these occur at wavelengths beyond the range of our ellipsometer ($\leq 300$ nm). Also provided are the Drude loss term (in fs), the background permittivity ($\epsilon_{\infty}$), oxide layer thickness and the interband transition center energy and width.

<table>
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<tr>
<th></th>
<th>ENZ (nm)</th>
<th>$\lambda_{\text{Re}{\epsilon} = -2}$ (nm)</th>
<th>Drude Loss (fs)</th>
<th>$\epsilon_{\infty}$</th>
<th>Oxide Layer (nm)</th>
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<th>Interband 2</th>
<th>Interband 3</th>
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<td></td>
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<td></td>
<td></td>
<td>Energy (eV)</td>
<td>Width (eV)</td>
<td>Energy (eV)</td>
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Figure B.2: Spectroscopic ellipsometry measurements of thin films, divided into real (left-hand plots) and imaginary (right-hand plots) parts of the permittivity divided into the material classes: (a-b) noble metals, (c-d) refractory metals, (e-f) transition metal nitrides, (g-h) conductive metal oxides.
Appendix C

Figures of Merit

C.1 Plasmon-Enhanced Hot Electron Devices

A significant amount of energy is transferred from incident light to a nanoparticles electrons upon LSPR excitation due to the resonant coupling as outlined in Section 2.2.3. The coherent oscillation of electron density has a corresponding energy distribution of electrons associated with their proximity to the lattice ion. [221] Higher energy electrons have a lower oscillation frequency than lower energy electrons, which then gradually grow out of phase in a process known as Landau damping. As the LSPR decays within a few femtoseconds, [222] the energy can be lost into two distinct pathways: radiative decay (emission of a photon) or nonradiative decay (generation of an electron-hole pair through interband or intraband electron transition) [51]. Although the nonradiative pathway can be deleterious to device performance due to the eventual rise in lattice temperature, a wealth of hot carrier devices have used the energy stored in the plasmon-excited electrons before they thermalize with the lattice.[223, 224]. Such devices circumvent the typical loss problems characteristic to plasmonic devices and give a larger window to harness the energy extracted from light. Such devices include photodetectors and photovoltaic devices that operate below the bandgap of the involved semiconductor as well as photocatalytic applications.
Appendix C. Figures of Merit

<table>
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<th>Heat Capacity $(MJm^{-3}K^{-1})$</th>
<th>Work Function $(eV)$</th>
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<td>4.3-4.6 [210]</td>
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<tr>
<td>Au</td>
<td>2.5 [209]</td>
<td>5.4 [210]</td>
</tr>
<tr>
<td>Cu</td>
<td>3.5 [209]</td>
<td>4.4 [211]</td>
</tr>
<tr>
<td>Pd</td>
<td>2.9 [209]</td>
<td>5.1 [212]</td>
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<tr>
<td>Rh</td>
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<td>5.0 [212]</td>
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Table C.1: Literature values of the volumetric heat capacity and electronic work function for the materials considered in this analysis (where available).

C.1.1 Sub-Bandgap Photodetection

A plasmonic-enhanced hot electron photodetector is developed operating at 1550 nm comprised of a spherical metal particle embedded in n-Si. As such, a metal is needed that forms a Schottky barrier with Si with height that is lower than the energy of the exciting photons (0.8 eV). With the electron affinity of Si $\chi_{Si}$ being treated as a fixed quantity (4.05 eV), it is the metal work function $\phi_M$ that determines the barrier height through $\phi_B = \phi_M - \chi_{Si}$. [73] If the barrier must be greater than 0 (to form a Schottky barrier) and below 0.8 eV this imposes the restriction $4.05eV \leq \phi_M \leq 4.85eV$. In addition to the electron Schottky barrier formed with n-Si, it is also possible to harvest energetic holes using a Schottky barrier formed with the valence band of p-Si (Figure C.1b). In some materials, such as gold, interband transitions result in higher energy holes than electrons based on the band and these holes can be harvested at a Schottky barrier. [225] The Schottky barrier in this case is defined as $\phi_B^h = E_g + \chi_{Si} - \phi_M$ [73] Using the bandgap of Si (1.1 eV), the metal work function is then restricted within the range $4.35eV < \phi_M^h < 5.15eV$ to form the required Schottky barrier. Figure C.1c shows the range of work function values in literature for each of the materials used in this study with shading corresponding to the whether it forms an n-type (red), p-type (blue), or either p- or n-type...
Knowing the compatible materials, it is now required to quantify a figure of merit for the corresponding operation of the embedded sphere in the Si. For this, both the generation of energetic carriers as well as efficient harvesting across the metal-semiconductor interface must be optimised. Through Mie theory, the electron excitation is quantified by the absorbed power via the absorption efficiency \( Q_{Abs} \). The collection efficiency at an energy \( E \) above the fermi level (here assumed to be 0.8 eV corresponding to 1550 nm) can be estimated using the modified Fowler yield, [226] where \( E_F \) is the Fermi energy of the material.

\[
Y_F(E) = \frac{(E - \phi_B)^2}{8E_FE}
\]

This quantifies the injection probability taking into account the relative energy between the electron, the barrier, and the electronic properties of the material through \( E_F \). To quantify the entire process the overall photodetection efficiency at 1550 nm \( \eta_{PD} = Q_{Abs}Y_F \) must be accounted for. This is shown in Figures C.1e and C.1f for n-type and p-type Schottky contact, respectively. When comparing the total figure of merit and the absorption cross-section at 1550 nm, shown in Figure C.1d, it is apparent that it is imperative to include the Fowler factor. As the extraction probability scales with the square of the difference between the electron energy and Schottky barrier height, the work function of the material is the most critical factor in determining the overall efficiency. This is exemplified with SRO in that, even with the large absorption cross-section, its large barrier limits its effectiveness particularly in the n-type configuration. Through efficient infrared absorption and low Schottky barriers, Mo, Ti, TiN and TiON can each form a low barrier with n-Si \( (\phi_B^n \approx 0.5\text{eV}) \) for photodetection at 1550 nm. Although the work function of Ti, TiN and TiON can vary over a wide range, the ability to tune this value has been demonstrated for use in field effect transistors (FETs). [200] For hole based photodetection at this telecom wavelength, Pd has the highest figure of merit, again due to the low Schottky barrier formed \( (\phi_B^p \approx 0.1\text{eV}) \). We also note the use of bimetallic material stacks such as Ti/Au, [110] in literature. Although not included in this study for simplicity, one can easily extend our model to account for these condition.
Figure C.1: Schematic of (a) n- and (b) p-type Schottky barriers formed between a metal with Fermi level $E_F^M$ and a semiconductor with bandgap energy $E_g$ and Fermi level $E_F^S$. When the two Fermi levels are equated, a barrier forms due to the interfacial charge layer for either electrons $\phi_B^e$ or holes $\phi_B^h$. (c) Reported work functions of the respective materials. Blue (red) shaded region shows range of possible work functions that form a hole (electron) Schottky barrier with silicon with barrier heights less than 0.8 eV (1550 nm). (d) Optimised absorption cross-sections at 1550 nm and their corresponding barrier formation with Si: blue (p-type), red (n-type), purple (either p- or n-type) and grey (neither/unknown). The final optimised figure of merit taking into consideration both absorption and injection probability for (e) n-type and (f) p-type Schottky contact.
C.1.2 Plasmon-Enhanced Solar Energy Conversion

The world is at a critical point in time where our dependence on fossil fuels must be reduced in favour of clean, renewable sources of energy to combat the effects of climate change and global warming. The strong interaction of the free electrons in metals with visible and ultraviolet light make plasmonics an ideal platform for this endeavour. The spectral irradiance of sunlight at sea level is shown in Figure C.2a. An ideal metal would have broadband absorption across this range with a plasmon resonance peak in the range of 500-700 nm. Three exemplary absorption cross sections are shown in Figure C.2a for Ag (red), Au (blue) and TiN (green) spheres in air with radii of 80 nm. The broadband absorption of TiN allows infrared light to be harvested in addition to the efficient visible absorption offering direct advantages over gold at this particular size, which has been demonstrated experimentally. [15] As it is critical to understand the interaction with sunlight to best implement a material, each figure of merit will be weighted by the sun's spectral irradiance denoted by $E(\lambda)$.

A previous review of refractory conductive plasmonics [132] considered this problem and introduced a figure of merit of an integrated absorption cross section $IQ_{Abs}$ defined as:

$$IQ_{Abs} = \int_{300\text{nm}}^{1300\text{nm}} [Q_{Abs}(\lambda)E(\lambda)d\lambda]$$

where $Q_{Abs}(\lambda)$ is the absorption cross section at a particular radius as a function of wavelength. As this characterises the efficiency of collecting energy in the form of energetic electrons, it is important to understand how this energy is then utilised for energetic applications. In this work two methods are examined: storing energetic electrons in chemical bonds, for instance to catalyse $H_2O$ resulting in $H_2$ fuel, and using plasmonic particles to enhance the absorption of photovoltaic cells. Use of this figure of merit does not account for variations in carrier mobility and electron-phonon scattering times, which can limit the number of electrons reaching the operative surface. However, as absorption is assumed to be related to the internal field generated by the surface plasmon mode, electrons are excited throughout the volume of the nanoparticle with the highest generation occurring at the nanoparticle surface. As such, this can still act as a useful comparison of materials for such applications as a larger $IQ_{Abs}$ will result in more carriers excited at the interface, but may underestimate the efficiency of high mobility materials.
In water splitting applications, energy from sunlight is converted into chemical energy. Both plasmon-excited electrons and holes participate in the photocatalytic reaction of converting $H_2O$ to $O_2$ and $H_2$ gases, the latter of which can be used as a fuel. During the reaction, photo-excited holes are responsible for the generation of the $O_2$ gas whereas the electrons participate in the generation of $H_2$. The reaction proceeds as follows [196, 163, 161]:

\begin{align}
H_2 + 2h^+ &\rightarrow 2H^+ + \frac{1}{2}O_2 \\
2H^+ + 2e^- &\rightarrow H_2
\end{align}

Through the use of co-catalysts, this reaction can occur spontaneously and has led to the development of autonomous photosynthetic devices.[73] Again, this relies on efficient generation of electrons within the plasmonic component using visible light and we look to the $IQ_{Abs}$ to quantify this. Figure C.2b shows the optimized values for spherical nanoparticles submerged in water where $IQ_{Abs}$ is maximized by varying the particle size. Not surprisingly, the noble metals are out performed by all other material groups as their high carrier concentrations and correspondingly high plasma frequencies make it difficult to absorb infrared light without more complex geometries. [227, 228] We observe that the partially oxidized $Cu_xO_y$ has the highest integrated absorption efficiency in water as a result of its broader resonance (increased Drude loss term) and red-shifted crossover wavelength compared to pure copper due to incorporation of oxygen and decrease in the free carrier concentration. A similar behaviour is also observed between TiN and TiON. Although, this was framed in the context of solar water splitting, it can be extended to catalysis of environmental pollutants such as $CO_2$ by changing the surrounding refractive index to air ($n=1$).

In silicon-based photovoltaic cells, the inefficient absorption of the indirect bandgap requires thick layers (hundreds of microns [229]) to achieve competitive conversion efficiencies which remain the largest cost in solar cell production. The inclusion of plasmonic particles can compensate for the weak infrared absorption and has the potential to make a considerable impact in the development of thin film photovoltaic cells. [230, 231] The broad absorption of plasmonic particles can be used to harness energy from photons with insufficient energy to excite electrons across the semiconductor bandgap[232, 160, 233] or to scatter light into the
For sub-bandgap absorption and collection using hot carriers, we use the integrated collection efficiency:

\[ \text{ICE} = \int_{300\text{nm}}^{1300\text{nm}} Q_{\text{Abs}}(\lambda)E(\lambda)Y_F(\lambda)d\lambda \]  

(C.5)

Figure C.2c shows ICE for the materials forming a Schottky barrier with n-type Silicon embedded in the semiconductor. Embedded particles provide the maximum collection area as transfer can occur at any surface leading to improved collection efficiencies. [13] The high refractive index of silicon dramatically changes the resonance behaviour of the sphere. The Fröhlich condition, for example, is now at the wavelength where \( \varepsilon \approx -7 \) rendering most of the oxides (SMO, SNO, SRO), W, and Ti inoperative due to their low magnitude of the real part of the permittivity. However, this new condition is advantageous for the noble metals as this redshifts the resonance giving a higher overall absorption, which gives Ag the highest figure of merit.

To examine the suitability of materials for light trapping via scattering, we must consider the relative amount of light scattered to absorbed and define our scattering efficiency as:

\[ \Delta P = \int_{300\text{nm}}^{1300\text{nm}} ((\sigma_{Sca}(\lambda) - \sigma_{\text{Abs}}(\lambda))E(\lambda)d\lambda \]  

(C.6)

Defining \( \sigma_{Sca} \) and \( \sigma_{\text{Abs}} \) for a spherical particle embedded in silicon and vary the particle radius between 10 nm and 200 nm to find the highest \( \Delta P \). The optimized size for each material is the maximum of the range (R=200 nm) as the scattering cross section scales with the size of the particle and the absorption cross section is much smaller at larger particle sizes. Nevertheless, the absolute value of P does vary between materials by over an order of magnitude. We observe the conventional noble metals (Cu, Au, Al, and Ag) outperforming all other materials due to their weak absorption across the solar spectrum for particles this large.
Figure C.2: (a) Absorption cross sections of R=80 nm particles of Ag (red), Au (blue) and TiN (green) plotted on top of the solar spectrum (grey) demonstrating the advantage of broadband absorption in the visible and near-infrared. (b) Optimized integrated absorption efficiency of particles in water for solar photocatalysis applications. (c) Optimized integrated collection efficiencies (ICE) of particles embedded for silicon for sub-bandgap excitation with sunlight and collection into the conduction band of silicon. (d) Integrated power differential in silicon for R=200 nm particles embedded in silicon for in-plane scattering to enhance semiconductor absorption efficiencies.
C.2 Photothermal Applications

Conventionally, the heat generated from the nonradiative relaxation of surface plasmon modes is believed to be deleterious to device performance. The elevated temperatures can deform the metallic particles, dramatically altering their performance [238] and heat the surrounding materials causing faster device degradation. [26] This has required materials with higher thermal stability, termed refractory metals, which includes metal nitrides and metals known to resist high temperatures such as Mo and W. However, recently there has been significant interest in harnessing the unavoidable heating of plasmonic structures for productive purposes. The ability to generate heat in the immediate vicinity of the metal particle has allowed for heating with nanoscale precision. This ability to selectively heat desired areas is of paramount importance to control chemical reactions [239] and the response of biological systems [240]. Here the use of heated plasmonic particles is investigated for use in nanotherapeutics such as cancer therapy [241, 242] and in vivo bacterial annihilation. [27] The use of plasmonic particles in integrated in vitro studies for compact lab-on-a-chip applications is also addressed. [243]

C.2.1 Photothermal Cancer Therapy

To maintain optimal functioning, homeostatic mechanisms have evolved in many organisms to maintain ideal conditions for cell function which includes controlling temperature, pH, and osmotic concentrations. Without these in place, cells within the organism can fail to perform their functions [244] or degrade altogether due to increased fluidity of the cell membrane. [245] The temperature sensitivity of cells is exploited in photothermal nanotherapeutics where nanoparticles selectively bind to the membrane of a targeted cell-type [246] and are then heated using pulsed or continuous wave (CW) laser illumination. The heat generated in the vicinity of the nanoparticle has the potential to degrade the cell membrane resulting in the release of cellular contents in a process termed cell necrosis. [247, 248] It has also been shown that heat generated from these particles can activate natural apoptosis pathways also resulting in cell death. [249] The targeted heating of noble metal nanoparticles has already been successfully used in the elimination of bacteria, [27] targeted drug delivery, [250] and destruction of tumor cells in mammals [241, 247, 249]. The selectivity provides a significant advantage over conventional
systemic cancer treatments such as radiation and chemotherapy as neighboring tissue remains unharmed.

For such in-vivo applications, laser excitation must be within the biological transparency window (800-1000 nm) where tissue is maximally transmissive. This coincides with absorption minima of water, hemoglobin (Hb) and oxygen-bonded hemoglobin (HbO$_2$) which make up the bulk of tissue. However, even in this regime the penetration depth of the infrared light is only several centimeters.[251] As such, the ideal material for such applications is one that is non-toxic to humans and animal life that heats efficiently in the infrared. This requires a close examination of both plasmonic and thermal properties to characterize the associated temperature change. Thus far, gold particles have dominated the field as gold is known to be inert and non-toxic. To improve absorption in the near-infrared, more complex geometries are required such as nanoshells and nanocages. [252, 253] This can potentially be avoided by looking to non-toxic materials with preferential absorption properties including titanium nitride and titanium oxynitride. [254]

Previous work has looked at quantifying a particles ability to generate heat for photothermal applications [255] and compared between noble metals and transition metal nitrides. However, the ability to generate heat does not directly quantify its applicability to photothermal applications as the relationship between thermal energy and temperature is determined by material-dependent thermal properties. For this reason, the temperature change corresponding to the energy absorbed by the plasmonic mode is estimated for both continuous wave (CW) and pulsed excitation. Under CW illumination, a spherical particle of radius $a \leq 200$ nm will reach a steady-state on the order of nanoseconds [256] $\tau_{tr} = a^2 C_V / 3 \chi_S$ where $C_V$ is the volumetric heat capacity of the particle and $\chi_S$ the thermal conductivity of the surrounding media [257]). Given an absorbed power $P_{Abs}$ by a particle of radius $a$, the steady state temperature of the particle is only determined by the surrounding medias thermal conductivity ($\chi_S$) by the following expression: [258, 257]

$$\Delta T_{CW} = \frac{P_{Abs}}{4\pi\chi_S a^4}$$ (C.7)

The power absorbed is quantified by the absorption cross-section ($\sigma_{Abs}$), which gives $P_{Abs} = \sigma_{Abs} S_0$ where again $S_0$ is the incident irradiance in $W \cdot m^{-2}$. In Figure C.3a, the steady state temperature change ($\Delta T$) is calculated under 830 nm CW illumination for an incident
irradiance of 1 mW/m$^2$ of a particle submerged in water. In addition, the plot is colour-coded according to known toxicity to humans with nontoxic materials shown in green, toxic materials in red, and grey for unknown toxicity. TiON and Ti show the most promise for photothermal applications due to their low toxicity and efficient infrared absorption showing an order of magnitude larger temperature increase than gold. SMO, SNO, and SRO also show very high equilibrium temperature changes but would be best suited for in vitro biological applications due to the inclusion of strontium, which is known to be toxic to humans.

Under ultrafast pulsed illumination, the thermal properties of the absorbing material strongly influence the maximum change in temperature experienced by the nanoparticle. Due to the absorption throughout the nanoparticle volume and the high thermal conductivity due to the free electrons present, we assume that the heat energy generated inside the particle results in a uniform temperature distribution. For lifetimes shorter than the transient lifetime $\tau_{tr}$ mentioned above a large nonthermal electron distribution is generated, which thermalize with other electrons (tens of femtoseconds) and phonons (picoseconds), which then dissipate to the environment. This results in a sharp increase of the maximum temperature over CW illumination and is determined by the energy absorbed and the volumetric heat capacity of the material ($C_V$) as [256]:

$$\Delta T_{\text{Pulse}} = \frac{\sigma_{\text{Abs}}}{V C_V}$$

where $F$ is the laser fluence and $V$ the particle volume. In Figure 6b, we show the calculated temperature change under pulsed illumination at 830 nm with a laser fluence of 2.5 mJ/cm$^2$ in water. The volumetric heat capacity values used are shown in Table C.1. There are currently no reported heat capacity values for NbN, SMO nor SRO and as a result these have been omitted from the calculation. Again, titanium is shown to be superior under these particular illumination conditions and with its low toxicity [259] has the potential to dramatically improve the efficiency over gold photothermal therapeutic treatments when considering only spherical colloids.
Figure C.3: Single particle temperature changes under (a) continuous wave (CW) [830 nm, 1 mW/µm²] and (b) pulsed illumination [2.5 mJ/cm²]. Colour indicates toxicity in humans: green (non-toxic), red (toxic) and grey (toxicity unknown). Lower images show the heating of a dimer system with 10 nm separation under (c) continuous wave (CW) [830 nm, mW/µm²] and (d) pulsed illumination [2.5 mJ/cm²].
C.2.2 Thermal Control of Biological Processes

Localized heating remains a common method of controlling the kinetics of chemical reactions by supplying the necessary activation energy. As many biological processes rely on chemical reactions and interactions, the ability to target and heat specific molecules is invaluable to understanding and controlling these complex processes. The strong photothermal conversion of plasmonic particles allows for nanoscale precision heating without influencing surrounding molecules. This specificity has allowed for the selective deletion of genes within a chromosome [260], phenotyping of cancerous cells [261], and protein manipulation.[262] By conjugating the surface of a plasmonic particle with DNA or RNA molecules, these photothermal processes can be reversible by allowing the molecules to naturally recombine with complementary strands.[243, 263] This can be extended to complex networks of gold-nucleic acid conjugates [261] allowing for larger-scale studies of single-cell properties. These applications take advantage of the enhanced absorption and electric field that occurs when the coupled resonance of two closely-spaced nanoparticles is excited, frequently called a plasmonic hot-spot.[264] The ability to control such processes is of particular interest to cancer probing techniques including DNA/RNA fluorescence in situ hybridization (FISH). [265]

The coupled resonance of two nanoparticles is a result of the Coulombic repulsion of the electrons of the respective particles acting as an additional driving force. The coupled mode is characterized by an increase in scattering and absorption as well as a red-shifting of the plasmon resonance described by the plasmon ruler equation.[266] This coupled interaction increases each of the particles interaction with incident light resulting in an increase in the effective polarizability of each particle caused by the presence of the other. We hope to use this increased absorption to control the heating of two coupled particles previously used in DNA melting and hybridization applications106. The influence of the coupling on the absorptive properties of the nanoparticles has been studied via this modified polarizability.[267] In this work, they quantify the enhanced power absorption of each particle through an expression depending on a ratio of particle diameter (D) and gap (g). Letting \( \eta = D/(D+g) \) the absorbed power enhancement is given by:

\[
\frac{P_{\text{Dimer}}}{P_{\text{Single}}} = \eta = \frac{16(\epsilon_r + 2\epsilon_s)^2 + \epsilon_s^2}{(\epsilon_r - \alpha^3\epsilon_r + [8 + \alpha^3]\epsilon_s)^2 + [4 - \alpha^3]^2 + \epsilon_s^2}
\]  

(C.9)
where $\epsilon_r$ and $\epsilon_i$ are the real and imaginary parts of the dielectric function, respectively. Through this we can now define a dimer enhanced absorption efficiency as $Q_{\text{Abs}}^2 = \eta Q_{\text{Abs}}^1$, where $Q_{\text{Abs}}^1$ is the absorption cross section of a single sphere. It is observed that $Cu_xO_y$ and TiN have the highest absorption enhancement in the presence of an adjacent particle almost over doubling its absorption cross section. However, when considering the resultant absorption cross-section, TiON outperforms TiN due to the proximity of the maximum absorption cross-section to the excitation wavelength.

For consistency, the maximum temperature difference of the dimer system is calculated in water under 830 nm illumination with both CW and pulsed illumination. Similarly to the previous section, using an exemplary CW excitation of 1 mW/m2 and calculate the steady state temperature of the system, shown in Figure C.3c. When accounting for the size of the particle, the most efficient materials at heating under these illumination conditions are $Cu_xO_y$ and TiON for their originally high absorption cross sections and efficient dimer coupling. However, when comparing Figures C.3a and C.3c the advantage of using a dimer system are apparent, with higher temperature changes under the same illumination conditions, requiring lower laser powers for the same effects and so potentially reducing interference with surrounding biological molecules. With pulsed illumination, again with an example fluence of 25 $J/cm^2$ a change in behaviour is observed compared to CW illumination as the thermal properties of the absorbing material are accounted for. Here, Ti has superior performance due to its strong infrared absorption and preferable thermal properties resulting in large temperature changes. Although CW illumination is typically used in biological measurements, pulsed excitation can be extremely useful in monitoring biological processes. This is due to the temporal width of the laser pulse being shorter than the typical timescales of many biological processes, so they can be measured without interference of the externally applied field.

C.3 Sensing and Near-Field Applications

A breadth of plasmonic applications relies on the interaction of the resonantly driven electrons and the particles environment via the generated dipole-like electric field. As outlined when discussing the LSPR resonance condition in Section 2.2.3, the spectral position of the resonance
peak depends on the contrast between the permittivity of the particle and its surroundings. Not only can this provide a means of tuning the plasmon resonance, but conversely, changes in the dielectric environment can be detected as changes to the plasmon resonance peak. This has led to sensors which can detect the presence of a target molecule ultra-low concentrations [268] that can easily be scaled for relatively low cost. [269] This principle has also been extended to enhance the functionality of solid state lighting which include light emitting diode (LED) and quantum dot (QD) televisions. By coupling a plasmonic antenna to a nearby emitter (LED, QD) the far field radiation can be enhanced over the efficiency of the emitter alone by emitting via plasmonic modes. [270] Such applications require both spatial proximity and spectral overlap, as well as a thorough understanding of the near-field properties of the particle.

C.3.1 Refractive Index Sensing

Metallic nanoparticles can be used to detect minute changes in the vicinity of the particle by exploiting the sensitivity of plasmon resonances to the properties of the surrounding dielectric media. This has proven invaluable in detecting biological molecules as conventional biological detection techniques (using labels [271] and mass spectroscopy [272]) can interfere with or completely destroy the target molecule.[273] LSPR biosensing was demonstrated to be an inexpensive, sensitive and high-throughput technique for the detection and observation of a wide range of membrane proteins [274] and protein interactions, [275] cancer cells,[276] and bacteria [277] even in ultralow concentrations down to 150 fg/mL. [268] By functionalizing the surface of the nanoparticle with specific antibodies, the target cell or molecule can be adsorbed to the surface. As this molecule has a different refractive index to the surrounding solution (n) the particles plasmon resonance peak shifts by \( \Delta \lambda = m(\Delta n)[1 - \exp(-2d/l_d)] \) [278] where \( m \) is the refractive index sensitivity, \( d \) is the distance of the analyte molecule from the surface and \( l_d \) is the decay length of the electromagnetic field. The refractive index sensitivity is dependent on the material being used as the resonance profile depends on the refractive index contrast between the material and its surroundings.

As detection relies on observing a shift in the plasmon resonance, the extinction profile of the colloidal particles and the ability to monitor these changes in the far-field must be considered. To determine the change in resonance wavelength with refractive index the ex-
Appendix C. Figures of Merit

The extinction cross section is calculated using our Mie theory calculations with refractive indices at \( n=1.33 \) and \( n=1.4 \) as an example. Although the change in refractive index is proportional to the change in resonance wavelength, the ability to resolve small changes relies on the sharpness of the far-field extinction profile. To quantify this, the full-width half-maximum (FWHM) of the resonance is calculated in water (\( n=1.33 \)). The following figure of merit is used to evaluate our materials: [279]

\[
F_\omega = \frac{\Delta \omega}{FWHM_\omega} \tag{C.10}
\]

This ratio is unitless and balances both requirements of a large spectral shift while maintaining a narrow bandwidth for better resolution. Figure C.4a shows the refractive index sensitivity in frequency units (\( F_\omega \)) with silver outperforming all other materials due to its small FWHM as a result of its low Drude loss compared to other materials.

C.3.2 Solid State Lighting

Light-emitting diodes (LEDs) have provided tremendous improvements over traditional incandescent light bulbs in terms of efficiency (lumens per watt), lifetime, cost, and color range. By electrically exciting electrons across a semiconductor bandgap, the subsequent recombination process results in emission of photon with energy equal to the bandgap of the semiconductor. RGB (red-green-blue) LED displays have been developed by choosing semiconductors with appropriate bandgaps where combinations of the three colors can generate the entire visible spectrum. Quantum dots (QDs), semiconductor nanocrystals, have also been used successfully in displays that take advantage of the fine tunability of emission properties with particle size. [280] The overall efficiency of such semiconductor-based systems is determined by three factors: excitation efficiency (\( \eta_{exc} \)), radiation efficiency (\( \eta_{rad} \)), and light extraction efficiency from the device (\( \eta_{ext} \)) [281] \( \eta_{exc} \) and \( \eta_{rad} \) are intrinsic properties of the system corresponding to the generation of excited carriers and the internal quantum efficiency (IQE) respectively. However, the light extraction efficiency into free space (\( \eta_{ext} \)) can be increased through device engineering to prevent subsequent total internal reflection or absorption. The overall emission efficiency can be enhanced further by coupling the semiconductor emitter to metallic antennas for more efficient radiation into the far field from the coupled system. [282]
Figure C.4: (a) Refractive index sensitivity calculated in terms of frequency for optimized particle size. The optimized antenna-enhanced far-field radiation enhancement factor are calculated for (b) blue (470 nm) (c) green (470 nm) and (d) red (660 nm) dipole emitters placed 10 nm from the surface of particle oriented perpendicular to the electric dipole mode of the antenna.
By bringing an antenna into close proximity with the emitter, the modification of the local density of states can provide additional far-field radiation channels enhancing the overall radiation efficiency of the coupled system. However, for metallic antennas this also provides additional nonradiative loss channels that must be balanced when including the antenna. From comprehensive theoretical studies it is known that the overall fluorescent enhancement can be quantified by the following expression at the emitter wavelength (\( \lambda_{Em} \)):

\[
q(\lambda_{Em}) = \frac{\Gamma_{RAD}/\Gamma_0}{P(\lambda_{Em}) + \frac{1-q_0(\lambda_{Em})}{q_0(\lambda_{Em})} + 1 - q_0(\lambda_{Em})^2} \tag{C.11}
\]

where \( \Gamma_{RAD}/\Gamma_0 \) is the radiation enhancement factor (with the antenna compared to the bare emitter), \( P \) is the Purcell factor and \( q_0 \) is the intrinsic quantum yield. It was recently shown that for high-yield emitters \((q_0 \leq 1)\) the emission of the emitter is quenched by the nonradiative losses of the antenna. In this case, low-loss dielectric antennas outperform metals. However, in the case of low-yield emitters, metals were shown to outperform dielectrics (Si and GaP) and it is in this range we restrict our analysis.

By comparing the various materials and particle sizes the radiation enhancement factor \( \Gamma_{RAD}/\Gamma_0 \) is maximised. Following a previous comparison between dielectric and plasmonic antennas coupled to a dipole emitter we describe the radiative efficiency of the dipole-dipole coupled system in terms of the Mie coefficients \((a_1 \text{ and } b_1)\) and a modified separation factor \( \rho = \frac{2\pi d}{\lambda n_d} \), where \( d \) is the separation of the dipole to the center of the antenna, \( \lambda \) is the wavelength of the emitter in vacuum and \( n_d \) is the refractive index of the surrounding media.

For parallel (\( \parallel \)) and perpendicular (\( \perp \)) orientation of the two dipoles with respect to the dipolar mode of the antenna, the modified radiation efficiency is given by:

\[
\frac{\Gamma_{RAD}^{\parallel}}{\Gamma_0} = 9 \left| \frac{j_1(\rho) - a_1 h_1^{(1)}(\rho)}{\rho} \right|^2 \tag{C.12}
\]

\[
\frac{\Gamma_{RAD}^{\perp}}{\Gamma_0} = 9 \left[ |j_1(\rho) - b_1(\rho)h_1^{(1)}(\rho)|^2 + \left| \frac{\rho j_1(\rho)'}{\rho} - a_1(\rho h_1^{(1)}(\rho))' \right|^2 \right] \tag{C.13}
\]

where \( j_1(\rho) \) and \( h_1^{(1)}(\rho) \) are the spherical Bessel and Hankel function of the first kind and \( f' \) denotes the derivative of \( f \) with respect to \( \rho \).

By fixing the spacing between the emitter and antenna surface to be 10 nm, we vary
C.4 Perspectives and Outlook

Figure C.5: The maximum (a) scattering enhancement factor ($Q_{Scat}$) and (b) absorption enhancement factor ($Q_{Abs}$) and the corresponding price in USD per mm$^3$.

The particle radius to optimise the radiation efficiency of blue (470 nm), green (540 nm), and red (660 nm) dipole emitters oriented perpendicular to the electric dipole of the antenna plotted in Figures C.4b, C.4c, and C.4d, respectively. Silicon is included as a reference to directly compare the performance of a comparable dielectric antenna. The parallel dipole had emission efficiencies below unity, except for Si. As seen for blue light emission (Figure 7b), silver is predicted to be more efficient than aluminum and both are much more efficient than gold.

C.4 Perspectives and Outlook

For the future development of plasmonics and the wider implementation in industrial settings, the tradeoff between efficiency and price must be considered as well. In Figure C.5 we capture this tradeoff by plotting the price (in USD/mm$^3$) against the maximum absorption and scattering cross sections. The low material cost is a primary advantage of some of the novel materials, as conventional materials (Au and Ag) are some of the most expensive. In many applications, the infrared materials (Ti, TiN, TiON, SNO, SRO) provide lower cost along with the ability to use smaller particles may make them more attractive even if it requires sacrificing some efficiency. In this work, both the material and size-dependence of the underlying physical processes of plasmonic applications have been investigated over a large material library.

With an ever-growing library of plasmonic materials and the continued development of novel applications, such a systematic method is critical to unite the material science and device engineering aspects quantitatively. Our quick and inexpensive method allows for such
Figure C.6: For each application the designated figure of merit and operation wavelength are included along with estimated figures of merit for the state-of-the-art found in the literature. Finally, the proposed optimal material, particle radius and predicted figure of merit are also presented, showing the possibility of marked improvement over existing devices. Asterisk (*) denotes FDTD calculated parameters. State-of-the-art examples taken from the following article: [288, 289, 290, 15, 291, 176, 292, 293, 35, 243].

predictions without any need for nanofabrication. It requires only simple descriptions of the electronic and optical properties of a thin film measured using standard optical characterisation techniques. From there, well-established mode calculations are used and a deep understanding of some of the cutting-edge plasmonic applications to make direct predictions on device functionality. The analysis has been performed for applications under three overarching categories: hot electron applications, photothermal applications, and sensing and near-field applications. Table C.6 consolidates the results along with benchmark comparisons with the state-of-the-art devices found in literature. Each of the proposed devices offers an advantage over the existing applications though either favourable optical properties, electronic properties, or easier fabrication. To accelerate the development of plasmonic devices to a point where the experimentally and theoretically-predicted advantages can begin to make a meaningful impact on our world, one must unite all aspects of the interdisciplinary research including theoretical modelling, material science, experimental characterisation and device engineering.
Appendix D

Two Temperature Model Fitting

Upon the pump pulse arriving, a nonthermal electron distribution with energy density \( N \) is excited. The distribution loses its energy to thermal electrons via electron-electron scattering events with a heating rate \( \alpha \).

\[
\frac{\partial N}{\partial t} = -\alpha N \tag{D.1}
\]

With the condition that \( N(t \to \infty) = 0 \), the time evolution of the nonthermal electron population is described by a decaying exponential function.

\[
N(t) = e^{-\alpha t} = e^{-\frac{t}{\tau_{ee}}} \tag{D.2}
\]

Where \( \tau_{ee} = \alpha^{-1} \) is termed the electron-electron lifetime and characterises the thermalisation of the excited electrons. This results in a corresponding increase in the overall electron temperature \( (T_e) \), mediated by the electronic heat capacity, \( C_e = \frac{\partial U}{\partial T_e} \). Subsequently, the electrons are out of thermal equilibrium with the lattice. As a result, energy is transferred from the electrons to the lattice via electron-phonon scattering.

The energy transfer rate is proportional to the temperature difference between the electrons and lattice with proportionality constant \( G \), termed the electron-phonon coupling constant. It is defined in terms of the electron relaxation time \( \tau_e(T_e) \), electron mass \( m_e \), speed of sound in the material \( v_s \), and the number density of electrons \( n_0 \) by [294]:

\[
G = \frac{\pi^2}{6} \frac{m_e v_s^2 n_0}{\tau_e(T_e) T_e} \tag{D.3}
\]
Appendix D. Two Temperature Model Fitting

and the time evolution of the electron temperature is described by:

\[ C_e \frac{\partial T_e}{\partial t} = -G(T_e - T_i) + \alpha N \quad (D.4) \]

By energy conservation, there must be a corresponding heating of the lattice temperature, \( T_l \), in terms of the lattice heating capacity, \( C_l = \frac{\partial U}{\partial T_l} \), according to:

\[ C_l \frac{\partial T_l}{\partial t} = G(T_e - T_l) \quad (D.5) \]

Taking first only the electron-electron and electron-phonon scattering (ignoring thermal conduction via phonon-phonon scattering), the difference of equations D.4 and D.5 resembles a Newton cooling problem between two bodies:

\[ \frac{\partial (T_e - T_l)}{\partial t} = -G \left( \frac{1}{C_e} + \frac{1}{C_l} \right) (T_e - T_l) + \frac{\alpha}{C_e} N \quad (D.6) \]

Due to the vastly different timescales of the two processes, it is possible to separate the solution into the heating and cooling components. The heating occurs with a timescale \( \tau_{th} \approx C_e/\alpha \) whereas the cooling occurs with the electron-phonon lifetime \( \tau_{ep} \approx G^{-1}(C_e^{-1} + C_l^{-1})^{-1} \). As the differential reflectivity is a direct result of the thermal electron distribution, the measured signal then follows:

\[ \frac{\Delta R}{R}(t) = \frac{\Delta R}{R} \bigg|_0 \left( 1 - e^{-\frac{t}{\tau_{ee}}} \right) e^{-\frac{t}{\tau_{ep}}} + \frac{\Delta R}{R} \bigg|_\infty \quad (D.7) \]

where \( \frac{\Delta R}{R} \bigg|_0 \) is the magnitude of the electron-phonon exponential and \( \frac{\Delta R}{R} \bigg|_\infty \) is the equilibrium value reached following the electron-phonon bottleneck. This bottlenecked value is determined by the equilibrium temperature formed between the two systems. From the Newton two-body cooling solution, this is known to be:

\[ T_\infty = \frac{C_e T_e(0) + C_l T_l(0)}{C_e + C_l} \quad (D.8) \]

As electron temperatures in pump-probe experiments reach thousands of Kelvin and the lattice is at room temperature, \( T_\infty \approx C_e T_e(0)/(C_e + C_l) \). We use the relationship between the
temperature and differential reflectivity to estimate \( \frac{\Delta R}{R} \) as:

\[
\frac{\Delta R}{R} \bigg|_\infty \approx \frac{C_e}{C_e + C_l} \frac{\Delta R}{R} \bigg|_0 = N \frac{\Delta R}{R} \bigg|_0
\]  

However, this is not what happens in the experiments, as phonon-phonon scattering can dissipate heat occurring in a timescale of \( \tau_{pp} \) related to the thermal conductivity of the material. The phonon system is being heated by the electrons at a rate of \( \tau_{ep}^{-1} \) and cool at a rate of \( \tau_{pp}^{-1} \):

\[
\frac{\Delta R}{R}(t) = \frac{\Delta R}{R} \bigg|_0 (1 - e^{-\frac{t}{\tau_{ee}}} + N \frac{\Delta R}{R} \bigg|_0 (1 - e^{-\frac{t}{\tau_{ep}}})e^{-\frac{t}{\tau_{pp}}}) \quad (D.10)
\]

\[
\frac{\Delta R}{R} \bigg|_0 \approx \beta \left[ \left(1 - \frac{\tau_{ep} + \tau_{th}}{(N-1)\tau_{th}}\right)^{-1} - N \left[ \frac{\tau_{ep} + \tau_{th}}{(N-1)\tau_{th}} \right]^{\frac{\tau_{th}}{\tau_{pp}}} \left( \frac{\tau_{ep} + \tau_{Th}}{(N-1)\tau_{th}} \right) \right]^{-1} + N \left[ \frac{\tau_{ep} + \tau_{Th}}{(N-1)\tau_{th}} \right]^{-\frac{\tau_{th}}{\tau_{ep}}} \quad (D.16)
\]
Therefore, the full phenomenological solution can be expressed as:

\[
\frac{\Delta R}{R}(t) = \beta \left[ \left( 1 - \left[ \frac{\tau_{ep} + \tau_{th}}{(N-1)\tau_{Th}} \right]^{-1} \right) - N \left[ \frac{\tau_{ep} + \tau_{th}}{(N-1)\tau_{th}} \right]^{-\frac{\tau_{th}}{\tau_{ep}}} \left( \frac{\tau_{ep} + \tau_{Th}}{(N-1)\tau_{th}} \right)^{-\frac{\tau_{th}}{\tau_{ep}}} + N \left[ \frac{\tau_{ep} + \tau_{Th}}{(N-1)\tau_{th}} \right]^{-1} \left[ 1 - e^{-\frac{t}{\tau_{ep}}} e^{-\frac{t}{\tau_{pp}}} + N \left( 1 - e^{-\frac{t}{\tau_{ep}}} \right) e^{-\frac{t}{\tau_{pp}}} \right] \right]
\]
Bibliography


[109] M. Casalino, L. Sirleto, L. Moretti, F. Della Corte, and I. Rendina, “Design of a silicon resonant cavity enhanced photodetector based on the internal photoemission effect at...


[148] L. Hultman, S. A. Barnett, J. E. Sundgren, and J. E. Greene, “Growth of epitaxial TiN films deposited on MgO(100) by reactive magnetron sputtering: The role of low-energy


[276] Q. Zhao, R. Duan, J. Yuan, Y. Quan, H. Yang, and M. Xi, “A reusable localized surface plasmon resonance biosensor for quantitative detection of serum squamous cell carcinoma


