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**Impact of Ga gradient and alkali
treatment on minority charge carrier
dynamics in CuInGaSe₂ solar cells**

by

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Abstract

CuInGaSe₂ solar cells, commonly known as CIGS solar cells, have achieved high device efficiency owing to two major research breakthroughs: the implementation of a Ga gradient into the CIGS absorber, and the alkali atoms treatment. Though many studies have been focused on optimising these two techniques to further enhance device efficiencies, the minority charge carrier dynamics inside such complex system are still under investigation. Hence, in this thesis, transient absorption spectroscopies (TAS) in the time range of picosecond to nanosecond and microsecond to second are utilized primarily to investigate the minority charge carrier dynamics inside such devices.

Chapter 3 presents the results of steady state and transient optical studies on CIGS (no Ga gradient and no alkali treatment), CuInSe₂ (CIS), and Sb₂Se₃ thin film, respectively. The study on CIGS/CIS is to set a foundation for the following two chapters. Additionally, the results of Sb₂Se₃ are included because Sb₂Se₃ also belongs to the Se-based chalcogenide family. In all three materials, two major transient absorption features are discovered: 1. A photobleach signal appeared in picosecond-nanosecond timescale, which is assigned to the ground state bleach, and 2: a positive absorption signal appeared in microsecond to second scale, which is linked to the presence of trapped charge carriers. Analyzing these two TA features, it is found that CIGS/CIS has a longer minority carrier lifetime and a smaller amount of trapped charges compared to Sb₂Se₃.

In Chapter 4, a Ga-graded CIGS device with RbF+NaF post deposition treatment (PDT) is investigated primarily by TAS, which allows to have a real-time observation of minority carriers dynamics. A drift-diffusion kinetic model is established, which successfully deconvolutes the two competitive kinetics, recombination and drift, in a Ga-graded CIGS device. Furthermore, the drift time constant obtained from the kinetic model enables to calculate the minority carrier mobility ($16.3 \pm 4.0 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) in the high Ga region of a Ga-graded CIGS solar cell. As far as I am aware of, this is the first time that

the minority carrier mobility in that region is determined.

Chapter 5 makes use of the kinetics model established in Chapter 4 to analyze the impact of Na and Rb atoms treatments on minority carrier mobility and recombination throughout the Ga-graded CIGS device. It is found that Na atoms prolong the minority carrier lifetime throughout the CIGS absorber regardless of the $[Ga]/([Ga]+[In])$ (GGI) ratio. On the other hand, passivation with Rb atoms works best in the domain with low Ga concentration, suggesting an ineffective passivation of Rb atoms in the regions of high Ga concentration.

Declaration of Authorship

I declare that the contents of thesis is the results of my own work unless stated except when the references are made to contributions by others.

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List of Abbreviations

Below listed the abbreviations commonly used in this thesis:

a-Si	A morphous Si
CBM	C onduction B and M inimum
CIGS	CuInGaSe ₂
CIS	CuInSe ₂
CGS	CuGaSe ₂
c-Si	C rystalline Si
EQE	E xternal Q uantum E fficiency
E_g	B andgap
E_F	F ermi level
GBs	G rain B oundaries
GIs	G rain I nteriors
GGI	$\frac{[Ga]}{[Ga]+[In]}$ ratio
H-BG	Region of a CIGS absorber which GGI=0.2–0.5 and the grain size > 2 μm
H-SG	Region of a CIGS absorber which GGI > 0.6 and the grain size < 0.5 μm
I-V	C urrent density- V oltage
J_{SC}	S hort- C ircuit C urrent D ensity
PDT	P ost D eposition T reatment
PL	P hotoluminecence
PV	P hotovoltaics
QNR	Q uasi N eutral R egion
SLG	S oda L ime G lass
SCR	S pace C harge R egion
SEM	S canning E lectron M icroscopy
SIMS	S econdary I on M ass S pectroscopy

TAS Transient **A**bsorption **S**pectroscopy

UV-VIS Ultra-Violet **V**isible spectroscopy

VBM Valence **B**and **M**aximum

V_{OC} Open-Circuit **V**oltage

Chapter 1

Introduction

1.1 Renewable energy

Renewable energies are an essential building block to decarbonize the global primary energy production and tackling climate change. Climate change refers to the change of the surface temperature of the earth by external forces, for example, human activities. The global temperature has risen by 1 °C compared to preindustrial levels[1], as shown in the black scattered line in Figure 1.1.

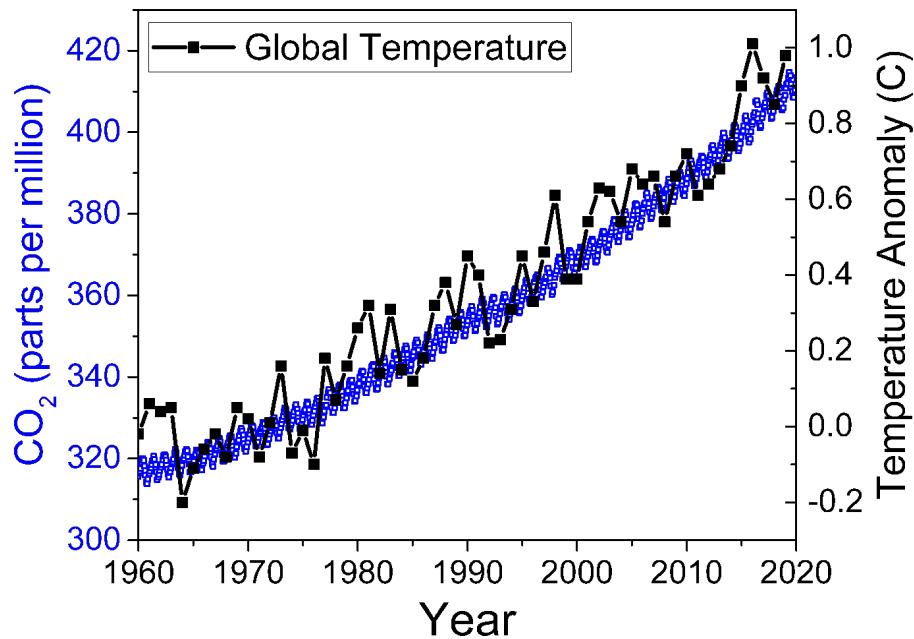


Figure 1.1: The correlation between CO₂ emission and the rising temperature of Earth from 1960 till now [1].

Even though this seems to be a comparable small increase of the global average temperature it poses a huge threat to all living beings on earth. More heatwaves and droughts, changes in precipitation patterns, rising sea levels by approximately 1 - 4 feet until 2100, and the Arctic becoming ice-free..etc are all part of predictions made by scientists[2]. Besides, all of these effects are irreversible.

The earth's climate is maintained by greenhouse gases[3]. When the Sun shines on the earth, most of the visible light will pass through the atmosphere and be absorbed by molecules at the earth's surface. Afterwards, these molecules will radiate infrared light as a form of heat back to space through the atmosphere. The radiated infrared light will then be absorbed by the greenhouse gases such as carbon dioxide (CO₂) and methane (CH₄)

in the atmosphere. The atmosphere is therefore heated and radiate infrared light (heat) back to the earth's surface as a return. This process is called the greenhouse effect and is essential so that the earth's climate is a suitable habitat. However, the concentration of greenhouse gases is significantly increased by human activities such as burning fossil fuels and agricultural activities over the past decades. This leads to an unusual growth of global temperature as well as other negative effects like sea water acidification [4][5]. A clear correlation can be seen between these two is shown in Figure 1.1.

Renewable energies emerged in an attempt to replace traditional fuels such as oil, gas and coal. It refers to using those renewable resources such as sunlight, water- and wind-power as well as biomass to produce energy. Most of the countries are now aware of the damage to the environment resulting from climate change and therefore invest renewable energy technologies to decarbonize their energy demand. Figure 1.2 (a) shows the primary energy demand in the UK from 2008 projecting to 2035[6]. The steady growth of the energy demand met by renewable energy sources is projected. On the other hand, a sharp decline of solid fuels (coal) is forecasted to happen, resulting in only 2 % of the overall UK energy demand will be met by coal in 2035. Among all the renewable energy sources in the UK, both offshore and onshore wind power as well as solar photovoltaics (PV) have a high share of the overall capacity[7], as shown in Figure 1.2 (b), indicating their high potential in facilitating the energy transition.

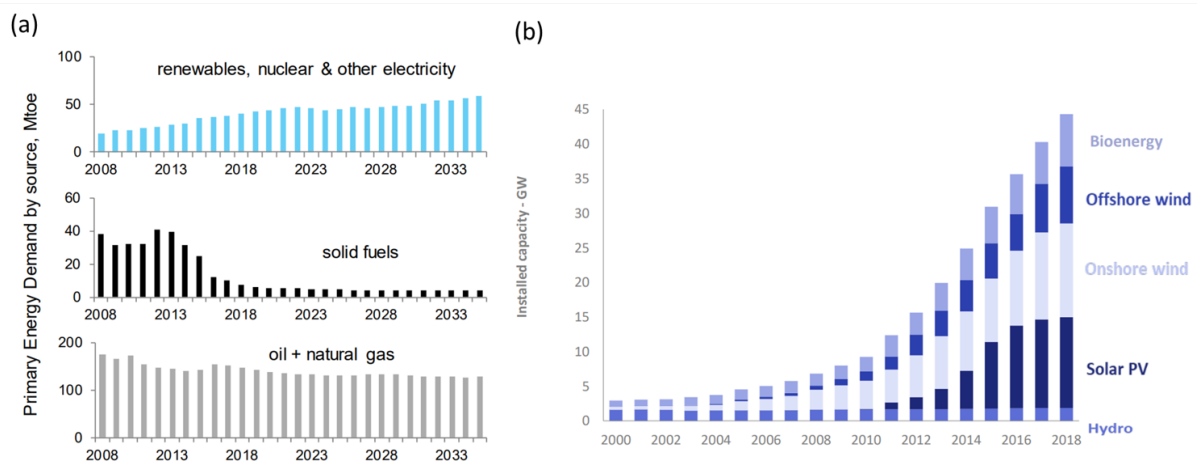


Figure 1.2: Primary energy demand in the UK from 2008 to 2035 (projection)[6] and electrical generating capacity by main renewable sources between 2000 to 2018[7]. Figure (a) and (b) are reprinted from reference [6] and [7], respectively. Both figures are reproduced with permissions from the Open Government Licence v3.0.

1.2 Introduction to solar cell technologies

The working principle of solar cells is to convert solar irradiation directly into electricity. The ratio of the incoming energy from sunlight to the released electric energy is termed the "Solar cell efficiency". Solar cells that are currently on the market can be categorized into five technologies[8] based on the type of the semiconductor: (1) Crystalline Si (c-Si), (2) Amorphous Si (a-Si), (3) III-V, (4) Chalcogenide, and (5) Emerging PV. Table 1.1 lists the semiconductor materials within these five technologies and their current state-of-the-art solar module efficiencies along with the manufacturing groups and the installed areas. In addition, these five technologies can be further classified into three generations based on the crystallinity of the material and their current research status.

1.2.1 First generation solar cells

The first generation solar cells are the cells made from c-Si, including both monocrystalline and multicrystalline Si. c-Si technology currently takes up 62% of whole solar cell market for their high module efficiency, reasonably cheap price and technology maturity[9]. Monocrystalline Si solar cells, which the cells are sliced from a large single Si crystal, have the highest efficiency (state-of-the-art module up to 24.4 %) among all Si-based solar modules. However, the downside is the energy-intensive fabrication process owing to the tightly controlled condition for growing single crystal Si in a large volume. On the other hand, for multicrystalline Si solar cells, due to the cell is grown from multiple Si crystals, the fabrication costs are much cheaper. Unfortunately, multicrystalline Si solar cells suffer from a lower device performance (state-of-the-art module efficiency up to 20.4%). Note that all Si solar modules suffer device efficiency losses under low irradiation levels and high temperature, which makes them difficult to generate energy in certain weather conditions..

1.2.2 Second generation solar cells

The second generation solar cells correspond to thin film solar cells, including a-Si, III-V, and chalcogenide technologies. This generation is estimated to own 5 % of the current market share [9]. They were developed owing to the following reasons: 1. Thin film solar cells can be fabricated on flexible substrates and therefore have more installation flexibility. 2. Comparing to traditional c-Si solar cells, thin film solar cells require much less raw

Table 1.1: State-of-the-art solar module efficiencies of the representative materials in the five technologies along with the corresponding manufacturing companies and the installed areas [8]. HJ stands for heterojunction and OPV stands for organic photovoltaics.

Technology	Generation	Detailed Description	Group(s)	Efficiency (%)	Area (cm ²)
c-Si	First generation	Multicrystalline silicon	Hanwha Q cells	20.4	14818
		Monocrystalline silicon; HJ rear junction; 108 cells	Kaneka	24.4	13177
a-Si	Second generation	amorphous Si	Solarex	9.8	933
III-V		GaAs, thin film, single crystal	Alta Devices	25.1	866.45
Chalcogenide		CdTe thin film	First Solar	19	23573
		CIGS thin film	Miasole	17.4	10850
Emerging PV	Third generation	Perovskite	Panasonic	17.9	802
		OPV	ZAE Bayern	11.7	204

material and are therefore more lightweight. Hence, there are less restrictions in integrating thin film solar modules to rooftop or buildings. Below provides brief information on each of the technology in this generation.

a-Si solar cells: Unlike c-Si solar cells, a-Si solar cells are made by deposited a thin layer of Si onto a substrate (for example: metal or glass). Consequently, a-Si solar cells can be made flexible, which allows them to be easily cooperated onto any surface. However, the downside of a-Si solar cells is that the cell efficiency is very low, approximately half of the efficiency of c-Si cells. As a result, a-Si solar cells require almost double the area of the installed panels to have the same electricity output as c-Si cells.

III-V solar cells: III-V solar cells correspond to the solar cells which the main

light absorbers are composed of group III (for example: Al, Ga, and In) and group V (for example: N, P, As, and Sb) elements. GaAs solar cells are the best known III-V solar cells for their outstanding device performance. The current state-of-the-art module efficiency of a single junction GaAs solar module is 25.1%, which is the highest among all solar technologies. Unfortunately, due to their high fabrication costs and the utilization of scarce material like Ga, GaAs solar cells are mainly implemented in aerospace-related applications (for example: satellites, space vehicles) for its high reliability and small temperature coefficients.

Chalcogenide solar cells: CdTe and CIGS solar cells are the most common and mature thin-film chalcogenide technologies in the market at present. CdTe solar cells is a promising candidate for thin-film PV production for its low manufacturing costs and fabrication with the earth-abundant material Cd. However, the toxicity of Cd posts significant challenges to the required safety and recycling procedures. CIGS solar cells have become a promising technology in thin-film PV industry after years of intensive research. The advantages of CIGS include low power loss to increasing temperature, high energy yield, the possibility to be deposited on flexible substrates and a lower energy payback time compared to Si solar cells. In 2019, the efficiency of CIGSe research cells surpassed CdTe research cells, as listed in Table 1.2, demonstrating its ability as a leading technology in thin-film photovoltaics in the future.

Table 1.2: Device efficiencies, the research groups, and the year of validation of the current state-of-the-art research cells in the Chalcogenide technology [10]. HUST stands for Huazhong University of Science and Technology.

Technology	Description	Group(s)	Efficiency (%)	Year
Chalcogenide	CIGS thin film	Solar Frontier	23.4	2019
	CdTe thin film	First Solar	22.1	2016
	CZTSSe thin film	IBM	12.6	2013
	Sb ₂ Se ₃ core-shell structured nanorod	Hebei/Jinan University	9.2	2019
	Sb ₂ Se ₃ thin film	HUST	7.6	2018

On the other hand, the downside of CIGS is the utilization of scarce materials such as

In and Ga. Consequently, many efforts have been put into developing solar cells that are made from earth abundant materials. $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ (CZTSSe) solar cells are therefore developed from this concept. Unfortunately, CZTSSe solar cells are struggling to reach high efficiency even though after 10 years of intensive development. The highest efficiency of a CZTSSe research cell, as listed in Table 1.2, was developed back in 2013 and is only half of the performance of the current state-of-the-art CIGS solar cells. The major issue of CZTSSe solar cells is the high amounts of secondary phases formed during the synthesis process, resulting in significant loss of device efficiencies [11]. Sb_2Se_3 , is another earth abundant semiconductor material that emerged as an alternative in thin film chalcogenide technology. As a binary compound, Sb_2Se_3 is easier to synthesis and therefore the cost of fabrication is reduced compared to making CIGS and CZTSSe. However, the current state-of-the-art efficiency of a Sb_2Se_3 solar cell is still far behind CdTe and CIGSe solar cells. High amounts of defect states in Sb_2Se_3 are suggested to be responsible for its low device efficiency. In chapter 3 in this thesis, a comparison of CIGS and Sb_2Se_3 from a charge carrier dynamics points of views is provided and discussed. **Note that an in-depth introduction of CIGS solar cells is given in chapter 1.4 as CIGS is the main topic of this thesis. An introduction of Sb_2Se_3 on its material and optical properties can be found in chapter 1.5.**

1.2.3 Third generation solar cells

Third generation solar cells refer to the solar cells that are not yet widely applied in industries and are still in the research phase. Hence, third generation solar cells can be also called as emerging PV. In this category, organic PV (OPV) and perovskite solar cells are the two types currently on the market. The cheap materials and the relatively simple fabrication procedure makes OPV and perovskite solar cells good candidates for large scale roll-to-roll manufacturing fabrication. In particular, perovskite solar cells receive numerous attentions in the solar cell research field for its rapid increase in device efficiency [12]. Both OPV and perovskites solar cell can be made thin and flexible. Therefore, they can be implemented in a wide range of applications such as building integrated PVs, mobile electronics, etc. The disadvantages of OPV and perovskite solar cells are that they degrade rapidly under exposure to air, which remains the biggest challenge that still awaits to be solved.

1.3 Basic principles of solar cells

Essentially, what happens in solar cells is the interactions between light and matter through time, space, and energy. In a solar cell, upon irradiation, charge carriers (e^- and h^+) are generated by absorbing photons in the absorber layer. The collection efficiency of these charge carriers is associated directly with the solar cell device performance. Below provides some basic semiconductor concepts to understand the solar cell material and how charge carriers behave after light absorption and how they determine device performance.

1.3.1 Photon absorption and charge carrier generation in semiconductors

Employing a semiconductor with a suitable bandgap as the main light absorber in a solar cell allows effective photon absorption and charge carriers generation. In solid state physics, bandgap corresponds to the energy levels in a solid that are unable to be occupied by electrons. It is also referred to the energy difference (E_g) between the valence band maximum (VBM) and conduction band minimum (CBM), where VBM corresponds to the highest energy level electrons stay at 0K and CBM corresponds to the lowest vacant energy level, as illustrated in Figure 1.3.

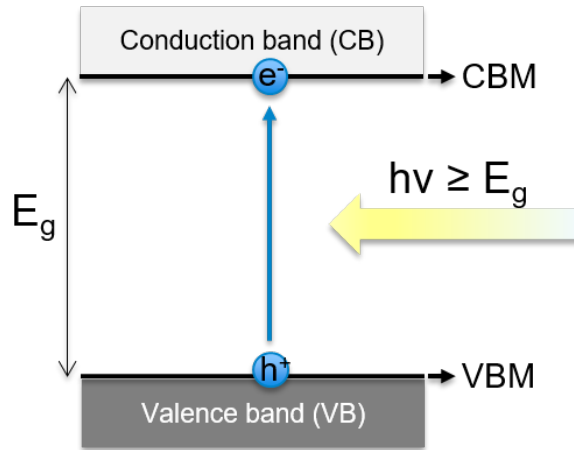


Figure 1.3: Schematic of charge carrier generation in a semiconductor. E_g corresponds to bandgap energy. $h\nu$ corresponds to the energy of light. CBM and VBM correspond to the conduction band minimum and valence band maximum, respectively.

In semiconductors, upon illumination, the $e^- - h^+$ pairs are generated by absorbing photons ($h\nu$), as shown in Figure 1.3. Whether the photons are absorbed by the semi-

conductor depends on the following two key factors. The first key factor is the energy of the photon. As long as the photons have energy equal to or higher than the bandgap of the semiconductor, they can be absorbed. The second key factor is the absorption coefficient (α) of the material, which refers to the distance a light of a specific wavelength can travel before it is fully absorbed. A higher α means a stronger absorption by the material. Figure 1.4 illustrates the α of the five solar technologies introduced in the previous section. It can be seen that the absorption onset of GaAs, CdTe, and CIGS solar cells is much sharper than that of Si-based solar cells. This is due to the fact that Si is an indirect bandgap material, whilst GaAs, CdTe and CIGS has direct bandgap. The difference between direct and indirect bandgap materials is that the electrons and holes do not have the same momentum in indirect bandgap material. This means to excite an electron in an indirect bandgap material would require not only photon absorption but also an extra momentum supply by a phonon. As a result, the absorption in indirect bandgap materials is weaker compared to direct bandgap materials, as can be seen clearly in Figure 1.4. This also means that the indirect bandgap semiconductors require thicker layers to absorb more photons. For example: the thickness of the absorber in c-Si solar cells is hundreds of μm , whilst in CIGS solar cells is only 2–3 μm .

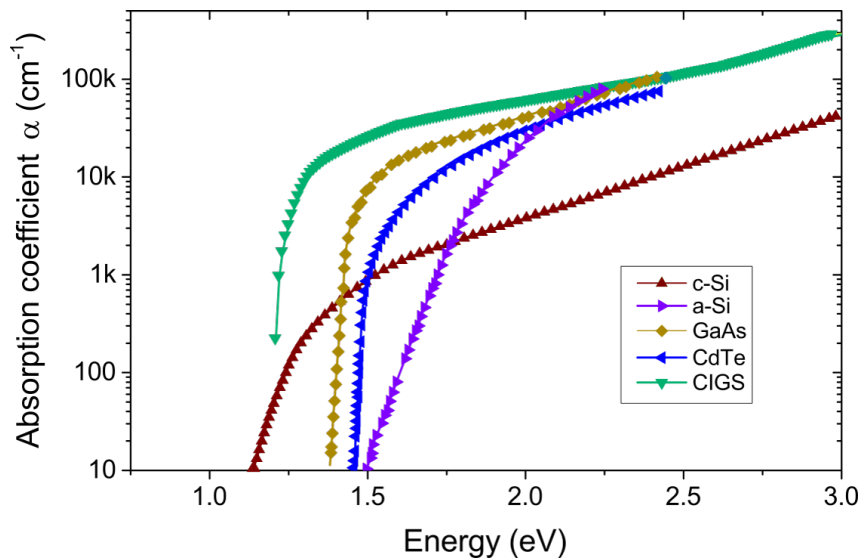


Figure 1.4: Absorption coefficient of c-Si, a-Si, GaAs, CdTe, and CIGSe solar cells. This figure is adapted with permission under CC BY-NC 4.0 license from reference [13].

Theoretically, the maximum solar cell (with a single light absorber layer) efficiency, also called Shockley-Queisser limit (SQ limit), is defined by the bandgap energy. SQ limit was calculated by William Shockley and Hans-Joachim Queisser using 6000K black

body radiation as solar spectrum (black curve in Figure 1.5(a)) in 1961 [14]. However, in reality, the irradiation from the sun will be absorbed and reflected by the earth's atmosphere. Consequently, Rühle recalculated the SQ limit by replacing the 6000K black-body spectrum with a measured AM 1.5G spectrum (red curve in Figure 1.5(a)) [15] in 2016. The AM 1.5G spectrum is now the stand solar spectrum utilized in measuring solar cell efficiency. The corresponding result showed the maximum efficiency (33.7 %) is reached on a solar cell with a bandgap of 1.34 eV[15]. Figure 1.5(b) illustrates different state-of-the-art solar cells relative to their corresponding S-Q limits. It can be seen that the highest solar conversion efficiency (> 32 %) lies in the bandgap range of 1.1 to 1.5 eV, suggesting choosing a semiconductor of which the bandgap in this range is favourable for high efficiency solar cells. The state-of-the-art GaAs solar cell, with a bandgap energy of 1.42 eV, performs the closest to its S-Q limit compared to all other existing technologies. For the state-of-the-art CIGS solar cell with a device efficiency of 23.5 %, the corresponding SQ limit reached 75 %.

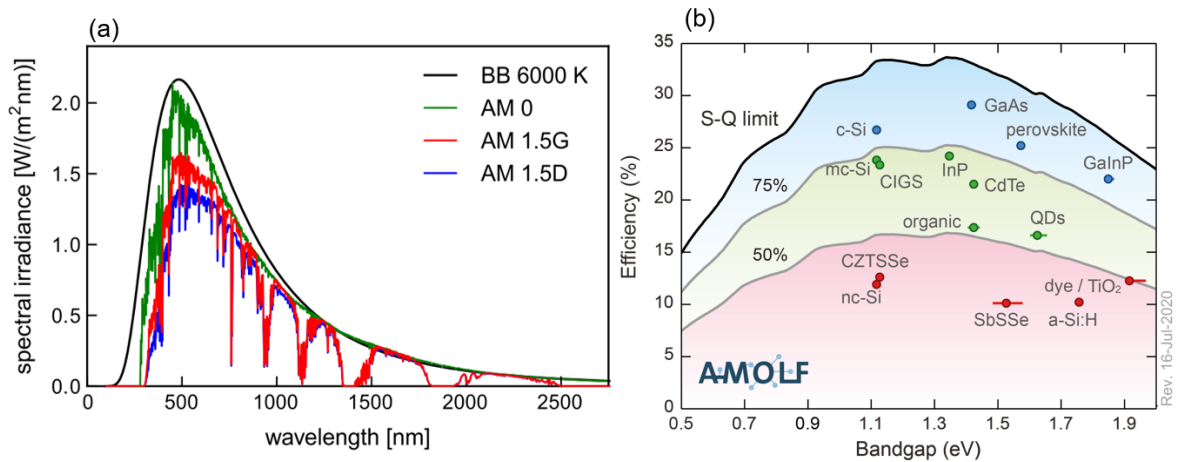


Figure 1.5: (a) Solar spectrum: BB 6000 K – 6000 K black body spectrum, AM 0: spectrum calculated based on irradiation outside of the earth's atmosphere. AM 1.5D: spectrum calculated based on sunlight irradiation considering absorption of earth atmosphere only, AM 1.5G: similar as AM 1.5D spectrum but with consideration of light scattering. This figure is adapted with permission of the copyright holder (Elsevier) from reference [15]. (b) Shockley-Queisser limit (S-Q limit, shown as the black line) as a function of bandgap of current record-efficiency cells. Two grey lines refer to the 75 % and 50 % of SQ limit. This figure is reproduced from reference [16] and [17] with permissions of the copyright holder (the owner and AAAS).

1.3.2 p-n junction

Once the $e^- - h^+$ pairs are generated, they need to be separated successfully so that electrons in the conduction band and holes in the valence band will have chances to be collected as electrical current. A material with high relative permittivity shows a good ability to separate electrons and holes.

Furthermore, to successfully collect electrons and holes, an ideal design of a solar cell is required to help transport of these charge carriers. Below gives introduction of the long-established and key model of a solar cell: A single p-n junction solar cell. To understand p-n junction, it is essential to understand first the idea of doping in a semiconductor.

1.3.2.1 Doping

Doping means introducing impurities intentionally (in most of the cases) into an undoped semiconductor. As a result, the electrical, optical, and structural properties of the semiconductor doped with impurities are modulated. Take Si as an example, since Si has 4 electrons in its outer shell, consequently, in a Si crystal, one Si atom will form four covalent bonds with its four neighbouring Si atoms, as illustrated in Figure 1.6(a). In a case when boron atoms (B) (or any III element) are doped into a Si crystal, the boron doped Si crystal will have extra holes since B only has three electron in its outer shell. As a result, holes become the majority charge carriers in this Si crystal. On the other hand, if phosphorous atoms (P) (or any V element) are introduced, the phosphorous doped Si crystal will have extra electrons since P has 5 electrons in its outer shell. As a result, electrons become the majority charge carriers in this case. The semiconductor which holes are majority charge carriers, it is called p-type. Whilst if electrons are majority charge carriers, it is called n-type. The doping atoms that lead to a p-type conductivity of a semiconductor are called acceptors, and the doping atoms that lead to a n-type conductivity of a semiconductor are called donors. The whole concept is clearly illustrated in Figure 1.6(a)-(c).

Fermi level, is an important concept in the physics of solar cells. It can be understood as a hypothetical level that it has a 50 % probability to be occupied by electrons in a thermodynamic equilibrium condition. It can be written as:

$$E_F = \frac{E_c + E_v}{2} + \frac{k_B T}{2} \ln \frac{N_v}{N_c} \quad (1.1)$$

, where E_c and E_v corresponds to the energy of CBM and VBM, respectively, k_B is boltzman constant, N_c and N_v is the carrier concentration of electrons and holes, respectively, and T is the temperature.

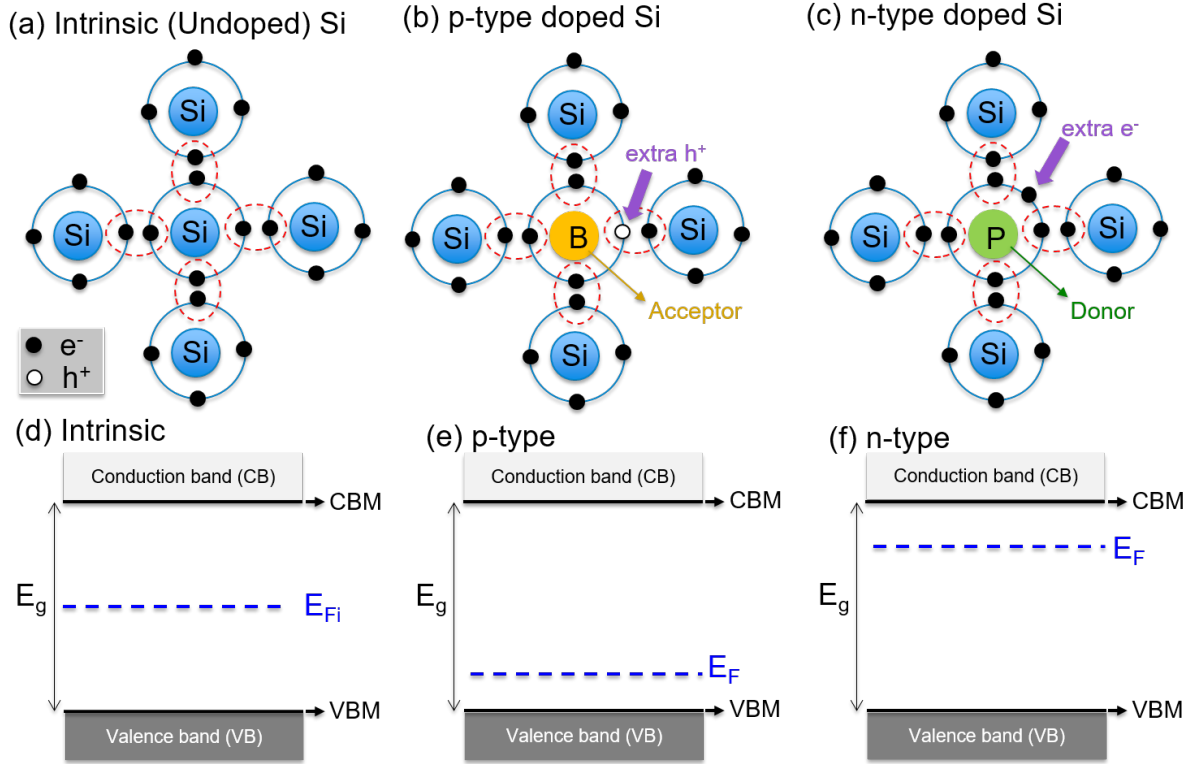


Figure 1.6: Schematic of bondings of (a) intrinsic Si, (b) p-type Si, and (c) n-type Si semiconductors. (d)-(f) illustrates the corresponding Fermi level (E_F) in a band diagram.

In an intrinsic semiconductor, since the numbers of electrons and holes are equal, the Fermi level is located in the middle of CBM and VBM, as illustrated in Figure 1.6(d). In a p-type semiconductor, since there are more holes than electrons, the Fermi level shifts closer to VBM, as illustrated in Figure 1.6(e). Whilst in a n-type semiconductor, which has more electrons than holes, the Fermi level shifts towards the CBM, as illustrated in Figure 1.6(f). With the concepts of what n and p type semiconductors are, one can understand a p-n junction as an interface where a n-type semiconductor is in contact with a p-type semiconductor. P-N junctions can be classified into two different types: Homojunction and Heterojunction. They will be introduced in the following.

1.3.2.2 Homojunction and Heterojunction

Homojunction occurs when the n and p semiconductors in contact with each other have the same bandgap energies despite the difference in doping. c-Si solar cells is a classic example of homojunction solar cells. Figure 1.7 illustrates the band diagram of a pn homojunction in the dark condition (without illumination and without bias) before and after equilibrium. When a p-type semiconductor is in contact with a n-type one, the excess holes in the p-type semiconductor will diffuse into the n-type semiconductor, and the excess electrons in the n-type semiconductor will diffuse into the p-type semiconductor. Those electrons that diffuse into p-type semiconductor will quickly recombine with the majority holes. Similarly, the holes diffuse into n-type semiconductor will recombine with the majority electrons. This mechanism results in the formation of a depletion region at the p-type semiconductor/n-type semiconductor interface. This depletion region, also named as space charge region (SCR), is charged by the immobilized ions and void of free charge carriers. The immobilized ions generates an electric field across the junction, which counteracts the charge diffusion and the equilibrium of the depletion region is reached once these two mechanisms counterbalance each other[18]. It is important to note that the fermi level of the p-type semiconductor and the n-type semiconductor, respectively, is lined up once the equilibrium is reached, as shown in the band diagram in Figure 1.7.

Heterojunction occurs when the n and p type semiconductors in contact with each other have different bandgaps. As illustrated in Figure 1.8, when two different semiconductors form a junction, due to the bandgap differences, a spike and/or a cliff may form at the interface. In a poor solar cell design, the spike/cliff serves as a blocker for charge carriers and lead to enhanced interface recombination. On the other hand, in an optimal design, the spike/cliff may prevent one type of charge carrier from flowing to a wrong direction, resulting in a more effective carrier collection.

Whether it is homojunction or heterojunction, the main purpose is to help transport electrons and holes effectively and aid charge carriers collections. In the following section, how charge carriers are transported and how recombination affects the transportation are explained.

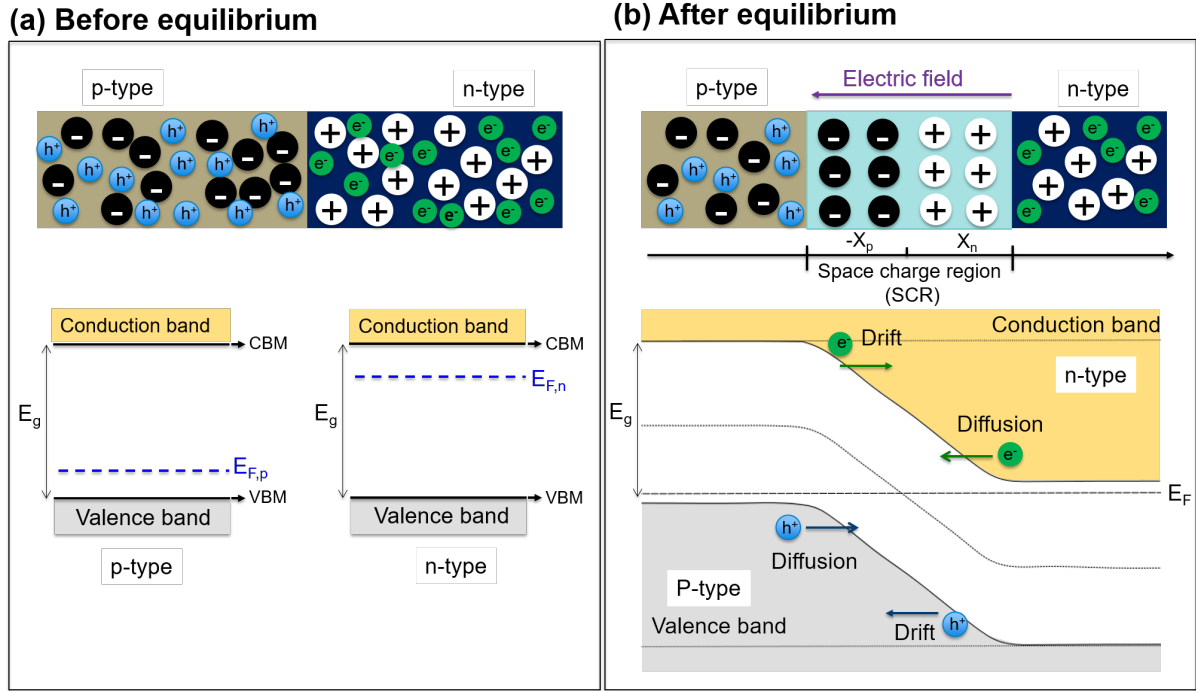


Figure 1.7: Schematic of a pn homojunction and the corresponding band diagrams in the dark condition (without illumination and without bias) before and after equilibrium.

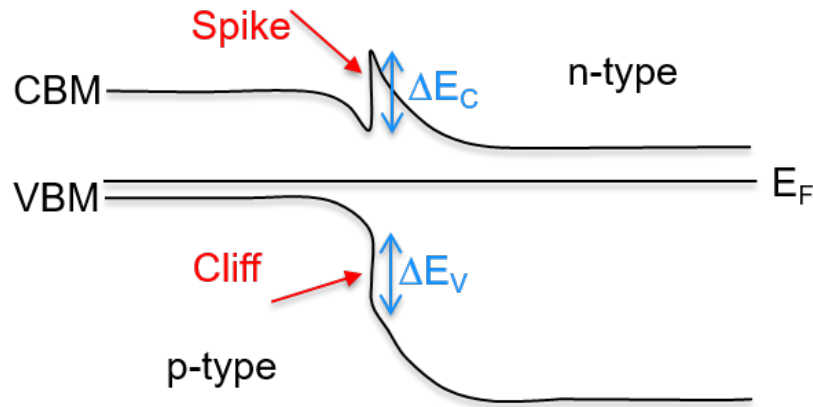


Figure 1.8: Schematic of a band diagram of a pn heterojunction. ΔE_c and ΔE_v corresponds to the conduction band energy and valence band energy difference at the interface, respectively.

1.3.3 Charge transportation and recombination

1.3.3.1 Transportation of charge carriers

Charge carriers can be transported by the following three mechanisms in a solar solar cell.

i. Diffusion: Upon illumination, the regions that are excited are in the non-equilibrium state due to the generation of free charge carriers. The concentration difference of the free charges at different regions facilitates a directional net current of charges from the region

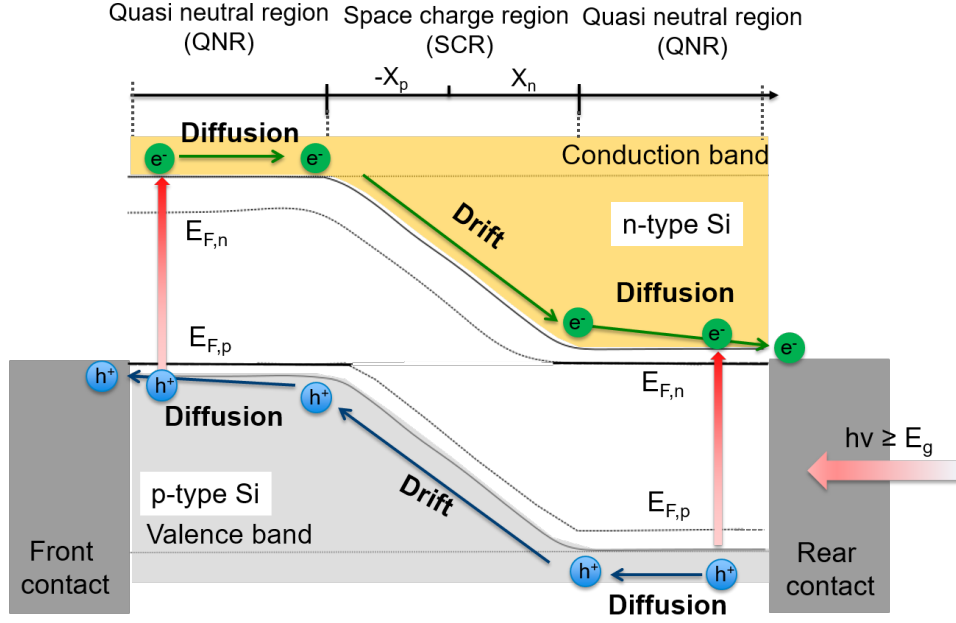


Figure 1.9: Schematic of transportation mechanisms of charge carriers in a Si solar cell.

with higher concentration to the region with lower concentration until the equilibrium is reached. This process is called "diffusion". As shown in Figure 1.9, if the free charges are generated in the quasi neutral region, there is no force that drives the free charges and therefore they only move via diffusion. The "diffusion length" is an important parameter in solar cells. It defines how far a free charge carrier can travel before it recombines. It can be expressed as:

$$L = \sqrt{D\tau} \quad (1.2)$$

, where D is the diffusion coefficient (cm^2/s) and τ is the charge carrier lifetime. Consequently, a higher charge carrier lifetime corresponds to a higher diffusion length, which is desirable for a high efficiency solar cell.

ii. Drift: Once the free charges reach the SCR, they are accelerated forward by the electric field. Figure 1.9 illustrates the drift process of the free charge carriers in a c-Si solar cell. The mobility (in conjunction with the strength of the electric field) is a measure of the speed of this transportation process and it can be expressed as follows:

$$\mu = \frac{v}{E} \quad (1.3)$$

, where v is the velocity and E is the electric field. The probability of a free charge carrier to be collected depends on the competition of recombination processes and transportation to the contact. A higher mobility leads to a shorter transportation time and therefore

increases the likelihood of the free charge carrier to be collected. Hence, determining the charge carrier mobility, especially the minority carrier mobility, is of importance to understand current performance constraints and eventually further advance solar cell efficiency.

iii. Tunnelling: The third mechanism of transportation is the tunnelling of charge carriers, as illustrated in Figure 1.10. In classical physics, to overcome a potential barrier (expressed as V in figure 1.10), the particle needs to have energy (expressed as E in figure 1.10) larger than V . Otherwise, the particle cannot pass through the barrier. However, in quantum physics, a particle is seen as a wave function. In the case of $E < V$, the wave can still pass through the potential barrier but with a probability that is exponentially decreased with the height and width of the barrier. This phenomenon predominantly occurs at the heterojunction interface due to the band discontinuity.

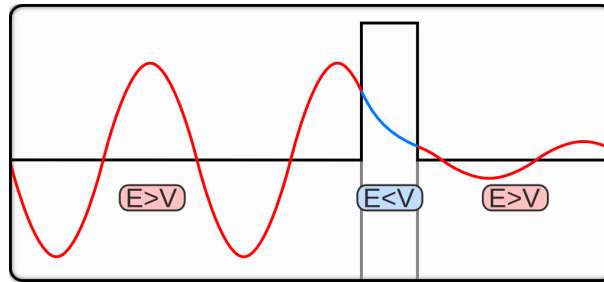


Figure 1.10: Schematic of a particle (with energy E) tunneling through a potential barrier V . This figure is reproduced with permission under CC BY-SA 3.0 license from reference [19].

1.3.3.2 Recombination of charge carriers

Recombination refers to the elimination of free charge carriers after photon-excitation. One can classify all recombination processes into two categories: Radiative recombination and Non-radiative recombination processes.

i. Radiative recombination: The radiative recombination processes can be divided into two categories: (1) spontaneous emission and (2) stimulated emission. Spontaneous emission refers to an electron decaying from an excited state to a lower energy state and emitting a photon during this process. As illustrated in Figure 1.11(a), spontaneous emission can be originated from (1) CBM to VBM (i.e. band to band), (2) shallow donor states to VBM, (3) shallow donor states to shallow acceptor states, and (4) CBM to acceptor states. In some cases, an emitted photon can stimulate another occurrence of

photon emission. This process is called stimulated emission, as shown in Figure 1.11(b).

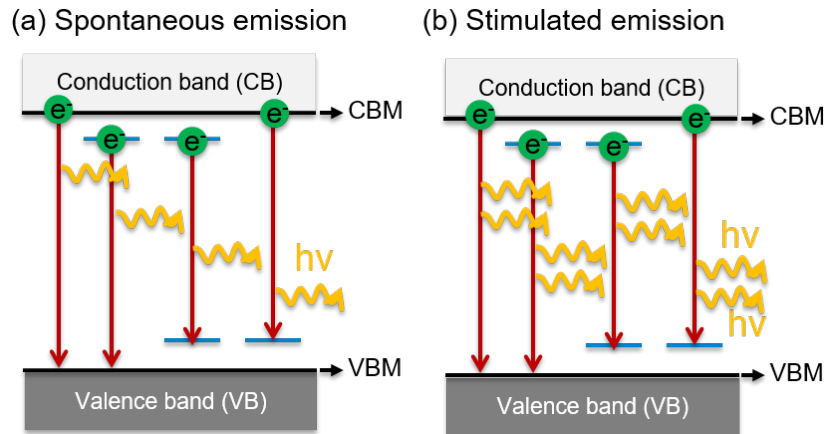


Figure 1.11: Schematic of (a) spontaneous and (b) stimulated emission in a semiconductor.

ii. Non-radiative recombination: The imperfection of the crystal structure and impurities induce the formation of defect states. Depends on their energetic level within the bandgap, defects can be categorized to two different types: 1) shallow traps, which refers to the defects that are localized ~ 0.4 eV lower (higher) from the CBM (VBM) and 2) deep defects. Deep defects are those localised energy-wise in the mid-bandgap and can capture both electrons and holes. Besides, once the charge carriers are captured, they cannot be easily released back to the band-edges via thermal emission. Hence, non-radiative recombination can occur when two charges of the opposite polarity are captured in the same deep defect state before one of either is re-emitted. This type of recombination is also called as Shockley-Read-Hall recombination (SRH recombination). In heterojunction solar cells, recombination centres are also formed at interfaces and surfaces, which result in a high recombination rate and poor open circuit voltage.

Auger recombination is also a non-radiative recombination process. When an electron releases its energy after decaying from a high energy state to a low energy state, part of this energy is transferred to another electron in the same energy state. The electron that received the energy can therefore be excited to an even higher energy state. this mechanism is called auger recombination. Note that Auger recombination is of importance in highly doped solar cells.

Here marks the end of the brief introduction of the physics of solar cells. If you would like to understand more in depth, I recommend the text book "The physics of solar cells" written by Professor Jenny Nelson [18].

1.4 Introduction to CIGS solar cells

The state-of-the-art CIGS module efficiency is up to 19.2 % and has surpassed CdTe solar modules, becoming a leading figure in the thin-film PV market. At laboratory scale, the efficiency of the current champion CIGS cell is 23.35 % [10], which holds a competitive position next to high efficiency mono-crystalline Si and perovskite solar cells. What has lead to the enhancement of CIGS device performance can be traced back to several research breakthroughs over the years, as detailed below. CIGS is a p-type semi-conductor that is obtained from the CuInSe_2 (CIS) material, which was first synthesized by Hahn in 1953 [20]. The first CIS solar cell was synthesized as a form of single crystal with a reported photovoltaic efficiency of 12 % [21]. The polycrystalline thin film CIS, on the other hand, suffered from low device performance until the employment of the co-evaporation technique in 1980 [22]. The record efficiency increased from around 5 % to more than 15 % [23]. This material was thus proved to be a potential candidate for thin-film solar PV and started to receive significant research attention that led to further progress in device performance. Band gap tuning by the introduction of gallium (Ga) atoms [24] [25] [26] and the alkali treatments [27] [28] are two of the most important breakthroughs that further promoted device performance. Further details of these two key performance techniques will be described in the following section. Overall, these achievements make CIGS an attractive material for further academic research as well as industrial upscaling. Currently, CIGS modules hold approximately 2 % of all PV markets [29] [30]. For a 15 % module efficiency, the production cost is about \$0.34 per W [29], which is competitive to c-Si production cost (trending to \$0.2 per W [31]). Solar Frontier, a PV company from Japan, is the biggest CIGS supplier and producer. The current capacity of their production line is 1 GW, and modules accumulating to 5 GW were already installed globally [32]. Even though CIGS is already considered a mature technology, there are still many unsolved puzzles underlying this complex material. This thesis is aimed at unravelling some critical effects in CIGS with the goal to enable significant advances in the future. In the following, the basic principles and properties of CIGS devices are described.

1.4.1 CIGS material properties

1.4.1.1 Crystal structure

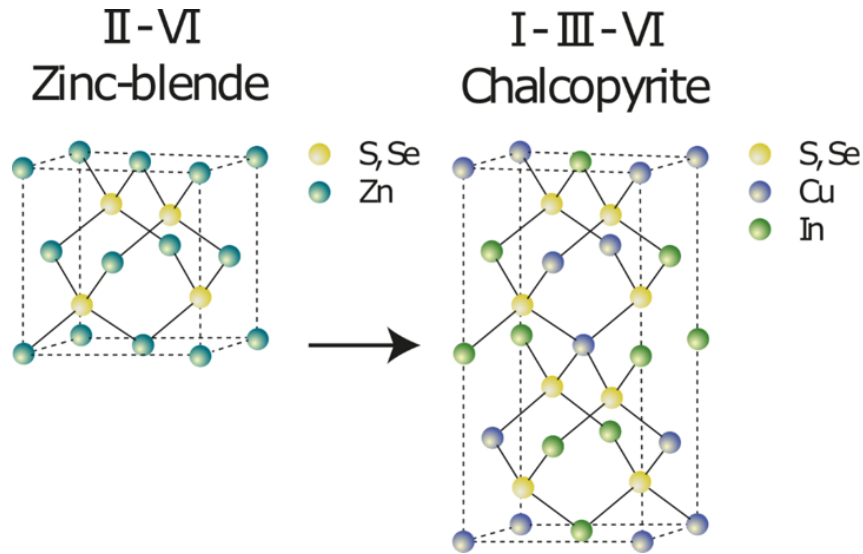


Figure 1.12: Schematic of zincblende and chalcopyrite structures. Figures reproduced with permissions under CC BY-NC 4.0 license from reference [13].

CIGS is a material of tetragonal chalcopyrite structure, as shown in Figure 1.12. The chalcopyrite structure is originally obtained from a cubic zincblende structure. Substitution of half of the Zn atoms with Cu atoms and the other half with In (and/or) Ga atoms leads to the formation of the chalcopyrite structure. Inside the unit cell, one Se atom forms two bonds with Cu atoms and another two bonds with In/Ga atoms. The asymmetry of Cu-Se bonds and In-Se/Ga-Se bonds induces a distortion (the lattice parameter ratio $(c/a) \neq 2$) in the lattice, which constitutes an additional difference to the symmetric Zincblende structure[33].

1.4.1.2 Band structure

CIGS is a direct bandgap material. The valence band maximum (VBM) is constituted of Cu 3d and Se 4p anti-bonding orbitals, whilst the conduction band minimum (CBM) is comprised of In/Ga 5s and Se 4p bonding orbitals[34]. Varying Ga to In ratio in the material (quantified by $GGI = [Ga]/([Ga] + [In])$) allows the modulation of the bandgap of the CIGS material[35]. The band-gap difference originates from the rise of the CBM with increasing Ga concentrations while the VBM stays relatively constant[34][36], as illustrated in Figure 1.13.

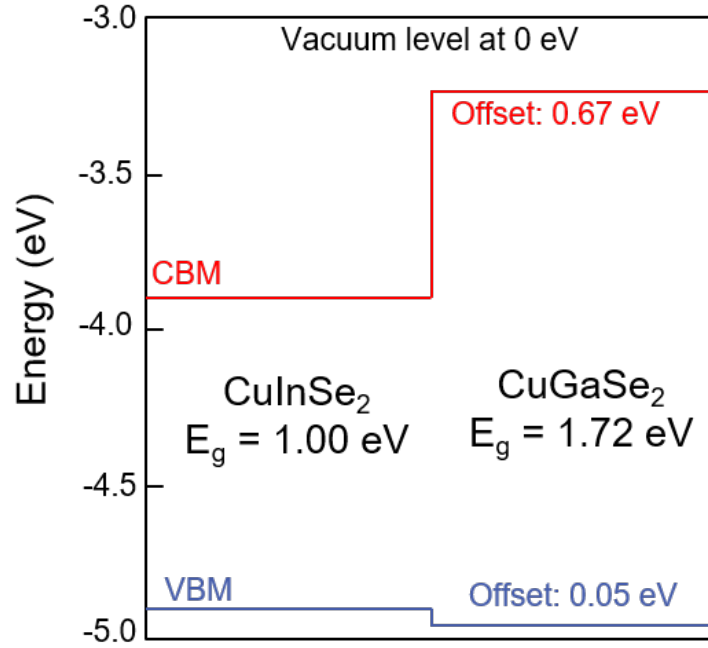


Figure 1.13: Comparison of the band alignment (VBM in blue, CBM in red) obtained by slab calculations of CuInSe₂ and CuGaSe₂. Figures reproduced with permissions of the copyright holder (ROYAL SOCIETY OF CHEMISTRY) from reference [34].

The band-gap in pure CIS is approximately 1 eV, whilst in pure CuGaSe₂ (CGS) the band-gap is around 1.7 eV [34][37][38]. The bandgap energy of CIGS can be approximated via the equation:

$$E_g(x) = E_{g,CIS}(1 - x) + E_{g,CGS}(x) - bx(1 - x) \quad (1.4)$$

,with x equal to the GGI ratio and b the measured bowing coefficient depending on growth conditions[36][39]. The GGI ratio along the CIGS absorber can be obtained by secondary ion mass spectrometry measurements, and bowing coefficients by a secondary polynomial fit of absorption coefficient spectrum[40].

1.4.1.3 Defects

Intrinsic defects play important roles in shaping the electronic properties of CIGS thin films. These defects can either act as shallow acceptors/donors or deep recombination centres. Numerous studies including theoretical calculations and experiments such as photoluminescence spectroscopy, neutron scattering and the Hall measurements have been performed in attempts to identify the origin of intrinsic defects. Different intrinsic defects based on the current findings[33][34][41][42][43][44] are categorized below, and Figure 1.14

from the publication of Spindler et.al illustrates the defect levels of different intrinsic defects[41].

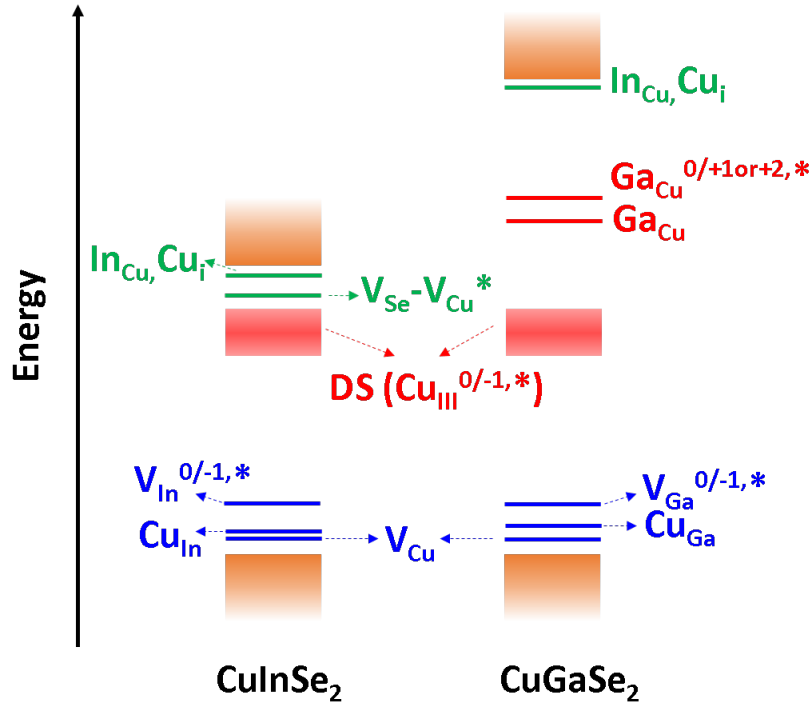


Figure 1.14: Illustration of the defect levels (including intrinsic defects and deep defects) in CuInSe_2 and CuGaSe_2 system. The one with a * mark means the defect assignment is with low certainty. This figure is adapted with permission under CC BY 4.0 license from reference [41].

i. shallow acceptors (coloured in blue in Figure 1.14)

The shallow intrinsic point defects determines the doping levels, and hence the electronic characteristics of the CIGS material. For CIGS grown under copper poor (Cu-poor) conditions, the dominant shallow acceptors are considered to be copper vacancies (V_{Cu}). For CIGS grown under copper rich (Cu-rich) conditions, copper atoms on indium sites (Cu_{In}) are the predominant shallow acceptors. Both V_{Cu} and Cu_{In} have low formation energies. Indium or gallium vacancies (V_{In} or V_{Ga}) are less likely to form due to their high formation energy (>2.5 eV). However, in some cases where CIS or low gallium CIGS has been grown under high selenium pressure, the presence of V_{In} was detected.

ii. shallow donors (coloured in green in Figure 1.14)

Indium atoms on copper sites (In_{Cu}) are regarded as the primary shallow donor states due to their low formation energy in Cu-poor CIGS. For Cu-rich CIGS, copper interstitials (Cu_i) are predicted to be the main shallow donors. In pure CGS, the dominant shallow

donor is considered to be Cu_i , since gallium atoms on copper sites (Ga_{Cu}) was calculated to be >0.4 eV below the conduction band.

Selenium vacancies (V_{Se}) have been viewed as the dominant donor states, especially in the material grown under a Se deficient atmosphere. However, recent studies revealed that the shallow donor states that were assigned to be V_{Se} before are rather a meta-stable defect complex ($V_{\text{Se}}\text{-}V_{\text{Cu}}$). So far, there is no consensus of the contribution of V_{Se} to the intrinsic doping in CIGS.

iii. Deep recombination centres (coloured in red in Figure 1.14)

Gallium atoms are suggested to be the major source for the formation of deep defects based on DFT calculations. Two charge states exist in Ga_{Cu} antisites, one is $+1/+2$, and the other is $0/+1$. Both of the charge states are buried deep below the conduction band (0.4 eV for the charge state $+2$, 0.25 eV for the charge state $+1$) in pure CGS. However, with the addition of In into the material, these deep defects become more shallow, and hence have less detrimental impact on the device performance, as shown in Figure 1.14. A broad density of defects located at approximately 0.8 eV above the valence band were detected in both CIS and CGS. Their origin is considered to be point defects such as Cu_{In} or Cu_{Ga} . This hypothesis is supported by both theoretical and experimental data. However, the existence of point defects does not explain such a broad energetic defect distribution in the bandgap as well as high defect densities. Grain boundaries and dislocations were also hypothesized to be a plausible source for these defects, but experimental results disprove this. Hence, the origin of these defects remain unknown so far.

1.4.2 CIGS device properties

CIGS is a p-n heterjunction solar cell. Figure 1.15 (a) shows the typical layer structure of a CIGS solar cell. A $0.5\text{--}1\mu\text{m}$ thick molybdenum (Mo) layer is deposited on the substrate and serves as the back contact of the device[45][46]. On top of the Mo layer is the p-type CIGS layer, which acts as the main light absorber of the cell. The typical thickness of the CIGS absorber is around 2 to 3 μm . Two deposition techniques include 1. three-stage co-evaporation process[47][48], and 2. selenization process[49] are commonly used as both lead to high device efficiency. A chemical bath deposition of CdS layer of approximately ≤ 50 nm thickness on top of the CIGS is the buffer layer of the device[50][51][52]. Among other functions, it naturally forms a p-n heterojunction with the p-type CIGS

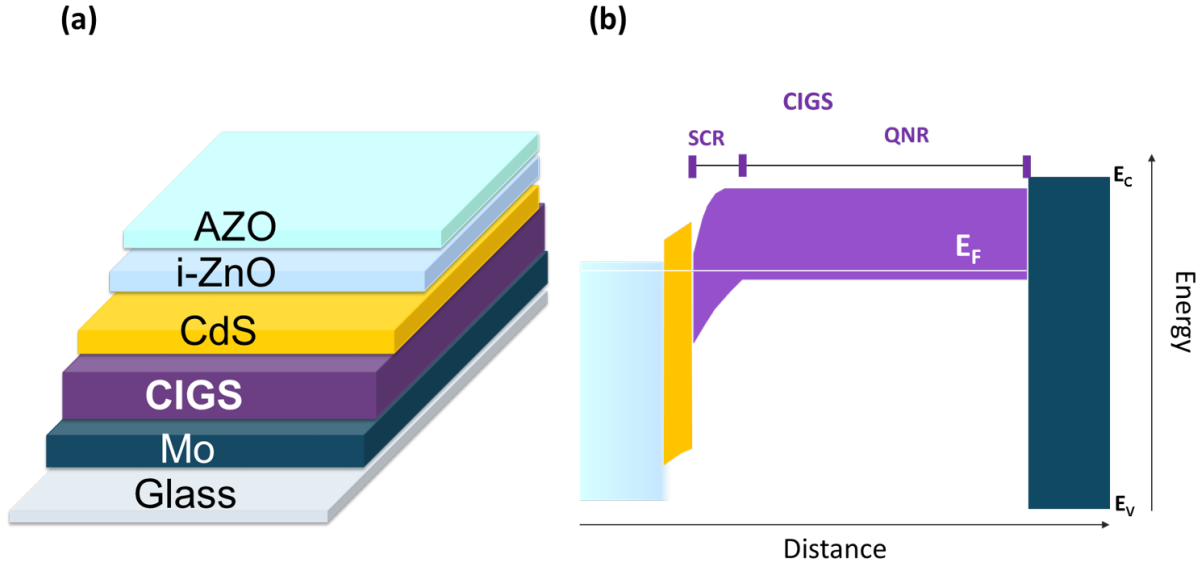


Figure 1.15: (a) Schematic of a typical CIGS solar cell stacks and its corresponding (b) band diagram at equilibrium in the dark.

absorber[53][54][55]. The window layer of the cell, ~ 60 nm of i-ZnO and ~ 100 nm of heavily aluminium doped ZnO (AZO), are deposited by sputtering[48]. Ni/Al metal grids serve as front contact and are deposited by e-beam evaporation. An anti-reflective coating layer (ARC) is often applied to further increase efficiency in solar cells[56].

Figure 1.15 (b) illustrates the band diagram of a typical CIGS solar cell shown in Figure 1.15 (a) at equilibrium in the dark. In CIGS solar cells, due to a high doping concentration of CdS, the SCR is primarily extended 300 nm to 600 nm into a CIGS of 10^{16} doping density at room temperature[33][57][58]. If free charge carriers enter the SCR, they will be accelerated forward by the electric field and possess mobilities. The mobility of the minority charge carriers differs greatly in CIGS field. It depends significantly on the choice of measurement tools and the results are in the range of 0.02 to 1000 $\text{cm}^2/\text{V.s.}$ **A more detailed discussion on the mobility of minority charge carrier is given in Chapter 4.** On the other hand, the diffusion length inside the CIGS film correlates highly with the GGI ratio. For pure CIS, the diffusion length is around 3 μm , whilst for pure CGS, it's only about 0.7 μm . To avoid recombination at grain boundaries, it is essential to have a diffusion length that has a similar range as the film thickness. Hence, one would expect to observe a higher recombination rate at grain boundaries in CIGS device with a high Ga concentration. Note that the band discontinuities present at the interfaces inside the CIGS device are due to the different bandgaps of materials[18].

1.4.3 Ga gradient for bandgap engineering



Figure 1.16: Schematic of the double Ga-gradient CIGS profile.

Looking back to the historical improvements in CIGS solar cell performance, varying the GGI ratio to modulate the device band gap, as introduced in Chapter 1.4.1.2, plays a very important role. A double Ga-gradient profile (Ga-rich/Ga-poor/Ga-rich) is commonly implemented in high-efficiency CIGS solar cells[25][48][59]. This double Ga gradient profile refers to an increasing GGI ratio towards the back and front contact, resulting in a GGI minimum region in between, as shown in Figure 1.16. The length of the front contact gradient is designed to be within SCR[60]. Also, the GGI ratio is designed to increase more towards the back contact than the front contact. Increasing Ga concentrations has been shown to induce a spatial gradient in the conduction band edge, whilst the valence band stays comparatively unchanged. The potential gradient in the conduction band edge from the back contact leads to an electric field that drives the minority charge carriers towards the SCR[61]. As a result, the reduction in the electron density near the back contact has been shown to suppress recombination losses, thereby considerably increasing device open-circuit voltage[59][62][63].

Optimisation of the CIGS film thickness, composition and the Ga-gradient profile has largely been carried out largely following observed improvements of device efficiency[26][48][64][65][66][67][68][69][70][63], yet the minority charge carrier dynamics inside a Ga-graded CIGS are still under investigation[69][71][72][73][74]. **In this thesis, a key aim is to elucidate these minority charge carrier dynamics in such devices via a series of optical measurements.**

1.4.4 Alkali PDT treatment in CIGS

1.4.4.1 Overview

The importance of alkali atoms was first realized in 1993 by Hedstrom, who observed a clear loss of open-circuit voltage (V_{OC}) and fill factor (FF) after changing the device substrate from soda-lime glass (SLG) to borosilicate glass[75]. It was proposed that diffusion of Na during CIGS synthesis resulted in the enhancement in crystal quality and electronic properties that eventually lead to the improvement of device efficiency. Later in 1997, Contreras et al. deposited a thin-MF precursor layer (M= Na, K, Cs) prior to CIGS deposition and discovered that Na, K and Cs all unexpectedly enhance device performance, but Na has the single largest positive impact[76]. Since then, alkali treatment in CIGS solar cells is considered as an essential procedure for achieving high device efficiencies. There are several ways of alkali atoms incorporation[77], for example, utilization of SLG substrates (in the case of Na incorporation), employment of an alkali atoms precursor on the device substrate prior to the CIGS synthesis, and alkali atom post deposition treatments (PDTs). With PDTs, it has been suggested that the amount of alkali atoms diffusing into the CIGS absorber layer can be controlled precisely[27][77]. Besides, PDTs are highly compatible with different CIGS synthesis routes and substrates. For example, PDTs are widely implemented in CIGS absorbers which utilize low temperature deposition processes, and also can be employed on a CIGS absorber that is grown on a flexible substrate[48]. In 2011, Chirila et al. utilized NaF and KF post deposition treatment on the CIGS absorber layer deposited on a polyimide substrate, boosting device efficiency from below 16 % to 20.3 %[48]. Jackson et al. raised the efficiency of CIGS cell to 22.6 % by implementing RbF PDT in 2016[78].

1.4.4.2 NaF PDT

The effects of Na have been intensively investigated in the CIGS research community. It is generally observed that the open circuit voltage and fill factor increase with the optimal Na incorporation[79][80][81][82]. Several studies correlated the increase in the open circuit voltage and fill factor with the increased p-type character of the sodium treated CIGS absorber[79][81][83][84], which can be explained by the following three reasons. First, DFT calculations[85][86][87] and experimental results suggest that Na is incorporated into the

CIGS lattice by migration via copper vacancies (V_{Cu}) or interstitial sites due to the low migration energy[88][89]. Consequently, a reduction of compensating donors such as In_{Cu} anti-sites is achieved by Na atoms occupying Cu or In vacancies (i.e. forming Na_{Cu} , Na_{In} anti-sites)[76][81][84][87][90]. Second, since the solubility of Na in CIGS is temperature dependent, it has been reported that Na is prone to diffuse out from the copper sites during the cool down process after the PDT, leaving behind V_{Cu} in the bulk[86][87][91]. Indeed, higher concentrations of V_{Cu} have been measured and account for the increased p-type conductivity observed after Na incorporation[91]. Last, it is proposed that Na atom acts as a catalyst, oxidizing Se vacancies that act as compensating donors[80].

Other studies showed that the increase in V_{OC} and FF can result from the passivation of non-radiative recombination centres at grain boundaries (GBs), supported by several atom probe topography studies showing Na accumulation predominantly at GBs compared to grain interiors (GIs)[90][92][93][94][95].

Transient optical studies also showed a correlation of increased minority carrier lifetime with optimal Na atoms incorporation[96][97]. Nevertheless, the passivate with Na atoms on grain interiors and/or grain boundaries are still under investigation. More discussion on how Na impacts minority carrier lifetime and whether it passivates grain interiors and/or grain boundaries will be followed in Chapter 5.

1.4.4.3 RbF+NaF PDT

In the case of applying a combined NaF+RbF PDT, Rb atoms can easily replace the position of Na atoms at grain boundaries and cause Na migrating into the grain, as evidenced by atom probe topography and secondary ion mass spectroscopy experimental results[98][99]. However, unlike Na atoms, Rb atoms are much more likely to form a secondary phase: Taguchi et al. discovered the formation of a RbInSe₂ thin layer on the CIGS ($GGI = 0.2\text{--}0.3$) surface via transmission electron microscopy[100], which was found to create an additional valence band offset at the CIGS/CdS junction, leading to reduced recombination at this interface[27][101]. Besides, the modified front interface of the CIGS absorber layer improves the coverage of CdS, and therefore, a less thick CdS layer is needed to form a good CdS/CIGS junction[102][103]. Since the parasitic absorption of CdS increases with its thickness, a thinner CdS layer allows more photons to enter the CIGS absorber, leading to an increase in J_{SC} [102]. A recent Kelvin-Probe force microscopy (KPFM) study demonstrated that the Rb segregation at GBs have a beneficial effect on the band bending at GBs, leading to an increase in open-circuit voltage in the CIGS device[104][105]. However, we need to put into consideration that KPFM detects the characteristics of grain boundaries only at the surface and the analysis was conducted solely on the area where the Ga concentration of the CIGS device is low ($[Ga]/([Ga] + [In])(GGI) = 0.32$). In addition to the beneficial effect of Rb on CIGS surfaces, it is also proposed that Rb incorporation reduces non-radiative recombination centres in the space charge region. Heinemann et al. indicated the Rb treatment reduces the rate of bulk recombination by utilizing J-V measurements along with device simulations[106]. Siebentritt et al. recently observed the radiative efficiency and the quasi-Fermi level splitting (i.e. photovoltage) both to increase by similar amounts in RbF-treated Ga-graded CIGS and concluded that the alkali treatment suppresses recombination in the space charge region due to a decrease in tail states[105]. However, these studies mainly revealed the influence of Rb on the regions within 1 μm depth (out of a $\sim 3\mu\text{m}$ film), where typically the GGI ratio is below 0.5. In a Ga-graded CIGS device, where GGI ratio varies strongly and may lead to a distinct microstructure throughout CIGS film, the effect of Rb on minority carrier dynamics is not yet understood.

1.4.5 Photophysics studies of CIGS

In the following, photo-physical studies on CIGS utilizing external quantum efficiency (EQE) measurement tools, steady state UV-VIS spectroscopy, steady state and transient PL spectroscopies, and pump-probe spectroscopy are given. Note that a detailed introduction of each instrument including theoretical principles and experimental details will be given in Chapter 2 instead.

1.4.5.1 External quantum efficiency studies

For the current state-of-the-art CIGS solar cell with a device efficiency of 23.5 %, the corresponding SQ limit almost reached 75 % [16] (see Figure 1.5(b)).

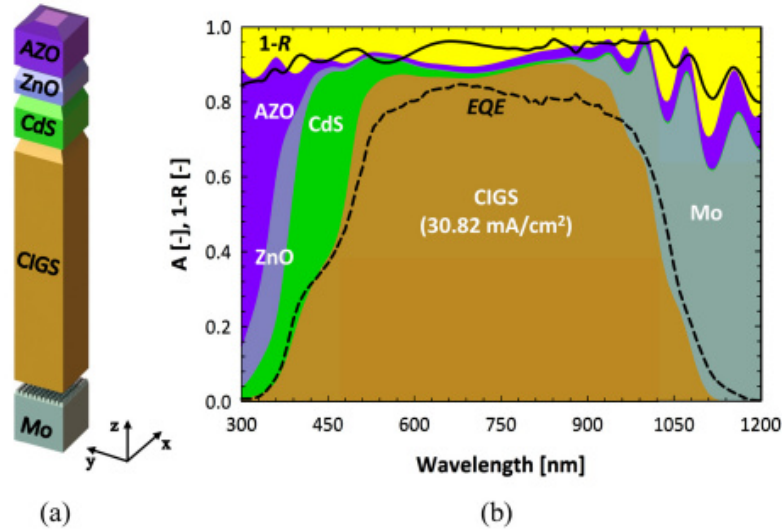


Figure 1.17: (a) CIGS device structure utilized for EQE simulation model. Thicknesses of layers from top to bottom are (in nm): 250, 60, 70, 1600 and 320. (b) Comparisons of simulation EQE results with the EQE measurement data (shown in dashed lines) and 1-R (shown in solid lines) data. The areas with different colour indicate the light absorption by each material. This figure is reproduced with permissions of the copyright holder (OSA Publishing) from reference [107].

EQE is equal to the ratio of the amount of charge carriers collected to the total number of incident photons. Since EQE efficiency is directly affected by both the light absorption and charge collection rate, simulating EQE performance of a solar cell allows to analyse the loss mechanisms in a solar cell [107]. Figure 1.17 illustrates a simulated EQE result compared to the measurement data of a CIGS device. Here, the EQE loss mechanisms

can be simply classified into three categories: reflection, absorption, and recombination losses. First of all, approximate 10 % of the overall incoming light is reflected and will not be absorbed CIGS (shown as the yellow area in Figure 1.17). Second, it is obvious that the window layer (AZO and ZnO) and buffer layer (CdS) absorbs majority of the light in the range of 300–450 nm. Furthermore, most of the light in the near-IR range (1050 nm onward) is either absorbed by Mo or will not be absorbed by CIGS due to the photon energy is smaller than the CIGS bandgap. Third, comparing the simulated EQE (brown area in Figure 1.17) to the measurement data of CIGS (dashed lines in Figure 1.17), an EQE loss in the range of 450 – 1000 nm is observed. This is because charge carriers recombine (due to the presence of defects) before they get collected.

Takuya Kato from Solar Frontier further analysed the EQE performance in correspondence with device properties with simulation techniques[49]. The analysis was performed on a 19.7 % CIGS solar cell and the results showed that this device (blue triangle with light grey square in Figure 1.18a) is just above 60 % SQ limit, as shown in Figure 1.18a. Figure 1.18b shows losses in the efficiencies of this device relative to SQ limit. First, for the loss channel of V_{OC} and FF, it is obvious that defects (yellow colour) are the main channels for elimination of charge carriers. These defects correspond to non-radiative recombination centres for charge carriers, as discussed in the previous section. On the other hand, the shortage of J_{SC} mainly results from the loss due to transmission (dark blue with diagonal lines), absorption (light blue with straight lines) and reflection (blue white stripes). This result agrees well with the simulation EQE simulation results presented in Figure 1.17.

1.4.5.2 Steady state UV-VIS studies

UV-VIS is a common tool to investigate the steady-state optical signals of a material. Figure 1.19 illustrates steady-state optical signals (transmittance (T), reflectance (R), and absorptance(A)) of a non Ga-graded ($GGI = 0.29$, $CGI = 0.82$) CIGS sample before and after Br wet polishing examined by Carron et al.[40]. The sample (*SLG/Epoxy/CIGS*) for the UV-VIS measurement was prepared by mechanically peeling of the CIGS layer from Mo back contact. This is to examine the optical properties of films deposited in the conditions as that of high-efficiency devices. The transmittance and reflectance were measured directly, in contrast, the absorbance was calculated by: $A = 1 - T - R$. The

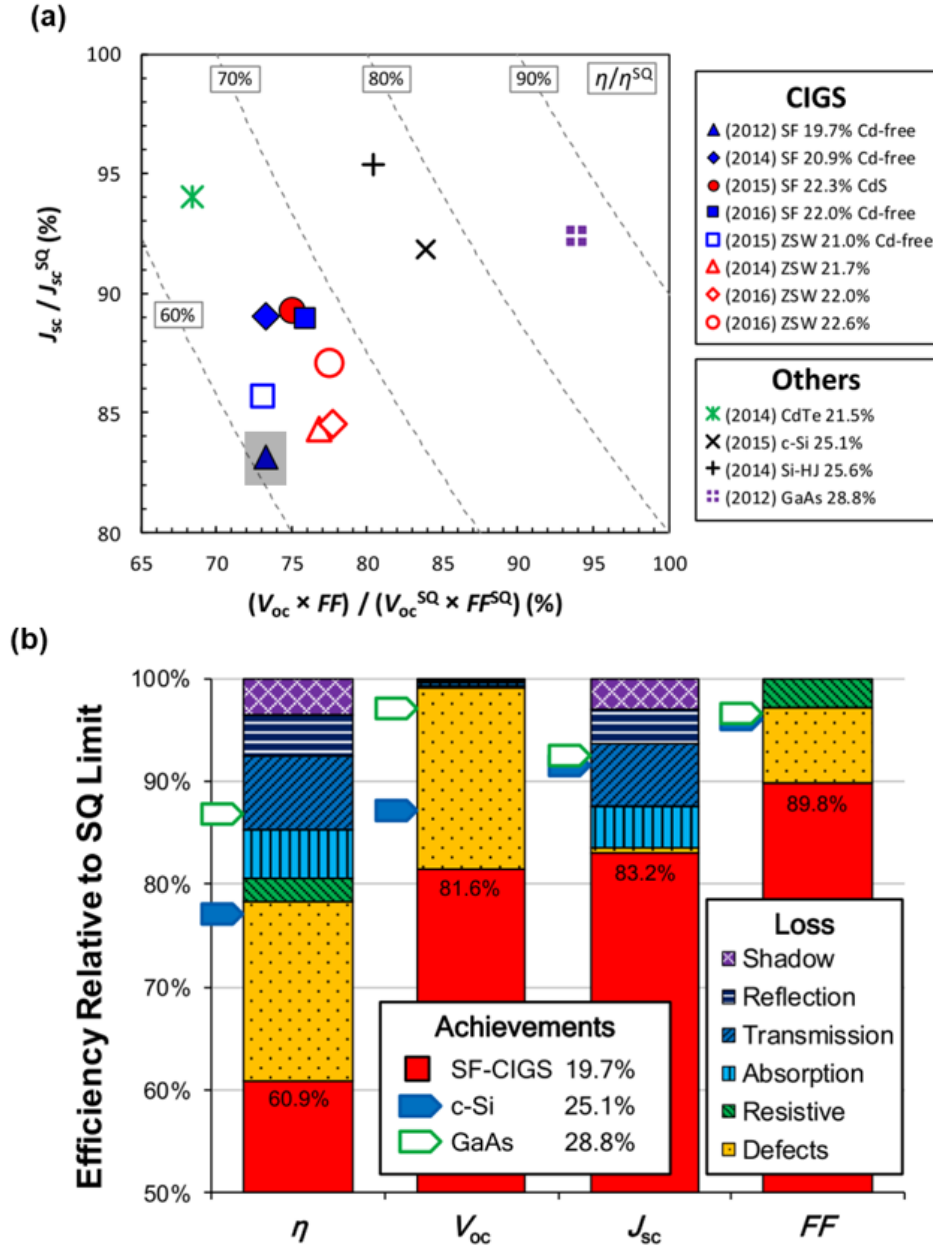


Figure 1.18: (a) Optical efficiency versus electrical efficiency with respect to SQ limit of different record solar cells. (b) Loss analysis on a 19.7 % CIGS device (blue triangle with light grey square in (a)). The analysis was performed by combining the simulated results of EQE and device performance. This figure is reproduced with permissions of Copyright (2017) The Japan Society of Applied Physics from reference [49].

Br wet polishing procedure is to reduce CIGS surface roughness. It can be seen that the optical signals in the infrared range oscillated much more significantly in the sample etched with Br than the one without, as shown in Figure 1.19a. Furthermore, 10% absorptance signal appearing in the infrared range in the non-polished sample disappeared after Br wet

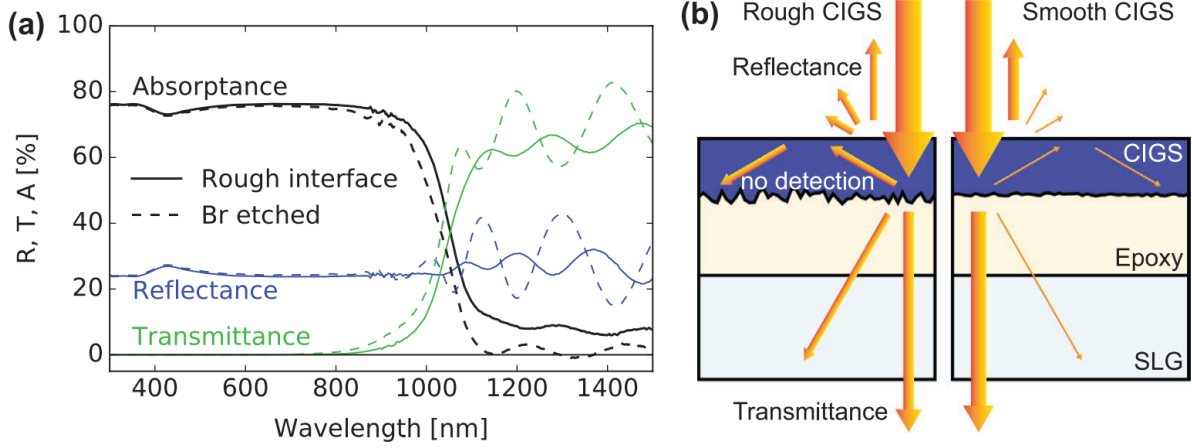


Figure 1.19: (a) Steady state optical signals (transmittance, reflectance, and absorptance) of a SLG/Epoxy/CIGS ($GGI = 0.29$, $CGI = 0.82$, $E_g = 1.198\text{eV}$) obtained from UV-VIS measurements. The continuous lines and dash lines correspond to CIGS with and without wet Br polishing, respectively. (b) Schematic of the light absorption affected by light scattering, reflection, and light trapping within layers owing to different scale of surface roughness of the CIGS layer. Figures reproduced with permissions under Creative Commons Attribution License from reference [40].

polishing. As illustrated in Figure 1.19b, when a light source passes through a sample with a rough surface, light is much more easily scattered and trapped within layers compared to a sample with a smooth surface, resulting in an overestimated absorption but reduced oscillation in transmittance and reflectance signal in the infrared range. UV-VIS optical signals are also utilized to estimate the optical bandgap of a material. For the CIGS sample without Ga gradient, plotting a Tauc plot following Equation 1.5 (α : absorption coefficient, h : Planck's constant, ν : photon's frequency, B : constant, E_g : optical bandgap, and γ : $\frac{1}{2}$ for direct bandgap material) is the most straightforward method. Figure 1.20 shows an estimation of the optical bandgap of a CIS thin film from a Tauc plot. In addition, extracting the optical bandgap from the 1st derivative of UV-VIS absorptance is also common in the circumstance when a dominant absorptance signal exists[109][110].

$$(\alpha h\nu)^{\frac{1}{\gamma}} = B(h\nu - E_g) \quad (1.5)$$

It is important to note that the optical bandgap of a Ga-graded CIGS sample cannot be simply calculated by constructing a Tauc plot. Instead, one can determine the optical bandgap along a Ga-graded CIGS film by Equation 1.4, as introduced earlier in Chapter 1.4.1.2.

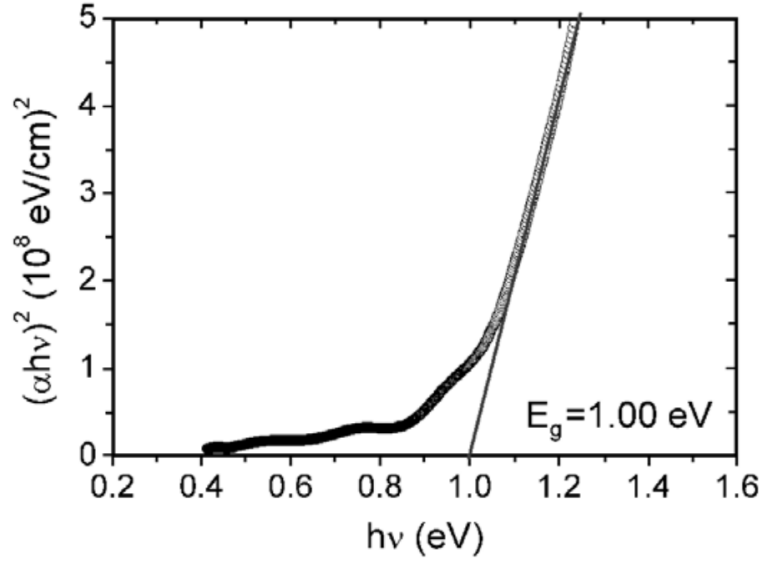


Figure 1.20: Tauc plot of a CIS thin film (thickness: $1.3 \mu\text{m}$). Figures reproduced with permissions of the copyright holder (Elsevier) from reference [108].

1.4.5.3 Photoluminescence (PL) studies

i. Steady state PL

PL spectroscopy can be utilized to characterize radiative transitions of charge carriers in materials. As illustrated previously in Figure 1.11, radiative recombination can occur via 1) band-to-band transition, 2) donor-to-acceptor transition, and 3) CBM-to-acceptor or donor-to-VBM transitions. One can distinguish and identify these transitions by measuring PL at low temperature[113][114][115]. At room-temperature, the PL signals often exhibit near-band-edge characteristics as band-to-band transitions are dominant[116]. An example can be seen in Figure 1.21a, both CIGS (GGI=0.41) cell and film showed a dominant near-band-edge PL peak at room-temperature[111]. However, the other two transitions may also appear or be dominant in the PL spectrum depending on the material quality. For example, in Figure 1.21a, the PL spectrum of the CIGS film showed two extra peaks below the near-band-edge peak. These two peaks were assigned to CBM-to-acceptor and donor-to-VBM transitions[111]. Another example is shown in Figure 1.21b, where two CIGS devices with bandgap energies of 1.21 eV exhibit PL peaks smaller than the bandgap. This blue-shifted PL originates from the donor-to-acceptor transitions due to the Cu-poor conditions of the CIGS devices[112]. Another important fact

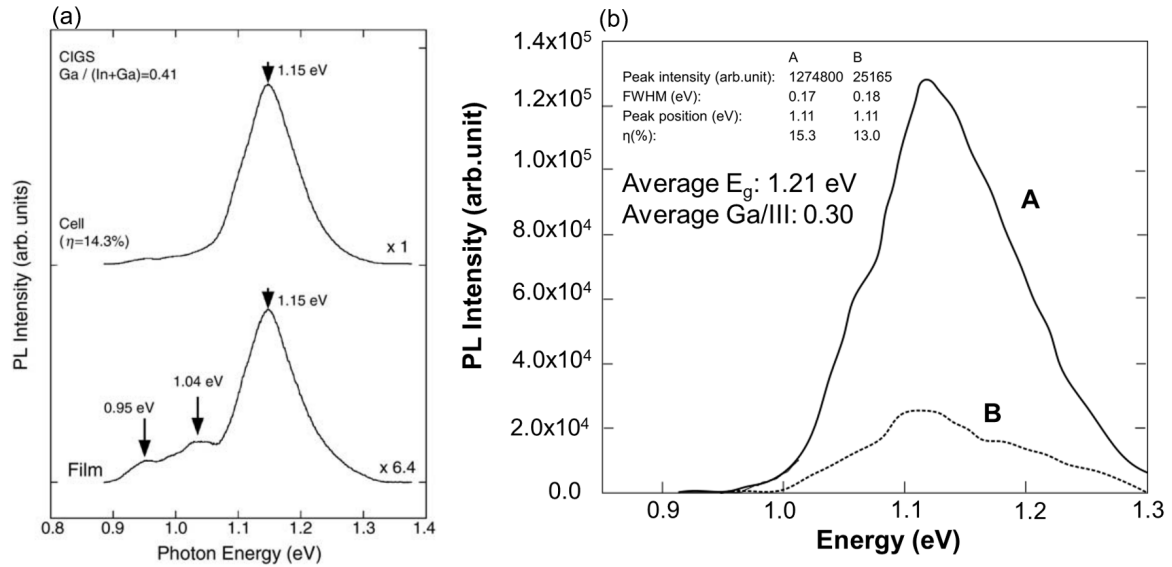


Figure 1.21: (a) Room temperature PL spectra of a CIGS cell and an as-deposited CIGS thin film. The GGI ratio is 0.41 for both the cell and the film. Figures reproduced from reference [111] with permissions from the copyright holder (Elsevier). (b) Room temperature PL spectra of two CIGS devices (device efficiency of A and B is 15.3% and 13.0%, respectively) of 1.21 bandgap energies. Figures adapted from reference [112] with permissions from the copyright holder (Elsevier).

to point out is that PL is also an indicator for material quality. In Figure 1.21a, the PL amplitude of the CIGS film is 6.4 times smaller than the one of the cell. In Figure 1.21b, the CIGS device with higher efficiency (device A) exhibited a higher PL amplitude than the one with lower efficiency (device B). To summarize, a material exhibiting a higher PL amplitude indicates reduced non-radiative recombination transitions.

ii. Time-resolved PL (TRPL)

Time-resolved PL is often utilized for the determination of the minority charge carrier lifetime in CIGS materials. Figure 1.22 shows a typical TRPL signal of a CIGS device of high device efficiency (18–19.4%). The TRPL data was fitted with a single exponential function and a decay time constant of 250 ns was obtained. This time constant was assigned to the minority charge carrier lifetime. The minority charge carrier lifetime obtained from TRPL measurements are sensitive to measurement conditions, injection levels, and material quality [69][117].

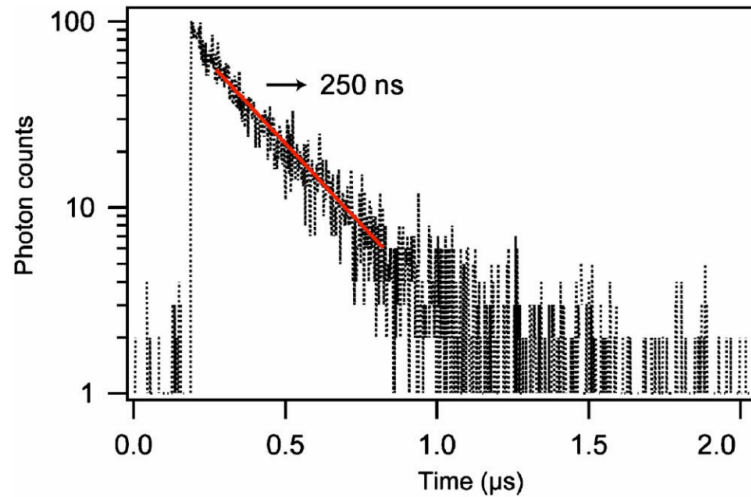


Figure 1.22: Time-resolved PL of a polycrystalline CIGS thin film corresponding to 18–19.4% devices. The red coloured line indicates a single exponential fitting of the TRPL data. This figure is reprinted from Appl. Phys. Lett. 93, 022110 (2008) [117], with the permission of the copyright holder (AIP Publishing).

1.4.5.4 Optical pump-probe spectroscopy studies

Optical pump-probe spectroscopy such as transient absorption spectroscopy (TAS), transient reflectivity spectroscopy, and optical pump terahertz probe spectroscopy allows to measure a wide range of charge carrier dynamics including electron-hole pair recombination, charge carrier transfer, charge trapping. Unlike PL spectroscopies which measure radiative recombination of a material, optical pump-probe spectroscopy measures non-radiative processes. Optical pump-probe spectroscopy has been utilized in the fields of organic and hybrid organic-inorganic perovskite photovoltaic materials[118][119][120][121], but so far only a few optical pump-probe studies have been conducted in the CIGS field. In 2012, Chen et al. studied the charge carrier relaxation processes in sputtered and co-evaporated CIGS devices and found the relaxation mechanisms vary significantly with different deposition processes[122]. Later in 2014 and 2015, Okano et al. published a series of transient absorption spectroscopy (TAS) studies, investigating the intraband charge carrier relaxation and localization processes in an ultra-thin film CIGS absorber layer (film thickness around 200 nm) at fs to ns timescales[123][124][125]. A TA spectrum of such CIGS film published in one of their studies is shown in Figure 1.23 as an example. It can be seen that a photobleach signal at 1.25 eV was dominant in the whole spectrum and this feature was assigned to the band to band transition of charge carriers.

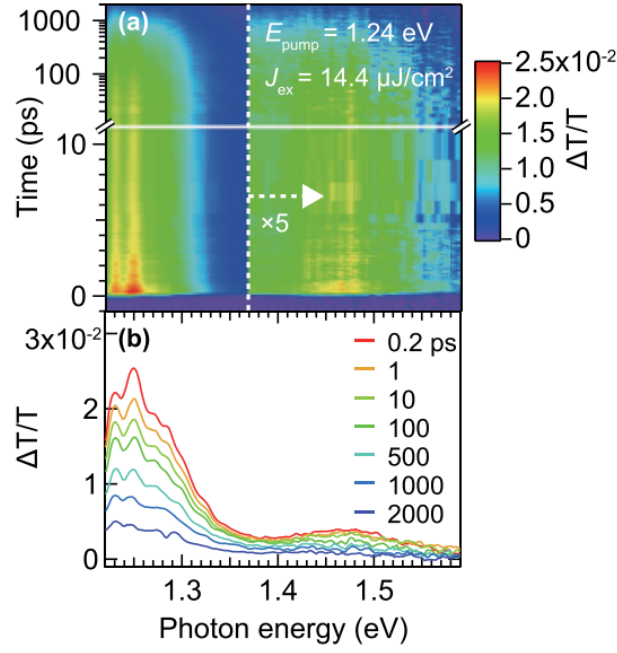


Figure 1.23: (a) Transient absorption map of a $E_g = 1.24$ eV CIGS thin film. (b) Transient absorption spectra of (a) recorded at 0.2, 1, 10, 100, 500, 1000, 2000 ps. The CIGS thin film is excited following 1000 nm excitation wavelength. This figure is reprinted from Appl. Phys. Lett. 106, 181903 (2015) [123], with the permission of the copyright holder (AIP Publishing).

Optical pump-probe spectroscopy can also be utilized to investigate the impact of different interfaces on charge carrier lifetime in CIGS devices. Lee et al. investigated charge carriers from the surface and the bulk by exciting the CIGS film with 400 nm and 800 nm excitation energies[126]. Parts of their results are reproduced here in Figure 1.24. As shown, a faster decay kinetics was observed in the 400 nm excitation case, which was proposed to be associated with a higher amount of V_{Cu} defects serving as electron scavengers close to the surface. In this thesis, TAS is utilized as the main tool for the analysis of charge carrier dynamics in alkali atoms treated and Ga-graded CIGS devices, and more optical pump-probe studies will be discussed along with the experimental results.

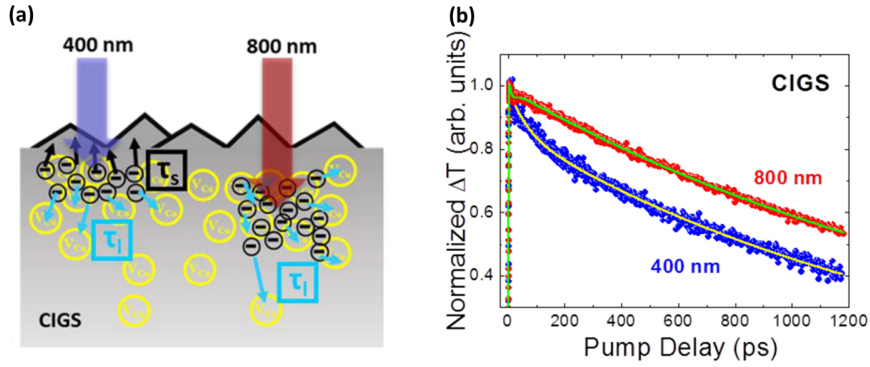


Figure 1.24: Schematic of electron dynamics of CIGS following excitation with 400 nm and 800 nm excitation energies. Yellow circles indicate V_{Cu} defect. τ_s and τ_l correspond to charge carrier trapped by defects at the surface and in the bulk, respectively. (b) Normalized ΔT (transmittance) signals as a function of time of the CIGS thin film following 400 nm and 800 nm excitation. This figure is adapted from reference [126], with permission from ACS Appl. Energy Mater. 2018, 1, 2, 522–530. Copyright (2018) American Chemical Society.

1.5 Introduction to Sb_2Se_3 solar cells

Sb_2Se_3 , a p-type semiconductor of bandgap ranging from 1-1.2 eV, high absorption coefficient, and earth-abundant constituents, is considered as a promising material for next generation solar cells/solar fuels. Below gives a brief introduction on the basic material and optical properties of Sb_2Se_3 .

1.5.1 Crystal structure

Sb_2Se_3 is a binary compound of orthorhombic crystal structure, as shown in Figure 1.25. The lattice constant is listed as follows: $a = 11.6330 \text{ \AA}$, $b = 11.7800 \text{ \AA}$, $c = 3.9850 \text{ \AA}$ [127]. It can be seen that the crystal exhibits a long ribbon-like structure of $[\text{Sb}_4\text{Se}_6]_n$ units along the $[001]$ direction. And between each ribbon, a clean plane is in between. Consequently, the bonding inside the ribbon is strong (covalent bond), whilst in between each ribbon is weak (van der Waals) [127]. It is claimed that the one dimensional ribbons are beneficial for charge carrier transporting.

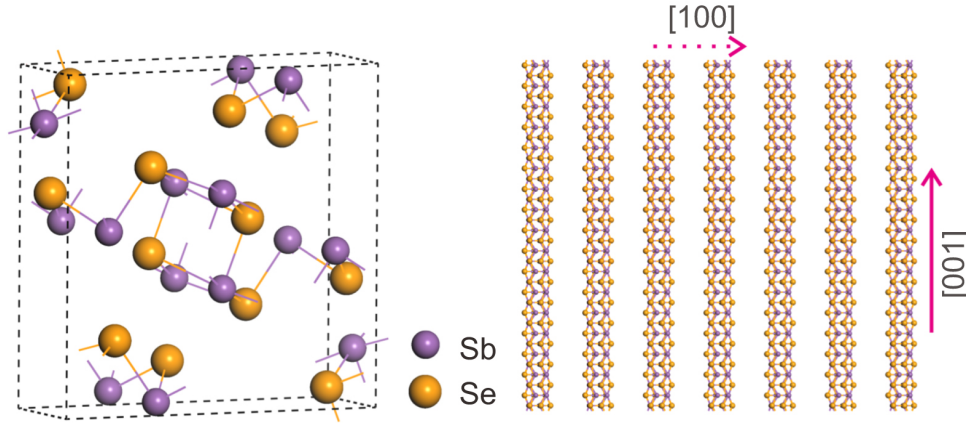


Figure 1.25: Crystal structure of Sb_2Se_3 . Se and Sb atoms are represented by yellow and brown balls, respectively. This figure is reproduced with permission of the copyright holder (IOP Publishing, Ltd) from reference [127].

1.5.2 Bandgap

Figure 1.26(a) shows both partial and total density of states (DOS) of Sb_2Se_3 . It can be seen that the highest occupied valence band is mainly contributed by Se 4p orbitals, whereas the lowest conduction band is mainly contributed by Sb 5p states. Figure 1.26(b) shows the first Brillouin zone allowing to see if Sb_2Se_3 a direct or indirect bandgap material. It can be seen that the VBM is located at Γ point, whereas the CBM is located between Γ and Y point. This indicates that Sb_2Se_3 can have both direct and indirect transition. It is often reported that the direct bandgap of Sb_2Se_3 is approximately 1.2 eV, whilst the indirect bandgap is close to 1 eV [127] [128]. As discussed in previous section 1.3.1, bandgap within the range of 1.1 to 1.5 eV allows to have maximum theoretical solar cell efficiency. For Sb_2Se_3 solar cell the theoretical efficiency is above 30%, though the current state of the art efficiency is still far from this target.

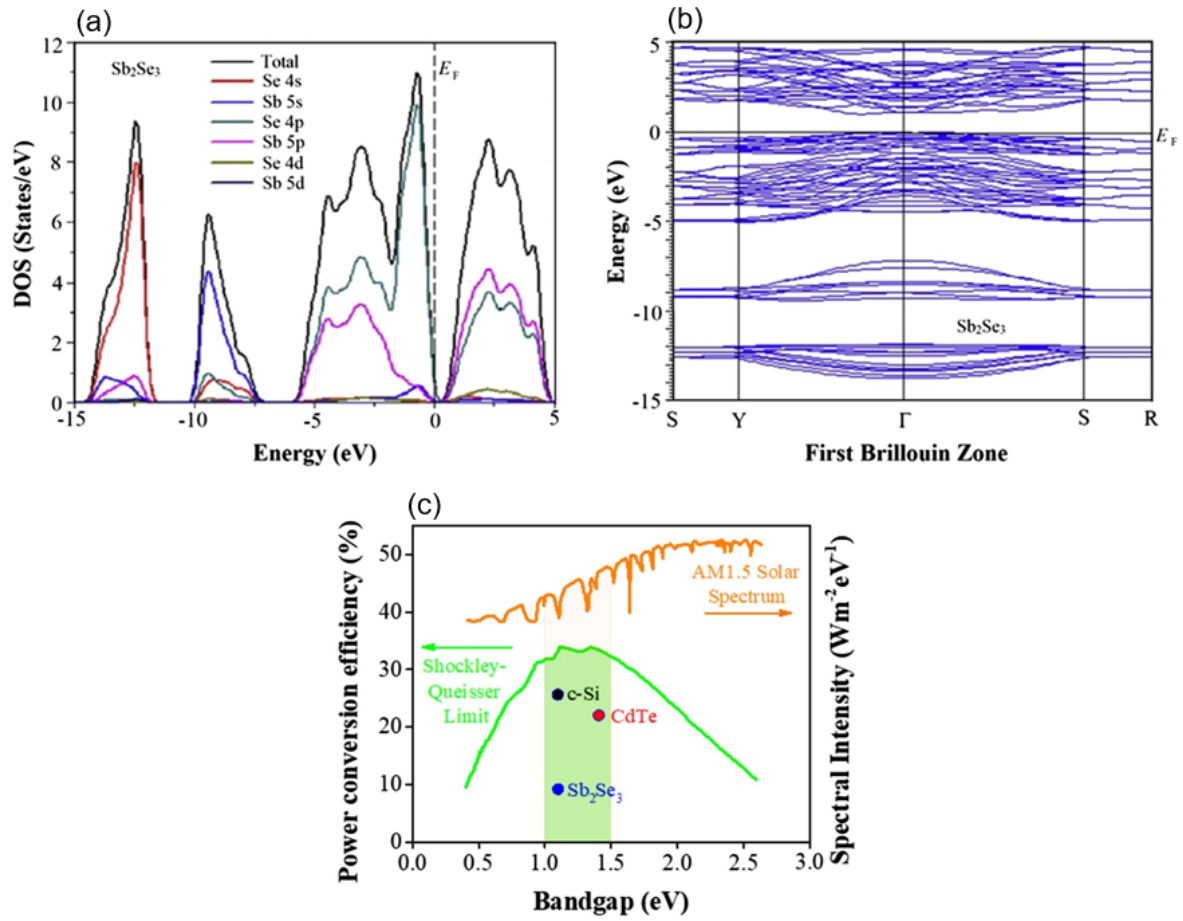


Figure 1.26: (a) Total and partial density of states (DOS), (b) energy band diagram in first Brillouin zone, and (c) the S-Q limit of Sb_2Se_3 . This figure is reproduced with permission of the copyright holder (Elsevier) from reference [129].

1.5.3 Device structure of Sb_2Se_3 solar cells

Here the device structure of the current state-of-the-art thin film Sb_2Se_3 solar cell (efficiency: 7.6 %) is given as an example [130], as shown in Figure 1.27.

It can be seen that the device structure is analogous to a typical CIGS solar cell. Sb_2Se_3 is the main light absorber with a thickness of 900 nm, fabricated by vapor evaporation method on top of the n-CdS/ITO/Glass substrate. Similarly to CIGS solar cells, the n-type CdS layer forms a p-n heterojunction with the p-type Sb_2Se_3 layer and serves as an electron transport layer. Figure 1.28 illustrates the band alignment of a wide range of transparent electrode (TE), window/buffer, hole transport layer (HTL), and back contacts (BCs) in Sb_2Se_3 solar cells. As illustrated, it is desirable to choose a buffer/window layer with relatively low conduction and valence band energies as it helps to transport electrons

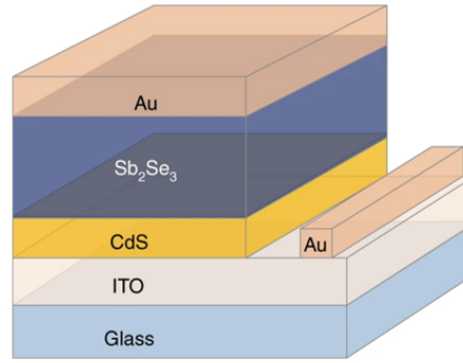


Figure 1.27: The device structure of the current-state-of-the-art thin film Sb_2Se_3 solar cell. This figure is reproduced with permission of the copyright holder (Springer Nature) from reference [130].

and at the same time block holes. The interface at absorber/back contact is notorious for having numerous interface recombination for its semiconductor/metal Schottky junction. Consequently, implementing a hole transport layer which not only assist holes transport but also serve as a buffer between the semiconductor/metal Schottky junction is found to improve device efficiency [131][132].

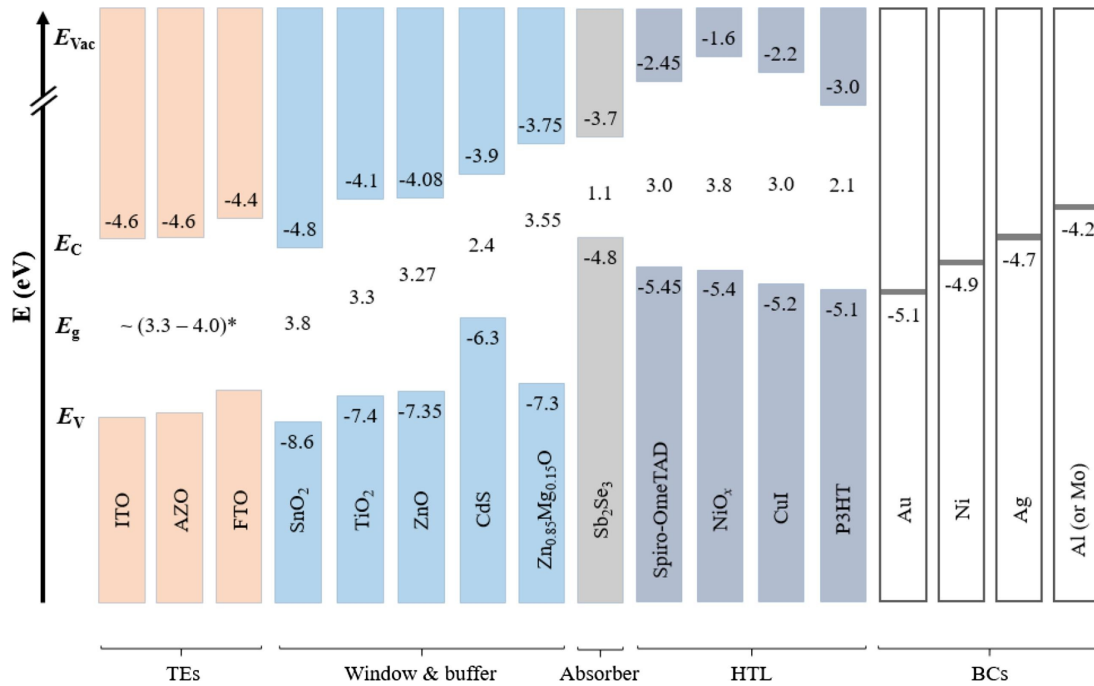


Figure 1.28: Band alignment of a wide range of transparent electrode (TE), window/buffer, hole transport layer (HTL), and back contacts (BCs) in Sb_2Se_3 solar cells. This figure is reproduced with permission of the copyright holder (Elsevier) from reference [129].

1.6 Thesis aim and outline

This thesis aims to unravel the impact of bandgap tuning by Ga grading and alkali atoms incorporation into the CIGS absorber layer on the device performance from a minority charge carrier kinetics point of view. The structure of the thesis is listed below:

i. Chapter 2 - Experimental methods:

This chapter will give a detailed introduction to the working principles of the measurement equipment including data interpretation and analysis. The main focus will be on optical spectroscopy including transient absorption spectroscopy, photoluminescence spectroscopy, and UV-VIS spectroscopy, as they are the main measuring techniques in this thesis.

ii. Chapter 3 - Transient absorption studies on CIGS and the correlation with emerging photovoltaic materials like Sb_2Se_3 :

Steady-state and transient optical studies on CIGS thin film to establish a firm ground for the next two chapters. Furthermore, the optical results of CIGS are compared with those of Sb_2Se_3 thin film to broaden the scope of this chapter.

iii. Chapter 4 - Transient absorption studies on electron dynamics along the Ga-gradient in CIGS solar cells:

This chapter is focused on the influence of the Ga gradient on the minority charge carrier kinetics in a high-efficiency CIGS device. Here, the charge mobility, recombination time, effective minority charge carrier lifetime throughout the whole GGI profile are investigated by using ultrafast transient absorption spectroscopy as well as other techniques. A Matlab fitting function was employed for supporting the experimental results. Also, scanning electron microscopy and secondary ion mass spectrometry were applied as additional characterization methods.

iv. Chapter 5 - Effects of incorporated alkali atoms (Na and Rb) on minority charge carrier kinetics in Ga-graded CIGS solar cells:

The impact of alkali atoms (Rb and Na) on minority charge carrier kinetics will be explored and discussed in this chapter. The three samples utilized for this study all include a Ga gradient but use different alkali treatments (without any

PDT, NaF only PDT and RbF+NaF PDT). By employing a TAS system in the picosecond-second time range along with other optical spectroscopy and material characterization measurements, the mobility of minority charge carrier and non-radiative recombination time between different PDT samples are obtained. From the experimental results, details of how minority charge carrier kinetics are affected by different alkali atoms are derived. Furthermore, utilizing a TAS system in the microsecond-second time range leads to novel experimental results that reveal the impact of incorporated alkali atoms on defects. This is the first time that minority charge carrier dynamics in the second time range have been discovered in CIGS solar cells

v. Chapter 6-Concluding remarks:

The overall conclusion based on the results from the previous chapters and the remaining challenges are given in this chapter.

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Chapter 2

Experimental methods

Note that all the optical measurements of CIGS thin films and devices in this thesis were performed by myself. On the other hand, fabrications of CIGS thin films/devices and the corresponding device characterizations in this thesis were all conducted by the research group of Professor. Ayodhya N. Tiwari in EMPA Switzerland.

2.1 Optical characterization

2.1.1 Ultraviolet–visible spectroscopy (UV-VIS)

Once the UV-VIS light (190 nm–750 nm) propagates into a thin film, several situations are likely to occur:

- (1) **Absorption:** Photon absorption induces an electron transition from the ground state to an excited state within the material. Hence, the intensity of the light will be reduced after absorption.
- (2) **Reflection:** There are two types of reflections, one is diffuse, the other is specular. Diffuse reflection is the reflection of the light at many random angles (i.e. scattering), whilst specular reflection is the mirror reflection of the incident light.
- (3) **Transmittance:** The residual light passes through the sample that is neither absorbed or reflected by the sample.

Though the absorption could not be directly measured, it can be calculated from the transmittance and reflection (both specular and diffuse) measurements and from using the equation below:

$$Absorption(\%) = 1 - Transmittance(\%) - Reflection(\%) \quad (2.1)$$

UV-VIS spectroscopy provides the information of the steady-state absorption characteristic of the sample. For example, the absorption onset of a semiconductor material in the UV-VIS spectrum, can be related to the material band gap, as only photons energy larger than the band gap could be effectively absorbed. In this thesis, a UV-2600 Shimadzu UV-Vis spectrophotometer with a two-detector integrating sphere module (Shimadzu ISR-2600Plus), or an Agilent Cary 60 spectrophotometer was utilized.

2.1.2 Steady-state photoluminescence spectroscopy (PL)

Steady-state photoluminescence spectroscopy detects the sum of the photons emitted from the specimen as a consequence of radiative recombination. In a solid semiconductor, after excitation, charge carriers may undergo four possible radiative recombination channels: CBM to VBM, CBM to acceptor levels, donor levels to acceptor levels, and donor levels to VBM, as illustrated in Figure 2.1.

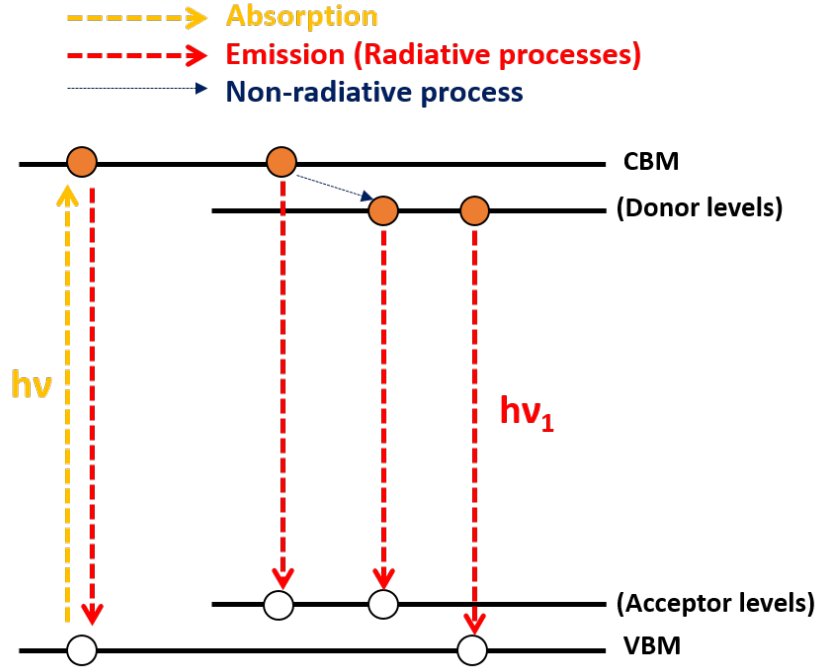


Figure 2.1: Schematic of radiative recombination channels (coloured in red) in a solid semiconductor.

The intensity of photoluminescence can be described as:

$$\text{PL intensity} = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}} \quad (2.2)$$

In principle, a higher PL intensity indicates less occurrences of non-radiative recombination in a material, and therefore the better quality of the material is. Literature reviews on PL studies on CIGS devices can be found in Chapter 1.4.5.3.

In this thesis, the sample was measured via emission mode in Horiba Fluorolog-3 modular spectrofluorometer. The emission mode refers to the sample excited by a fixed light source (LED white light in our case), with its emitted photons scanned after a monochromator and collected by an IR detector, generating a spectral distribution profile of all emitted photons.

2.1.3 Transient absorption spectroscopy (TAS)

TAS is the main spectroscopic tool utilized in this thesis. A detailed introduction of this technique is described below for better comprehension of the TAS data in the following result chapters.

2.1.3.1 Principle

TAS is commonly used to study the charge carrier dynamics in photovoltaic and photoelectrolysis systems. In a TAS experiment, a pulse laser (pump) in nJ range is pumped directly to the sample, exciting charge carriers from the ground state to the excited state. Subsequently, a continuous white light beam (probe) is then sent through the sample with a delay time ranging from ps to ns scale (τ) relative to the pump. An absorption difference between pumped and unpumped sample is then recorded at each time delay as a function of wavelength and τ profile. This profile contains information of carrier dynamics process such as electrons trapping, bimolecular recombination, and carrier separation process...etc. in the desired system. In comparison to steady-state absorption spectroscopy (ex: UV-vis), which we observe long-lived intermediates due to continuous excitation of the sample, with TAS both short-lived and long-lived intermediates will be able to detect due to short laser pulse. Furthermore, compared to photoluminescence and fluorescence spectroscopies with TAS, we can observe the evolution of non-emissive states in TAS.

2.1.3.2 TAS data calculation and analysis

In TAS measurement, an absorption difference (ΔA) of the specimen before and after pump excitation is recorded and calculated. Due to the excitation, the charge carriers are generated and excited from the ground state, which induce the change of the probe light spectrum with respect to the time. By subtracting the ground state absorbance from the excited state absorbance at each wavelength (equation 2.3), as shown in Figure 2.2(a), we will be able to obtain a transient absorption profile as a function of time (ps) and wavelength.

$$\Delta A = A_{EX} - A_{GS} \quad (2.3)$$

The absorption profile holds three main processes, as shown in Figure 2.2.

A. Negative signals ($\Delta A < 0$)

i. Ground-state bleaching. After excitation, charge carriers are excited from the ground states to the excited states. Due to the occupation of charges on the excited states in the pumped sample, the amount of charges that can be excited by the upcoming probe light is reduced. Hence, a decreased absorption is observed in the pumped sample than the

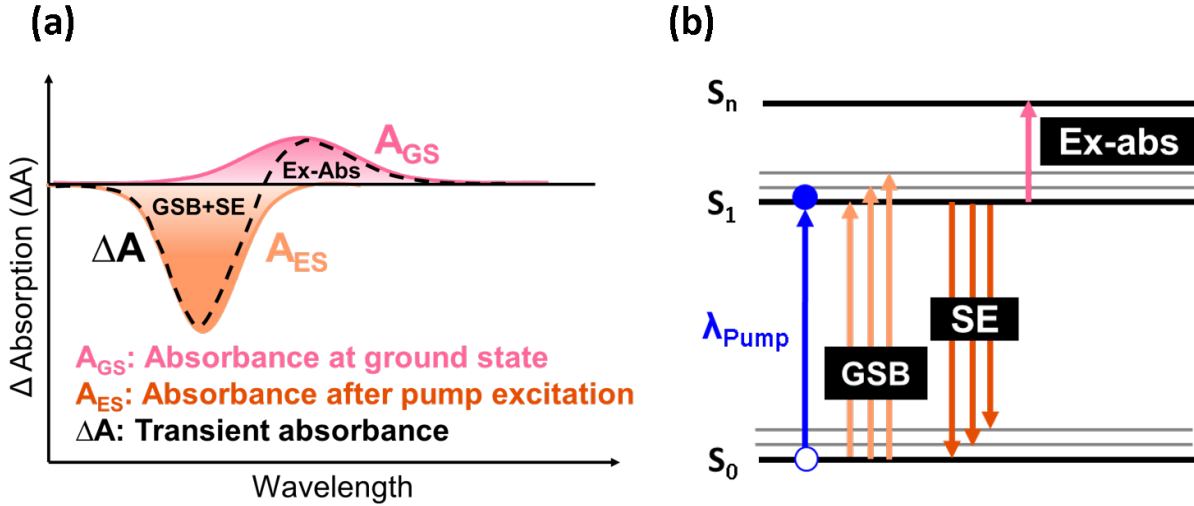


Figure 2.2: (a) TAS profile demonstrating the change of absorbance of the sample before and after pump excitation at each wavelength. (b) Schematic of the three main charge carriers processes after pump excitation in the energy band. GSB denotes Ground state bleach, SE denotes Stimulated emission, Ex-abs denotes excited states absorption

unpumped sample, leading to a negative signal shown in the TAS spectrum.

ii. Stimulated emission. The origin of stimulated emission comes from a pulse light passing through an excited sample, inducing the photons in the excited states to return to the ground states. Also, the direction of the emission is the same as the probe light, thus both of the emission will be detected. Stimulated emission only occur in an optically allowed transition and the photon usually contains less energy, thus a stoke shift is commonly observed.

B. Positive signals($\Delta A > 0$)

i. Excited-state absorption. After pump excitation, the charge carriers generated to the excited states might further absorb the energy from the probe light to an even higher excited states or other transient states, such as charge transfer states or triple states, contributing to an overall absorption spectrum at absorbed wavelengths.

2.1.3.3 fs-TAS set-up

The fs-TAS system employed here is commercially designed as shown in Figure 2.3. The laser output is from the Ti:Sapphire laser system (Solstice, Spectra-Physics), generating 800 nm laser energy with a width of 92 fs at a repetition rate of 1 kHz. This 800 nm laser light will be split into two light paths, pump pulse and probe pulse, after passing through

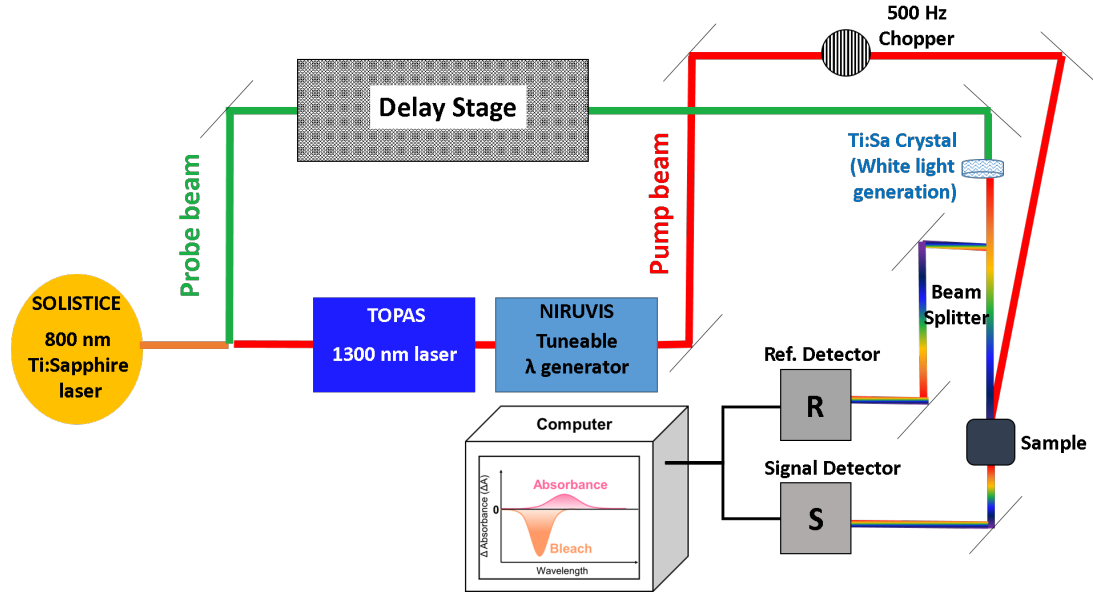


Figure 2.3: Schematic representation of the fs-TAS system.

an amplifier inside Solstice. First, we describe the pump pulse, which is shown in the red path. With Ti:Sapphire laser alone, the laser wavelength is restricted to 800 nm only. To broaden the range of wavelength for pump pulse, the initial 800 nm laser passes through a transient Optical Parametric Amplifiers (TOPAS, Light Conversion) to generate 1300 nm pump pulse, and then enter a frequency mixer (NirUVIS, Light Conversion) to generate specific wavelength ranges for experimental purposes. In our set-up, the pump wavelength ranges from ~ 290 nm up to the NIR region. An optical chopper with 500 Hz rotating frequency is applied before the pump pulse hits the specimen. The probe beam is shown in the green path. After splitting from the pump pulse, the probe pulse enters a delay stage which is up to 6 ns delay with respect to the pump pulse. This process defines when exactly the sample is probed. After the probe pulse leaves the delay stage, it passes through a Ti:Sapphire crystal and generates a continuum white light. Subsequently, the continuum white light is then divided into two paths by an adjustable semitransparent mirror, one probes through the sample directly, the other acts as a reference. The probe pulses from the sample and the reference pulses are collected by either a Si or InGaAs multi-channel detector depends on the measurement wavelength range. The change of absorption (ΔA) with respect to time and wavelength of the specimen before and after pump excitation is then successfully recorded. In this thesis, the measurement wavelength range is NIR (from 850 nm to 1600 nm). The pump excitation energy is measured via a power meter (VEGA P/N 7Z01560, OPHIR Photonics) with a $500 \mu\text{m}$ diameter aperture.

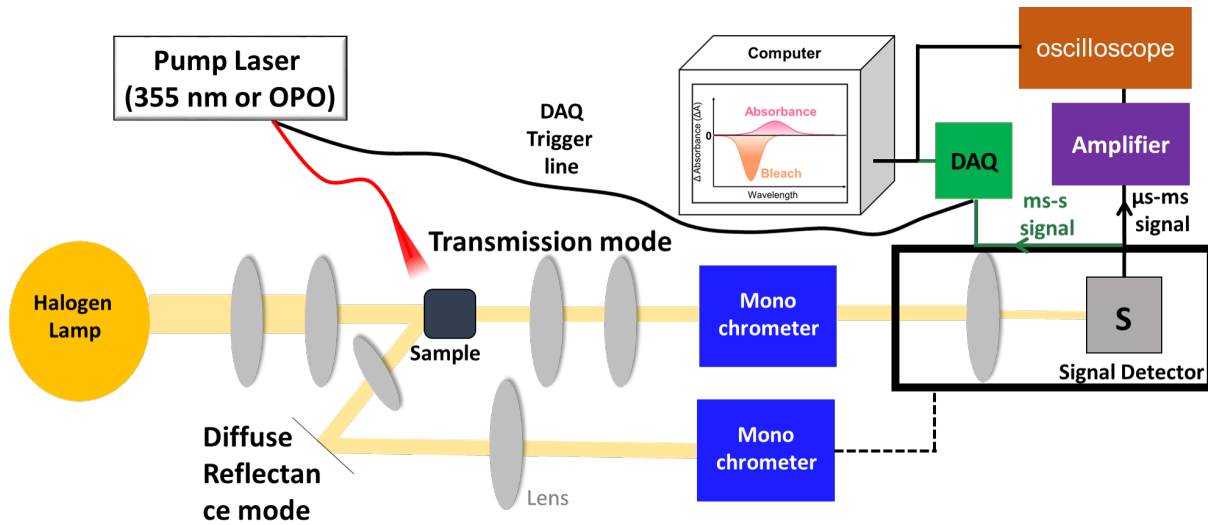
2.1.3.4 μ s-TAS set-up

Figure 2.4: Schematic representation of the μ s-TAS system.

Figure 2.4 shows the configuration of our home-built μ s TAS system. The source of the pump beam is the 1024 nm Nd:YAG laser (Big Sky Laser Technologies, Ultra CRF) with a pulse width shorter than 10 ns. The 1024nm laser generates a fixed 355 nm pump excitation via 3rd harmonic output port, and a tunable pump pulses (400 nm–2200 nm) via an optical parametric oscillator (OPOTEK Opolette). The pump excitation intensity can be adjusted via placing neutral density (ND) filters in between the sample and the pump pulse, or tuning the Q-switch delay. The source of the probe beam is the 100 W halogen lamp (Bentham, IL 1), and it's stabilized by a stabilized power supply (Bentham, 605). A monochromator is placed after the sample to filter the specific wavelength for measurements. The signal is then detected via a silicon photodiode (Hamamatsu S3071) at the end of the set-up. Note that the detectors are placed inside a black box to minimize the scattering and emission effect. The signals are acquired differently based on their time scales. The μ s–ms timescale signal will go through an amplifier (Costronics 1999 amplifier) before being recorded in an oscilloscope (Tektronix DPO 2012B). On the other hand, the ms–s timescale signal is recorded in a DAQ card (National Instruments USB-6211 or USB-6361) without being amplified. Last, all signals are processed with a home-built LabView software in a computer.

2.2 CIGS device fabrication and characterization

2.2.1 Device fabrications

All the CIGS samples studied in this thesis were fabricated by the research group of Prof. Ayodhya N. Tiwari in EMPA Switzerland via a modified three-stage co-evaporation process[1]. The substrates of the CIGS devices studied here are Mo coated soda lime glass. CIGS layers were deposited on top of the substrates by co-evaporating Cu, In, and Ga elements at a maximum substrate temperature of 450 degrees through three-stage processes, as shown in Figure 2.5.

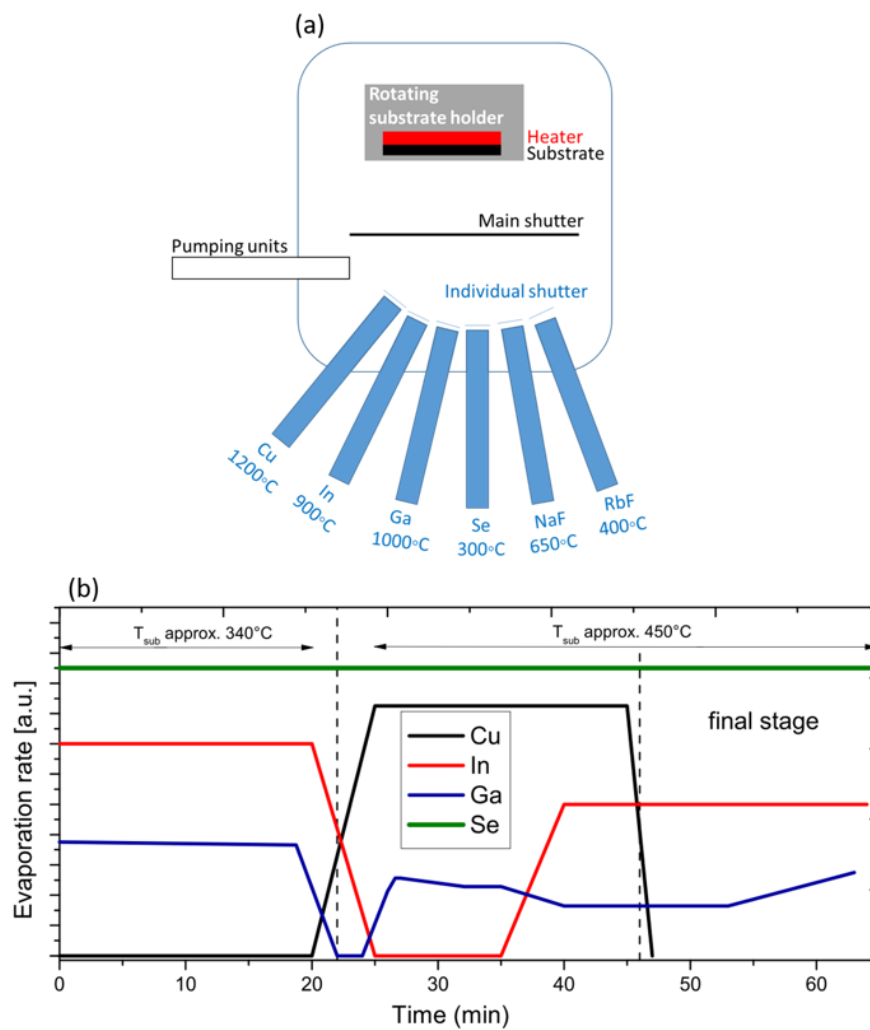


Figure 2.5: Schematic representation of (a) deposition setup and (b) a three-stage deposition process of CIGS thin films. Figures are adapted from references [1] and [2], respectively.

Once the co-evaporation process was finished, the CIGS film was taken out from the chamber and then a 30 – 50 nm CdS layer was deposited on top of it via a chemical bath deposition method. Window layers ZnO and Al:ZnO (Al_2O_3 , 2 wt%) were deposited by RF magnetron sputtering after CdS deposition. Finally, the device was finished by coating an anti-reflective layer MgF_2 and Ni/Al grids by e-beam evaporation.

Note that for NaF PDT treated samples, evaporation of NaF was conducted in a Se atmosphere in the same chamber following the standard three-stage coevaporation process. For RbF+NaF PDT sample, RbF was evaporated in the same manner following the NaF PDT deposition. Standard deposition rate for both NaF and RbF PDT was approximately 1-2 nm/ min, and the duration was 20 minutes each[3][4]. After the PDT processes, the CIGS samples were taken out from the vacuum chamber and rinsed gently with diluted ammonia to wash away the unreacted alkali fluorides on the surface. Note that in PDT treated samples, a silicon oxide layer was deposited between Mo and SLG to stop the unwanted diffusion of Na atoms from SLG to CIGS absorber.

2.2.2 Device characterizations

- **Time-of-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS)**

TOF-SIMS is an analytic tool that can reveal the composition of solid surfaces and the element depth profile from few angstroms to tens of micrometers. The physics behind this technique is illustrated in Figure 2.6 and explained in the following. First, a certain area of a sample is bombarded by a high energy analysis beam, resulting in ionized particles (also often called as secondary ions) emitting from that area. Afterwards, these secondary ions are individually detected and analyzed by a mass spectrometer. To obtain the element depth profile of the sample, a sputter beam is utilized simultaneously to etch the sample gradually.

It should be noted that the SIMS profile reveals the relative concentrations of each element instead of absolute quantities. Figure 2.7 gives an example of comparing Na concentrations in the CIGS absorber with and without additional RbF/KF PDT. It can be seen that the Na concentration decreased by half in the absorbers with additional KF and RbF PDT compared to the one without.

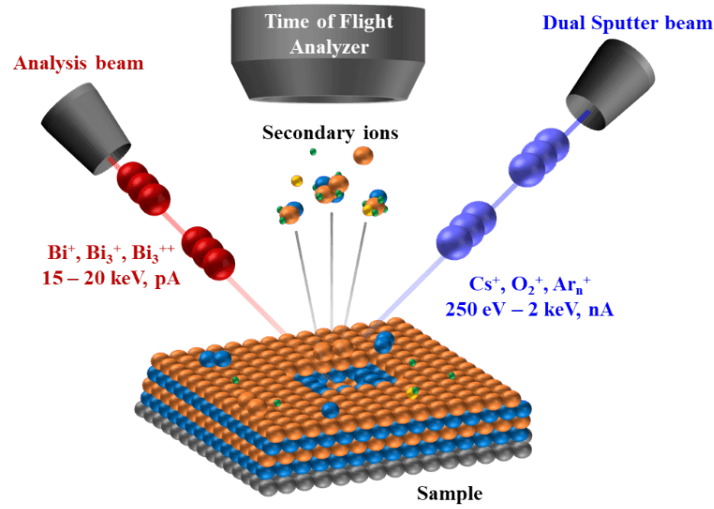


Figure 2.6: Principles a TOF-SIMS system. This figure is reproduced with permission of the copyright holder from reference [5].

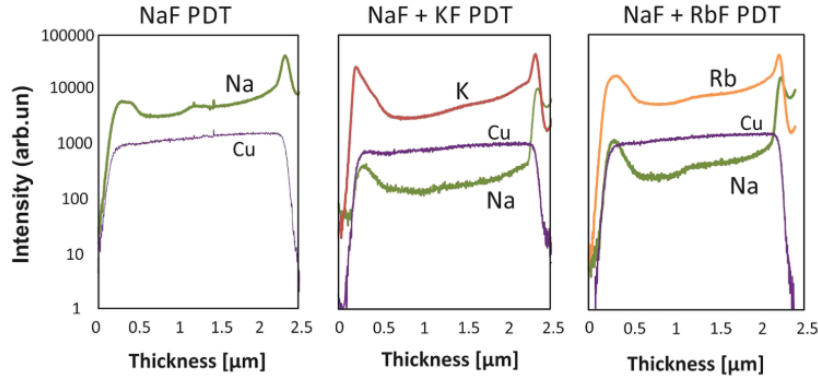


Figure 2.7: SIMS depth profiles signals from Na, K, Rb, and Cu in the CIGS absorbers treated by NaF PDT, NaF and KF PDT, and NaF and RbF PDT. This figure is reproduced with permission from Copyright © 2017, American Chemical Society from reference [3].

In this thesis, a TOF-SIMS system (ION-TOF GmbH TOF SIMS5) is utilized to detect the $[\text{Ga}]/([\text{Ga}]+[\text{In}])$ (GGI) concentration ratio across the $2.7 \mu\text{m}$ CIGS film. The analysis beam is Bi^+ with 25 keV acceleration and the sputtering beam is O_2^+ with 2 keV acceleration.

- **Scanning electron microscopy (SEM)**

Scanning electron microscopy provides information of the morphology, topography, and the cross-section of the sample. The physics behind this technique is given as follows: After being scanned by a focused and relatively low energy electron beam, the atoms of the detected sample interact with the injected electrons and generate various typed

of signals, for example, secondary electrons, cathodoluminescence, etc, as illustrated in Figure 2.8. In SEM, only the secondary electrons generated close to the surface are collected to produce three dimensional image of the sample. Secondary electrons are low energy electrons (10-50 eV) resulting from the collisions between the injected electrons and the loosely bonded electrons of the atoms. Figure 2.9 gives an example of utilizing SEM to obtain a cross-section image of a CIGS device, demonstrating that the difference in grain size and layer structures can be easily spotted and distinguished in a SEM image.

The SEM image in this thesis was taken on a Hitachi S-4800 electron microscope that has an interaction volume of $>1 \mu\text{m}$.

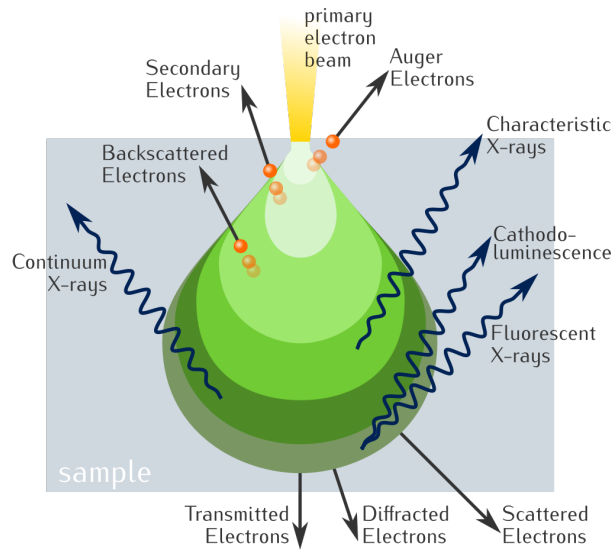


Figure 2.8: Schematic of interactions between primary electrons and the atom and the signals generated due to this interaction. Reproduced with permission under CC BY-SA 4.0 license from reference [6].

- **Current (I) - Voltage (V) measurement**

An I-V measurement corresponds to applying a series of voltages to a solar cell under either dark or illuminated condition and measuring the current flow through the device at each voltage simultaneously. Figure 2.10 shows a typical I-V curve of a solar cell measuring under dark and illuminated condition.

Several important parameters of a solar cell can be obtained from the I-V curve. The open circuit voltage, V_{OC} , corresponds to the voltage which the net current through the device is zero. V_{OC} is influenced by several factors such as the optical bandgap and recombination of the material as well as the device temperature. The short circuit

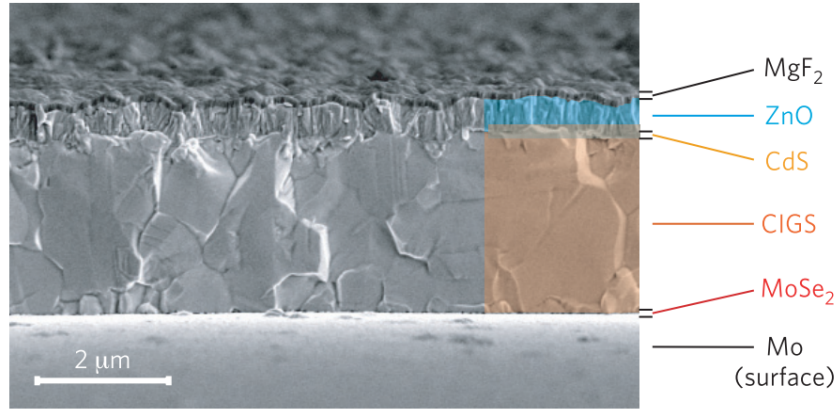


Figure 2.9: SEM cross-section image of a high efficiency ($> 18\%$) CIGS device grown on a polyimide substrate. Reproduced with permission of the copyright holder (Springer Nature) from reference [7].

current density, J_{SC} , corresponds to the maximum current flow through the device when the applied voltage is zero. J_{SC} reflects how many charge carriers are generated and collected in the solar cell after illumination. The power (P) of a solar cell is defined by the generated current and voltage ($P = I \times V$), hence, the maximum power point of a solar cell can be defined, as indicated in Figure 2.10a. The maximum power point (P_{MP}) refers to the point where the overall output of current density (J_{MP}) and voltage (V_{MP}) is maximized. Fill factor (FF) is employed for indication of the ratio of the actual maximum power to the overall output of the short circuit current (J_{SC}) and open circuit voltage (V_{OC}).

$$FF = \frac{P_{MP}}{V_{OC} \times J_{SC}} \quad (2.4)$$

The device efficiency η is therefore defined as below:

$$\eta = \frac{P_{MP}}{P_{illumination}} = \frac{V_{OC} \times J_{SC} \times FF}{P_{illumination}} \quad (2.5)$$

, where $P_{illumination}$ refers to the standard 1 sun condition (AM1.5G, $25^\circ C$, 100 mWcm^{-2}).

The behaviour of a single junction solar cell can be represented by a single diode with two resistors, the series resistance (R_s) and the shunt resistance (R_{sh}), as illustrated in Figure 2.10b. The presence of R_s reduces the voltage of the device. In the open circuit condition, due to the overall current flows through the solar cell the V_{OC} remains unchanged. Consequently, R_s can be extrapolated by simply calculating the slope of an IV curve at the V_{OC} point. The presence of R_{sh} reduces the current flows through the

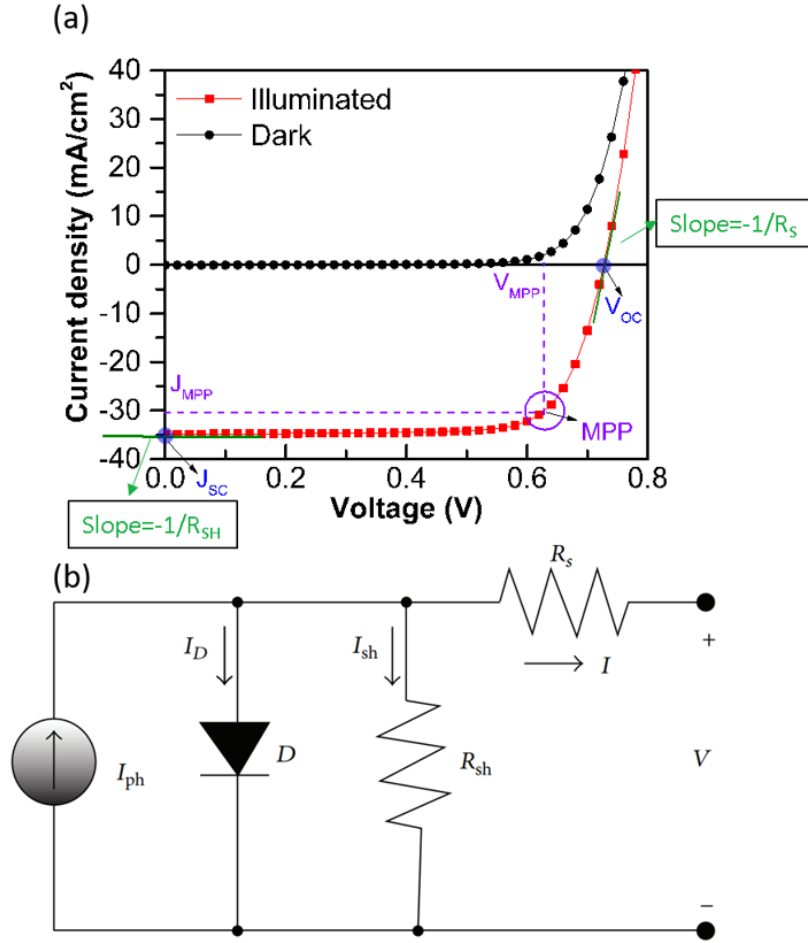


Figure 2.10: (a) An typical I-V curve of a single junction solar cell (19.3% CIGS solar cell as an example). The label MPP stands for maximum power point, R_{sh} stands for shunt resistance, and R_s stands for series resistance. (b) An equivalent diode circuit of a single junction solar cell under illuminated condition. The label D stands for diode and I_{ph} stands for photocurrent.

solar cell. R_{sh} can be obtained from the slope of an IV curve at the J_{SC} point. Both R_s and R_{sh} impact the FF (i.e. the shape of the IV curve) of the device significantly.

The I-V measurement in this thesis was conducted under 1 sun condition with the solar simulator (LOT-QuantumDesign) that was calibrated with a certificated Si diode. The electrical measurements was performed by a Keithley 2400 in four-points measuring mode.

• External Quantum Efficiency Measurement (EQE)

EQE efficiency is equal to the ratio of the amount of charge carriers being collected to the total number of incident photons. The J_{SC} is the result of integration of a spectral EQE, as described in the following equation:

$$J_{PH|V=0} = J_{SC} = \int_0^{\infty} G(\lambda) * EQE(\lambda) d\lambda \quad (2.6)$$

, where $J_{PH|V=0}$ is the photocurrent at 0 V, and $G(\lambda)$ is the incident photon flux.

The EQE result not only reflects the ability of a solar cell to absorb the sunlight but also reveals the losses due to charge carrier recombination, parasitic absorption, and reflection. In Chapter 1.4.5.1, a detailed analysis on the EQE results of a CIGS solar cell is given.

In this thesis, a calibrated chopped (260 Hz) white light source (900 W halogen lamp) with a monochromator was utilized for EQE measurement.

2.3 CIGS samples for optical measurements

All the TAS measurements in this thesis were performed in a **transmission mode** and in ambient atmosphere with low humidity. If the CIGS and CIS samples are measured in reflection mode, the optical signals have to be reflected back by the Mo back contact and re-absorbed by CIGS and CIS absorbers. However, due to the thickness of the absorber layers, the TA signals obtained are small such that the signal-to-noise ratio is very low. To measure CIGS samples in a transmission mode, the Mo back contact was detached from the rest of the CIGS stacks. To achieve this, a peeling-off method was utilized, as shown in Figure 2.11, and step-by-step procedures are given as follows.

First, the CIGS solar cell (named as "Sample") is glued with epoxy to another 2 mm thick glass substrate (named as "Substrate A") for support, as shown in Figure 2.11(a). A small droplet of transparent epoxy glue DP100 is then placed on top of the CIGS solar cell, as shown in Figure 2.11(b). A glass substrate (named as "Substrate B") is then used to cover the epoxy droplet and placed starting with an angle to avoid air enclosure, as shown in Figure 2.11(c). A small weight is placed carefully on the assembly and kept for 1 day, as shown in Figure 2.11(d). Afterwards, the sandwiched sample is heated to 50 °C for 1 hr and allowed to cool down before the top glass piece is pulled from the bottom piece, thereby, peeling off a circle of the solar cell stack from the Mo back contact.

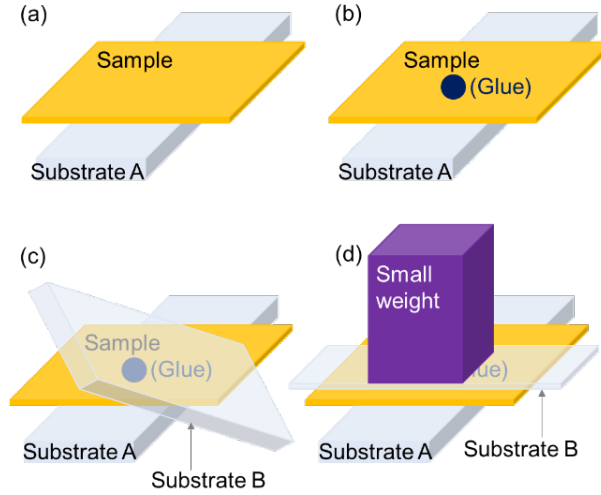


Figure 2.11: Schematic of the procedure of peeling off the rest of the CIGS cell stacks from its Mo back contact.

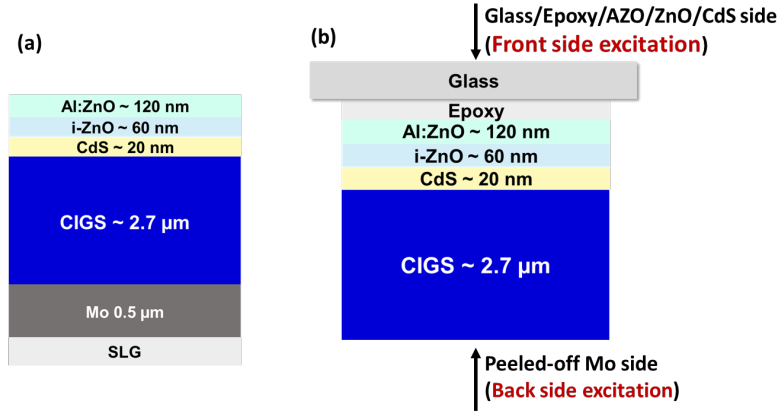


Figure 2.12: (a) CIGS device structure (b) CIGS sample utilized for TAS measurements

Figure 2.12 (a) illustrates the CIGS device structure studied in this thesis. The 2.7 μm p-type CIGS absorber layer is deposited on a Mo coated glass substrate. The absorber is then coated with n-type CdS and contacted via ZnO and Al:ZnO. Figure 2.12 (b) illustrates the resulting architecture of the CIGS stacks for TAS measurement after the peeling off procedure. **Note that in TAS measurements, the excitation impinges either from the peeled-off Mo side (denoted as back side excitation throughout this thesis) or the glass/epoxy/AZO/ZnO/CdS side (denoted as front side excitation throughout this thesis).**

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Chapter 3

Transient absorption studies on
CIGS and the correlation with
emerging photovoltaic materials like
 Sb_2Se_3

3.1 Introduction

The aim of this thesis is to unravel the influence of Ga gradient implementation and alkali atoms PDT on charge carrier dynamics in a high efficiency CIGS device. However, before stepping directly into studying such a complex system, a series of steady state and transient optical studies are being discussed on a less complex system: a CIGS thin film without any Ga gradient and no PDT treatment. This is to lay a foundation for the following studies presented in the next two chapters.

A detailed introduction of the CIGS material and its photo-physical characteristics is presented in Chapter 1. In short, in the CIGS research field, numerous PL studies have been carried out to understand the dynamics of charge carriers in CIGS absorbers and devices. It is generally observed that the PL emission of CIGS arises from either free-to-bound or donor-to-acceptor transitions within the bandgap (see Chapter 1.4.5.3 for more details). For CIGS, the PL decay time, which corresponds to radiative recombination processes, can measure up to hundreds of nanoseconds depending on the quality of the film[1]. On the other hand, there is much less focus on understanding the charge carrier dynamics in CIGS at the timescale of picosecond to nanosecond, which is the regime of non-radiative processes such as charge carrier trapping[2][3][4]. Besides, there are currently no optical studies in CIGS on the microsecond to second timescale. Here in this chapter, transient absorption spectroscopies in picosecond to nanosecond (ps-ns) and microsecond to second (μ s-s) timescales are utilized for investigating the charge carrier dynamics in a polycrystalline CIGS thin film. This is the first time that the transient absorption (TA) features of CIGS over such a broad time range are revealed.

To broaden the scope of this chapter, the TA results of CIGS are compared with another member of the CIGS family: CIS, and another type of chalcogenide material - Sb_2Se_3 . CIS, as introduced previously in Chapter 1, without the incorporation of Ga atoms, it has a smaller bandgap compared to CIGS. Due to the low bandgap energy, the device performance of CIS has a higher J_{SC} but a much lower V_{OC} . Recently, Sb_2Se_3 has been utilized as absorber layer for thin film photovoltaics[5][6][7][8][9] and solar fuel applications [10][11][12][13], though after years of development, the device efficiency remains low. The highest efficiency for a thin film Sb_2Se_3 solar cell so far is 7.6 % [7], which is far behind the record of CIGS solar cells (23.35 %)[14]. The main loss of device efficiency in Sb_2Se_3 results from a high V_{OC} deficit, which is twice as much as in the CIGS device of

the same bandgap[15][16]. Trap states in the bulk and at surfaces and interfaces[7][17][18] are considered to be the main reason. Though CIGS devices are still suffering from V_{OC} deficit due to defects[19][20][21], nevertheless, after 40 years of intensive research and development, an obvious improvement is achieved.

Comparing different materials with similar features can help to deepen understanding of processes in complex material systems. Therefore, a series of TA studies are also performed on Sb_2Se_3 , and the results are compared with those of CIGS with an attempt to find any similarity or difference in charge carrier dynamics between these two.

3.2 Experimental methods

In this chapter, steady state UV-VIS, PL spectroscopy, ps-ns and μs -s TAS are the main tools for the investigation of the photo-physics in CIGS, CIS, and Sb_2Se_3 materials. The details of each instrumental set-up and fundamental principles are described in detail in Chapter 2.

The fabrication methodology of the CIGS and CIS thin films investigated here is described previously in Chapter 2.2.1. Both samples have a structure as shown in Figure 3.1a. The thicknesses of CIGS/CIS film is $2\ \mu m$. The samples for TAS measurements are prepared by peeling off the Mo back contact from the rest of the CIGS/CIS stack and the corresponding sample structure is illustrated in Figure 3.1b. As described in Chapter 2.3, the reason for peeling off Mo is to measure CIGS/CIS in a transmission mode in TAS to maximize the signal-to-noise ratio. The CIGS/CIS samples can be either excited from the front side or the back side.

Sb_2Se_3 thin films were fabricated via a sputtering method by Prabhakar et al.[13]. The 300 nm Sb_2Se_3 film is deposited on a 5 nm Au layer on a glass substrate, and covered with a ~ 30 nm amorphous MoS_x layer. The fabrication details can be found in reference [13]. The Sb_2Se_3 thin film is measured in a transmission mode using a ps-ns TAS system. However, the signals obtained from the transmission mode using the μs -s TAS system suffers from a low signal to noise ratio, therefore the sample was measured in reflection mode instead. For the Sb_2Se_3 samples, all the TA measurements are carried out in N_2 atmosphere as the film decays rapidly in air.

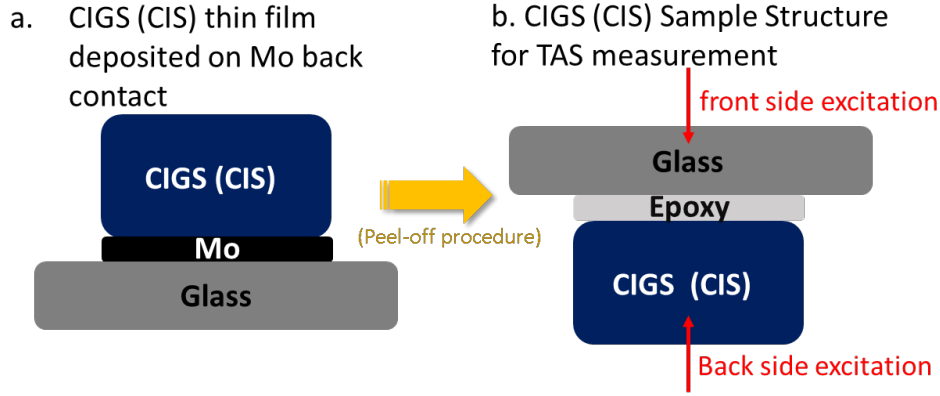


Figure 3.1: Schematic of a (a) CIGS (CIS) thin film deposited on Mo back contact and (b) the corresponding CIGS sample utilized for TAS measurement. For TAS measurements, since now the sample can be measured in transmission mode, it allows to excite the sample from the front side (epoxy side) and the back side (the peeled-off Mo side), as illustrated in the schematic

3.3 Results and Discussion

3.3.1 CIGS (no Ga gradient, no alkali post deposition treatment)

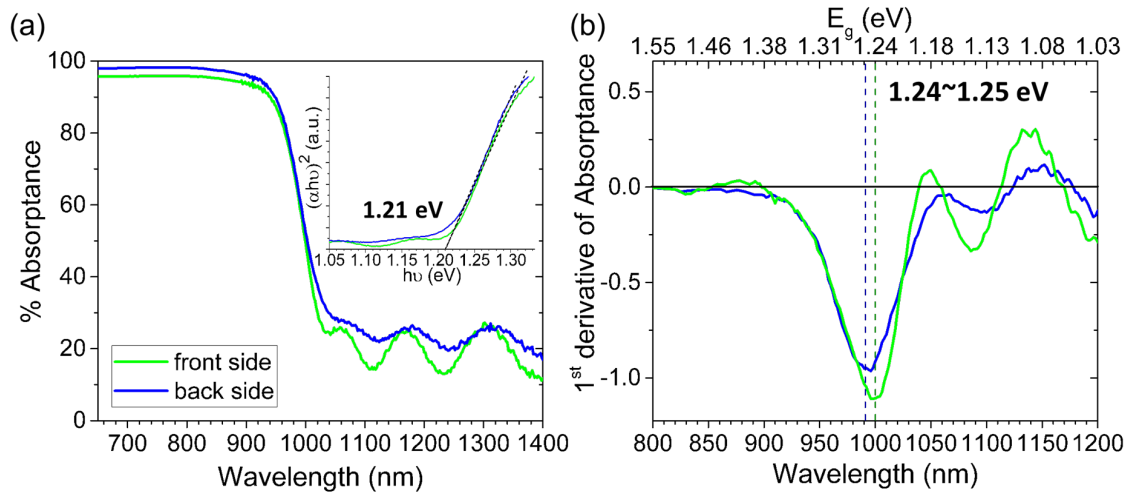


Figure 3.2: Steady state UV-VIS results of a CIGS (GGI=0.4) thin film sample. (a) Absorbance spectra following excitation from the front and back side, respectively. (b) The corresponding 1st derivative results of UV-VIS absorbance.

First, the results of UV-VIS steady-state measurements on CIGS thin film are presented. As shown in Figure 3.2a, the CIGS absorbance spectra obtained from the back side excitation showed a slightly higher absorption than the one from the front side. This

is due to a lower reflectance response when the sample was excited from the back side, as shown in Appendix Figure A.1. Nevertheless, a Tauc plot analysis shows that both spectra exhibit a 1.21 eV bandgap energy, which agrees well with previous literature. Note that in both spectra, the signals oscillate in the IR region, especially when the sample is excited from the front side. Since the CIGS thin film was fabricated via a three-stage co-evaporation method, the film is of high thickness uniformity and low surface roughness. These characteristics lead to a strong light interference effect during an optical measurement. As a result, intense oscillations appear in the weak absorption and transparent regions of the investigated material[22][23]. It should also be noted that the 20% absorptance detected in the IR region is considered to be an experimental artifact resulting from light trapping and scattering in the tested samples[24] (More details of UV-VIS experimental artifacts can be found in Chapter 1.4.5.2). Figure 3.2b shows the results of the 1st derivative of UV-VIS absorptance spectra. The 1st derivative spectra of both samples have shapes similar to a Gaussian distribution, ranging from 900 nm to 1050 nm. The 1st derivative absorptance peaks are between 990 nm to 1000 nm (equivalent to 1.24–1.25 eV). A 0.03 eV mismatch between the Tauc plot and the 1st derivative absorptance is likely to be originated from the scattering light.

To observe the transient absorption features, the CIGS sample was excited following an excitation wavelength of 600 nm at a $3.3 \mu\text{J}/\text{cm}^2$ fluence from both the front side and the back side, and the results are shown in Figure 3.3a,b, respectively. With 600 nm excitation, charge carriers within 160 nm depth beneath the excitation surface were excited, as shown in Appendix Figure A.2. In both cases, a prominent photobleach signal with a shape similar to a Gaussian distribution and a peak at 960–970 nm, was detected during the first hundreds of picoseconds. This prominent photobleach decayed with time in both cases and in the front side excitation case the photobleach is found to red-shift to 990 nm over the next 3 ns, which aligns well with the peak of the first derivative of UV-VIS absorptance. Therefore, this photobleach signal is assigned to the ground-state bleach. Note that the decay is more pronounced in the back side excitation case. The decay kinetics probed at the maximum TA peak wavelength of both cases (970 nm for front side excitation case and 960 nm for back side excitation case) were shown in Figure 3.3c. First of all, it is clear that the signal from the front side excitation decays much slower than the one from the back side excitation. Furthermore, the signal from the

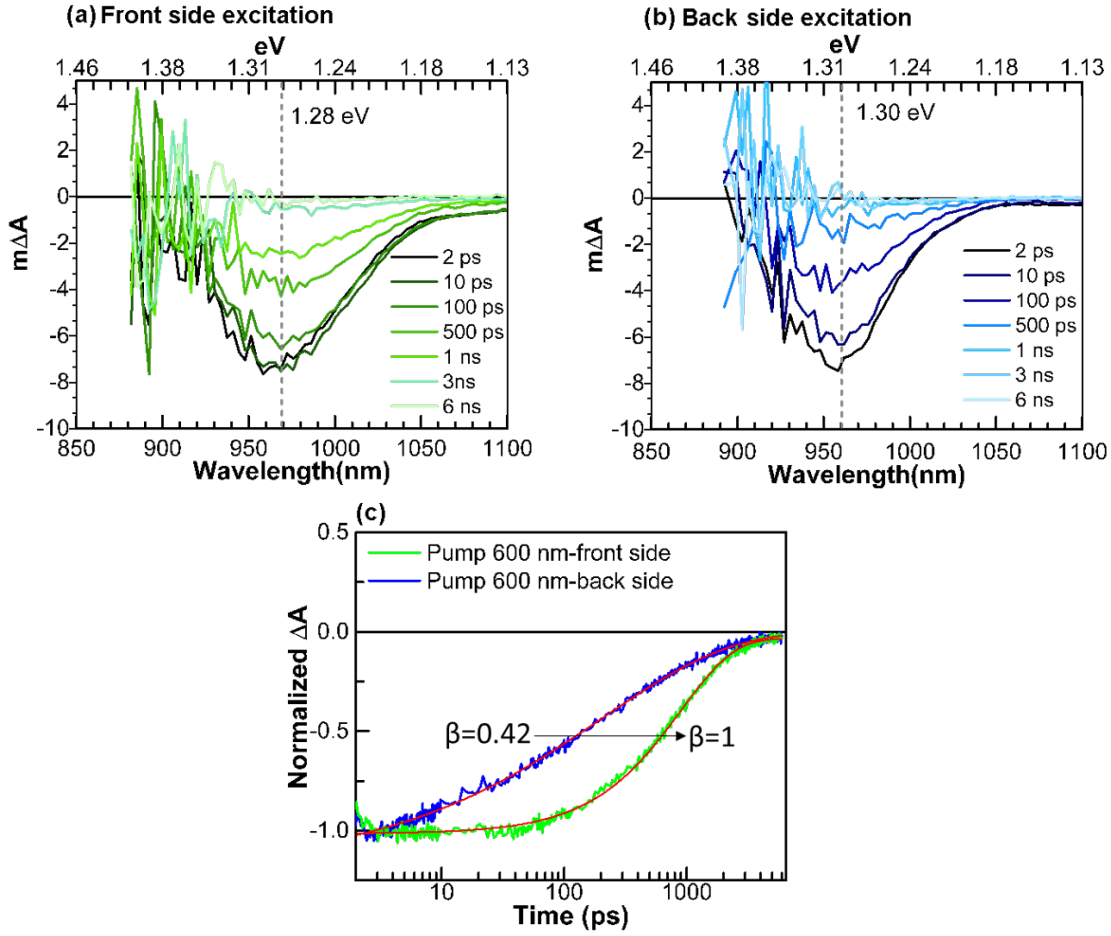


Figure 3.3: Transient absorption spectra of a CIGS (GGI=0.4) thin film sample recorded at 2 ps, 10 ps, 100 ps, 500 ps, 1 ns, 3 ns and 6 ns using an excitation wavelength of 600 nm from the (a) front and (b) back side. The fluence is $3.3 \mu\text{J}/\text{cm}^2$, equivalent to 10^{13} photons/ cm^2 . (c) Normalized TA kinetics probed at the maximum peak wavelength of the TA spectra a and b. Both kinetics were fitted with a stretched mono-exponential function ($y = a * \exp - ((kx)^\beta)$, β : stretching component). The fitting result of the kinetics of front side excitation case shows $\beta = 1$, whilst for the kinetics of back side excitation $\beta = 0.42$.

front side excitation can be fitted well with a mono-exponential function. In contrast, the kinetics from the back side excitation were fitted very well with a stretched exponential function ($y = a * \exp - ((kx)^\beta)$, β : stretching component = 0.42) rather than a mono-exponential function. A stretched exponential decay is commonly seen in disordered materials or materials with a distribution of defect states[25][26][27][28], which leads to dispersed recombination lifetimes rather than a single recombination lifetime which can be fitted with a mono-exponential decay model. This further indicates that there is a larger distribution of defects in the back region than in the front region. This can be

further supported by the PL experiments showing that the PL signal was only detected when the sample was excited from the front region (see Appendix Figure A.3), which again indicates a higher number of non-radiative recombination centres in the back region than in the front region. Here, the charge carrier lifetime is determined by the period in which the signal amplitude decays to 50% of its initial value ($t_{50\%}$). This is because the rate constant of a single exponential function has different units if the stretching exponent is different. Consequently, for the back side excitation case $t_{50\%} = 140$ ps, whilst for the front side excitation, $t_{50\%} = 650$ ps. A 4–5-fold increase $t_{50\%}$ in the front side excitation case further implies charge carriers are longer-lived in the front region.

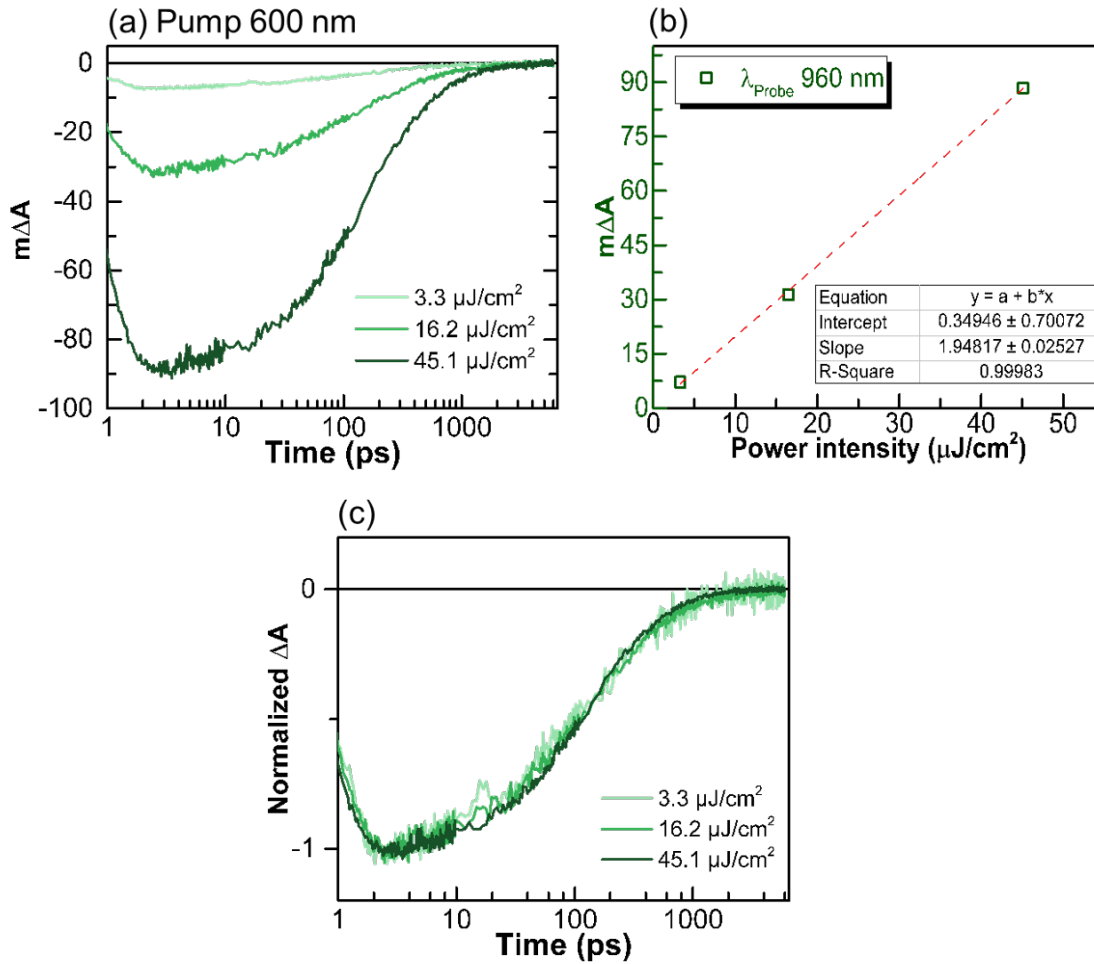


Figure 3.4: (a) Fluence-scaled study on TA decay kinetics probed at 960 nm of a CIGS (GGI=0.4) thin film sample following an excitation wavelength of 600 nm from the back side with 3.3, 16.2, and 45.1 $\mu\text{J}/\text{cm}^2$ fluences. (b) The maximum signal amplitude as a function of fluences. (c) Normalization of 960 nm kinetic trace at 2 ps. 3.3 $\mu\text{J}/\text{cm}^2$ equals to 10^{13} photons/ cm^2 absorbed.

In addition, a fluence dependant TA experiment (fluences range from $3.3 \mu\text{J}/\text{cm}^2$ to $45.1 \mu\text{J}/\text{cm}^2$) was also performed, as shown in Figure 3.4. Note that the fluence $3.3 \mu\text{J}/\text{cm}^2$ was chosen because it allows to obtain signals with high signal to noise ratio. The results show that the amplitude of the photobleach increases linearly with excitation fluences. However, the normalized kinetics are insensitive to the excitation fluence. With fluences ranging from $3.3 \mu\text{J}/\text{cm}^2$ to $45.1 \mu\text{J}/\text{cm}^2$, the population densities of photo-excited charge carriers are within the range of 10^{17} to 10^{18} cm^{-3} , which is higher than the suggested intrinsic carrier concentration of a GGI=0.4 CIGS absorber layer ($\sim 10^{16} \text{ cm}^{-3}$)[29]. In the high-injection regime, the Shockley-Read-Hall (SRH) recombination rate is directly proportional to the population of photo-excited charge carriers (n), whilst for radiative recombination and Auger recombination it is directly proportional to n^2 and n^3 , respectively[30]. Therefore, if radiative and Auger recombination are the main recombination pathways of the free charge carriers observed at this timescale, a significant power dependent decay signal would be expected. Instead, the observation that the decay kinetics are insensitive to the excitation fluence indicates that the decrease of the photobleach is mainly via free charge carriers which undergo SRH recombination[31].

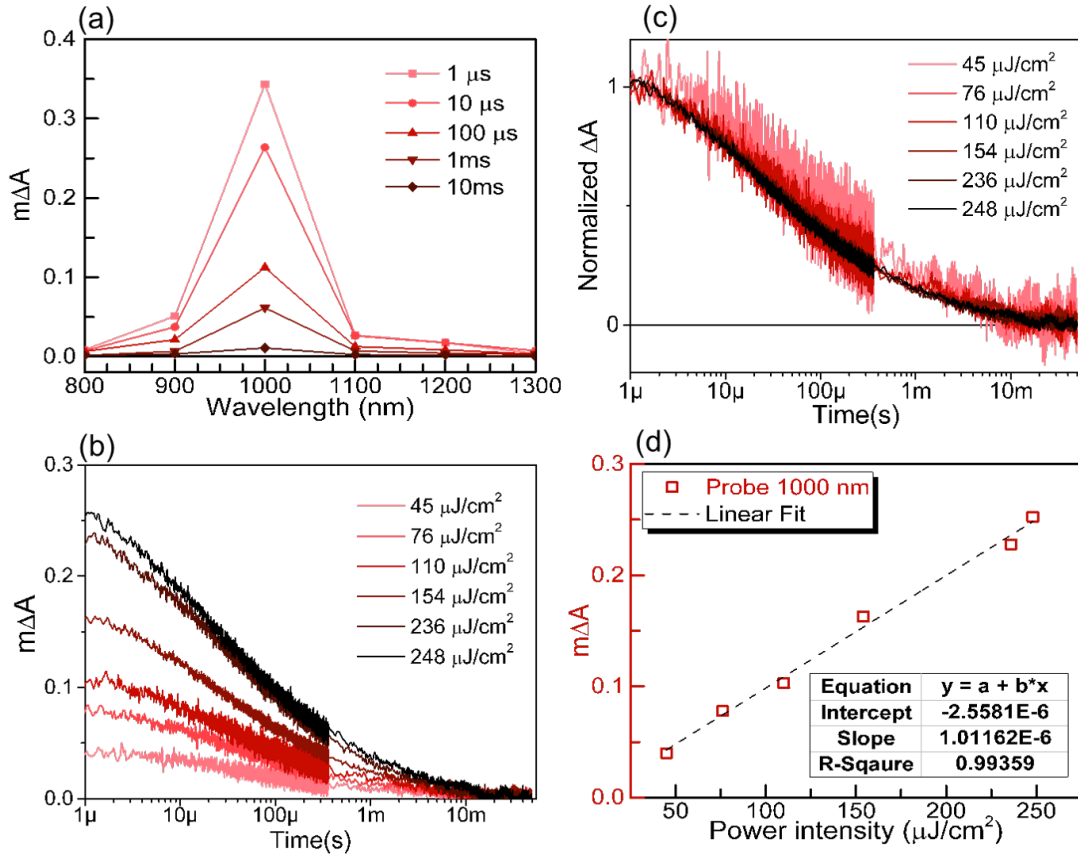


Figure 3.5: (a) Transient absorption spectra recorded 1 μs , 10 μs , 100 μs , 1 ms and 10 ms after excitation of a CIGS (GGI=0.4) thin film sample from the back side using 355 nm excitation wavelength. The fluence was 0.33 mJ/cm^2 , equivalent to $5.9 \times 10^{14} \text{ cm}^{-2}$ photons absorbed. (b) The TA decay kinetics probed at 1000 nm with fluences from 45 to 248 $\mu\text{J}/\text{cm}^2$. (c) Shows the corresponding kinetic trace normalized at 1 μs and (d) shows the highest ΔA amplitude as a function of fluence.

Figure 3.5a shows the TA feature after 355 nm excitation from the back side in the time range of 1 μs to 10 ms. With a 355 nm excitation, it is expected to excite charge carriers within a 100 nm region from the back surface. Instead of observing a photobleach signal as in ultrafast TA measurements, an absorption feature centred at 1000 nm was detected. Another interesting point is the shape of this absorption feature which fits well with the 1st derivative of the UV-VIS absorptance (Figure 3.2b). Within our measurement time window (1 μs to 50 ms), it is clear that the signal magnitude is the highest at 1 μs and decays to almost zero by the end of the measurement. Figure 3.5b to 3.5d illustrate the decay kinetics of this absorption feature under different fluences. The transient absorption signal increases linearly with increasing fluence, yet the normalized decay kinetics remain

unchanged. Furthermore, the decay kinetics fit well with a stretched exponential function, with a stretching constant (β) of 0.2, as shown in Appendix Figure A.4. Note that the fluence chosen for μ s TA study is much higher than the one chosen for ps-ns TA study. This is because if fluence chosen is lower than $45 \mu\text{J}/\text{cm}^2$ in μ s TA measurement, the signal-to-noise ratio is too low that the data did not seem to be trustworthy.

An absorption feature with such a long time scale can be assigned to the presence of localized charges (i.e. charges are being trapped)[32][33]. Furthermore, the decay kinetics following a stretched exponential behaviour indicate that the charge carriers decayed in multiple processes owing to varying carrier localizations[34][35][26]. Consequently, the species at 1000 nm is speculated to be trapped charge carriers that are generated in a larger number with higher light intensity and recombine on the ms timescale. Note that the two highest fluence chosen (236 and $248 \mu\text{J}/\text{cm}^2$) in μ s TA fluence-scaled measurement are both above 1 sun level, indicating a potentially higher impact of this type of defect on solar cell performance under concentrated light illumination.

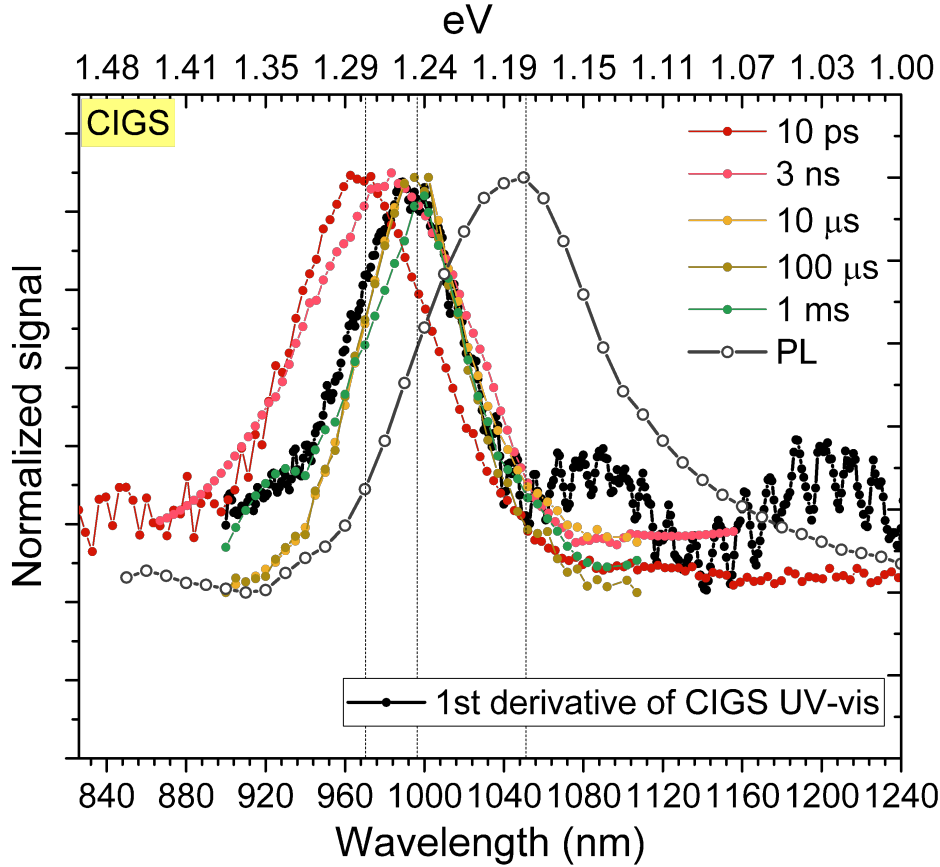


Figure 3.6: The comparison of peak positions among (1) normalized TA spectrum probed at 10 ps (red dots) and 3 ns (pink dots), (2) normalized TA spectrum of 355 nm excitation probed at 10 μ s (yellow dots), 100 μ s (brown dots) and 1 ms (green dots), (3) 1st derivative of UV-VIS absorbance spectrum (black dots), and (4) steady state PL emission following 1 sun white light illumination from the front side of a CIGS (GGI=0.4) thin film sample . Note that the 10 ps and 3 ns signal here are mirrored on the x-axis for an easier comparison with the other signals (absorbance).

Figure 3.6 is shown for an overall comparison of peaks positions of TA signals recorded at ps, ns, and μ s timescales, 1st derivative of steady-state UV-VIS absorbance, and steady state PL emission signal of the CIGS thin film sample. Note that the 10 ps and 3 ns TA signals here are mirrored on the x-axis for an easier comparison with other signals.

First of all, it is clear that TA signals obtained from the measurements followed the 1st derivative of UV-VIS absorbance spectrum. Though at ps timescale, the peak of the TA signal shows an approximately 30 nm blue shift compared to the peak of the 1st derivative of the UV-VIS absorbance spectrum, it can be seen that this signal gradually shifts

towards the 1st derivative absorptance peak with time. Therefore, the TA photobleach signal in the time range of ps to ns is assigned to the ground state bleach of the CIGS sample. Analysing the decay kinetics of this TA photobleach allows to extract the $t_{50\%}$ lifetime of charge carriers, and results show a $t_{50\%}$ lifetime of 140 ps in the back region and 650 ps in the front region. This decay is regarded primarily as SRH recombination of free charge carriers. A short $t_{50\%}$ lifetime in the back region of CIGS indicates that the non-radiative recombination is more pronounced than in the front region. From 1 μ s onward until 10 ms, a positive TA was detected and the shape matches almost exactly to the peak of the 1st derivative of the UV-VIS absorption spectrum. This long-lived and structured TA signal is proposed to originate from trapped charge carriers. Last, it should also be noted that the steady-state PL signal shows a ~ 50 nm difference in peak position compared to the peak of the 1st derivative of the UV-VIS absorption spectrum. This further suggests that the stimulated emission does not contribute significantly to the transient absorption signal.

3.3.2 CIS

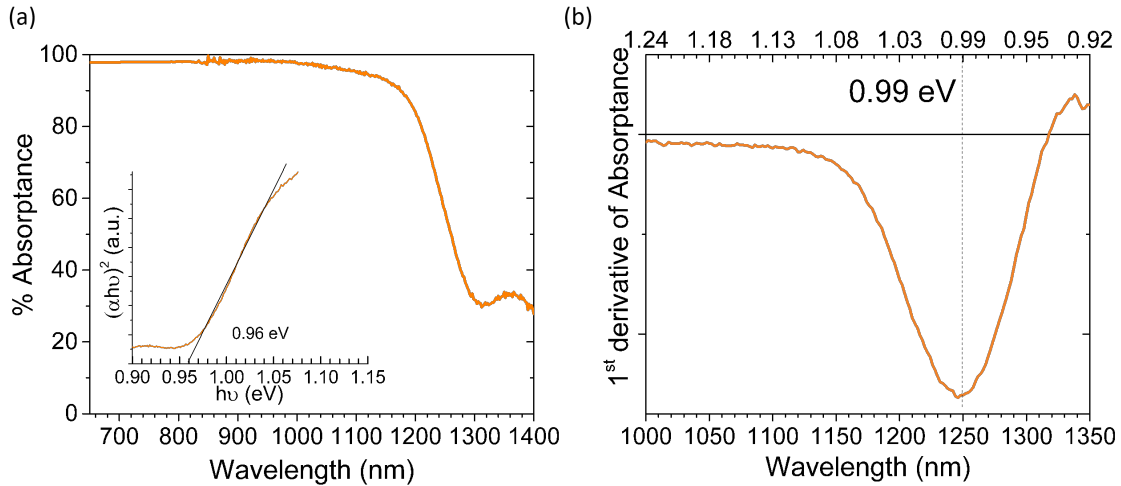


Figure 3.7: Steady state UV-VIS results of a CIS thin film sample. (a) Absorptance spectra following excitation from the back side. (b) The corresponding 1st derivative of the UV-VIS absorptance spectrum.

Figure 3.7 shows the steady state UV-VIS results of a CIS thin film sample. Similarly to the UV-VIS results of the CIGS sample, CIS shows a strong absorption of the light with energies above the bandgap energy. The bandgap energy determined by the Tauc

plot is 0.96 eV and using the peak of the 1st derivative results (as shown in Figure 3.7b) in 0.99 eV. These values align well with literature[36][37]. On the other hand, the sub bandgap absorption presumably originates from light scattering and light trapping in the material as in the case of CIGS.

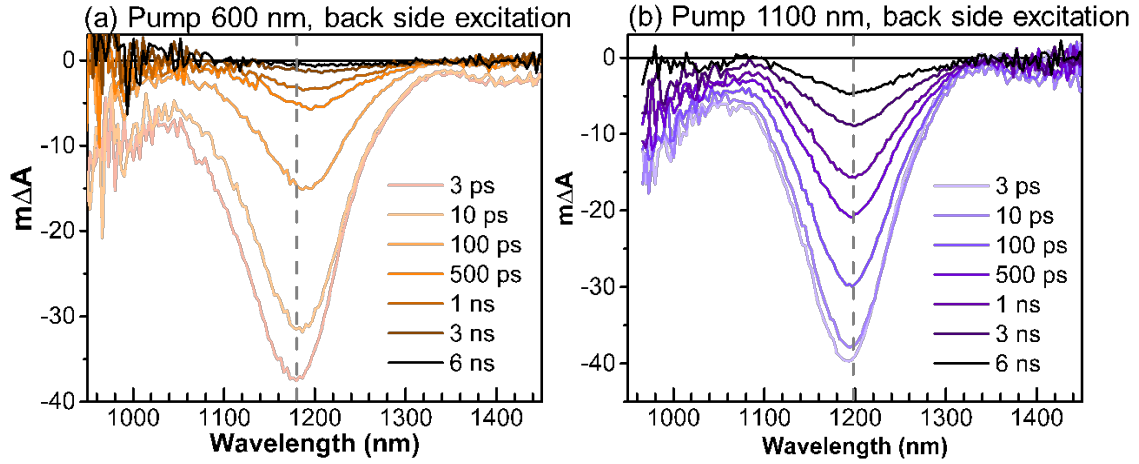


Figure 3.8: Transient absorption spectra recorded at 3 ps, 10 ps, 100 ps, 500 ps, 1 ns, 3 ns and 6 ns of a CIS thin film sample following excitation wavelengths of (a) 600 nm and (b) 1100 nm from the back side. The fluence is $11.5 \mu\text{J}/\text{cm}^2$ for the 600 nm excitation, and $25.5 \mu\text{J}/\text{cm}^2$ for the 1100 nm excitation so that the photons absorbed per volume are the same.

Figure 3.8 shows the TA results of the CIS thin film sample following an excitation wavelength of 600 nm and 1100 nm from the back side. Note that here the fluence of each wavelength was adjusted so that the photons absorbed per cm^3 is the same in both cases. With 600 nm excitation, charge carriers were generated up to 130 nm deep with respect to the back surface. On the other hand, with 1100 nm excitation, charge carriers were generated up to 540 nm deep with respect to the back surface, which allows the observation of the kinetics of charge carriers generated in different regions of the film (Appendix Figure A.5). In both cases, an intense photobleach with a single peak was detected. For 600 nm excitation, the peak starts from 1180 nm and gradually red-shifts to 1200 nm. For 1100 nm excitation, the peak starts from approximately 1190 nm before it shifts to 1200 nm after a few picoseconds and remains in its position until the end of the measurement (6 ns). In addition, the photobleach signals decay with time in both cases, yet it can be seen that in the case of 1100 nm excitation, the decay is slower than in the case of 600 nm excitation.

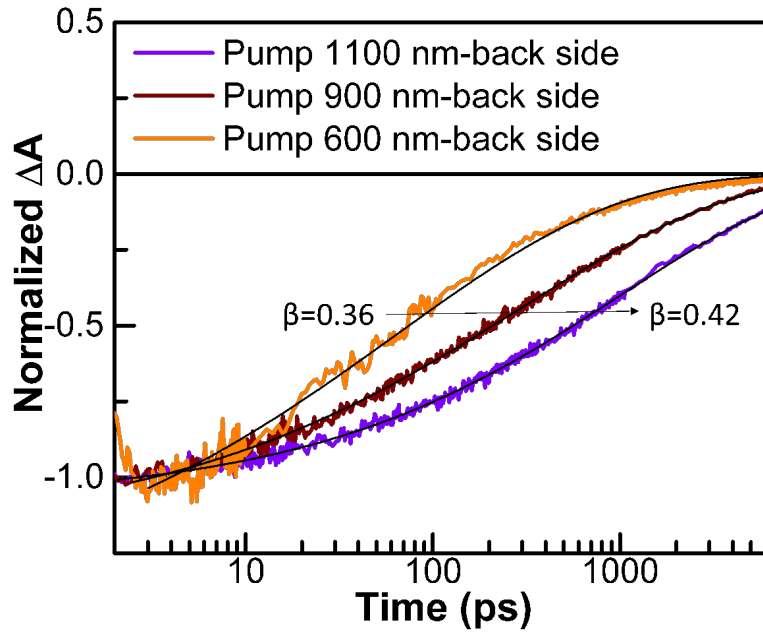


Figure 3.9: TA kinetics of a CIS thin film sample probed at 1200 nm normalized at 2 ps in the case of utilizing 1100 nm, 900 nm (spectrum shown in Figure 3.10a), and 600 nm excitation from the back side. All kinetics were fitted with a stretched mono-exponential function ($y = a * \exp - ((kx)^\beta)$, β : stretching constant). The stretching constant is 0.36, 0.39, and 0.42 for 600 nm, 900 nm and 1100 nm excitation cases, respectively.

Figure 3.9 illustrates the normalized TA kinetics probed at 1200 nm with different excitation energies, and it is clear that the TA kinetics decay faster with increasing photon energy and thus being located closer to the surface. Furthermore, all these kinetics can be fitted well with stretched exponential functions. The fitting results show that the stretching constant is larger when the sample is excited with lower photon energies, and the $t_{50\%}$ for each excitation case is 580 ps, 200 ps and 72 ps for 1100 nm, 900 nm and 600 nm excitation, respectively. A higher stretching constant indicates a broader distribution of defect states/tail states, resulting in higher dispersed recombination kinetics. These results indicate that the closer the charge carriers are generated to the back surface, the shorter is their lifetime, which may be attributed to the increased non-radiative recombination near the back surface, as in the case of CIGS film.

A fluence-scaled TA measurement was performed and the results are shown in Figure 3.10. The CIS sample was excited following 900 nm excitation wavelength from the back

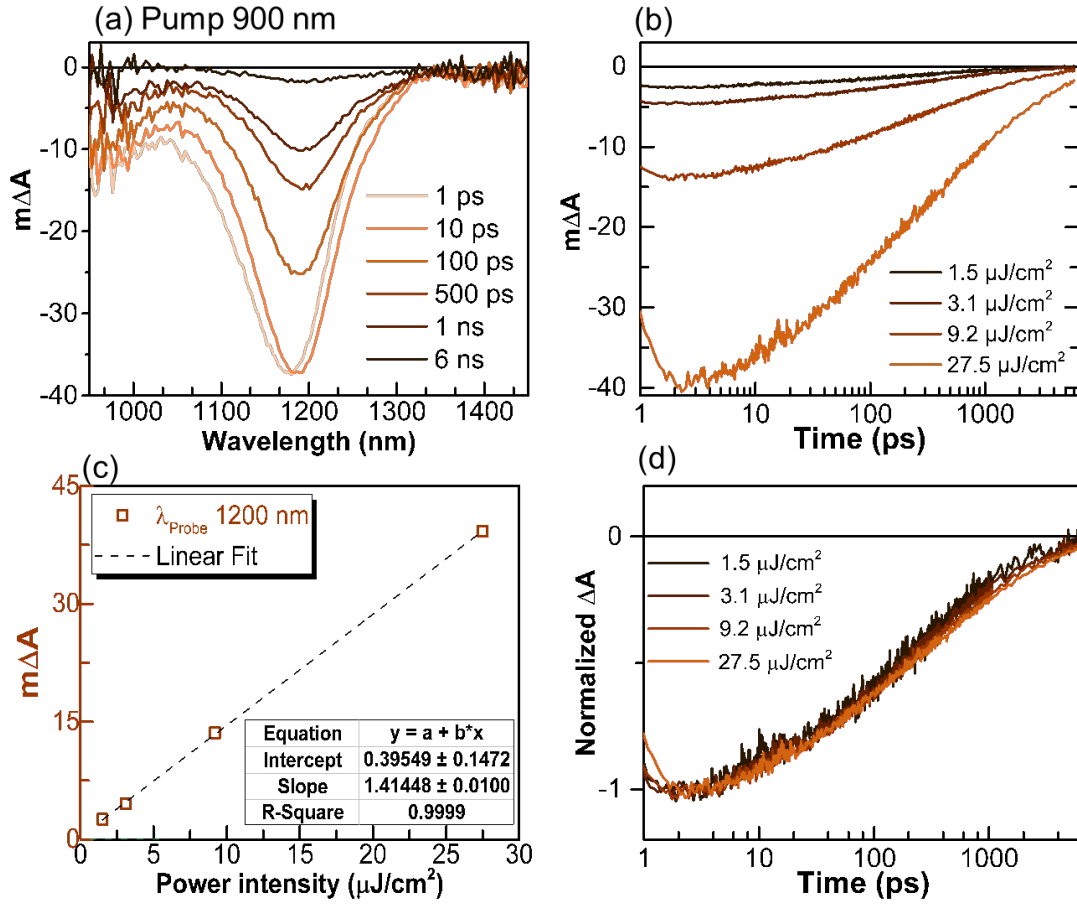


Figure 3.10: Fluence-scaled TA study on a CIS thin film sample following an excitation wavelength of 900 nm from the back side with 1.5, 3.1, 9.2 and 27.5 $\mu\text{J}/\text{cm}^2$ fluences. (a) TA spectrum recorded at 1 ps, 10 ps, 100 ps, 500 ps, 1 ns, and 6 ns. (b) TA kinetics probed at 1200 nm. (c) The maximum signal amplitude as a function of fluences. (d) TA kinetic trace of 1200 nm normalized at 2 ps. 3.3 $\mu\text{J}/\text{cm}^2$ equals to 10^{13} photons/ cm^2 absorbed.

side at 1.5, 3.1, 9.2 and 27.5 $\mu\text{J}/\text{cm}^2$ fluences. It can be seen that the photobleach amplitude increases linearly with fluence (Figure 3.10c), yet the normalized kinetics (Figure 3.10d) shows almost no change upon increasing fluence. This indicates that the recovery of the photobleach in CIS is primarily due to SRH recombination of free charge carriers, as in the case of CIGS film.

Figure 3.11a shows the TA feature of the CIS film after 355 nm excitation from the back side in the time range of 1 μs to 10 ms. The signal almost decayed to zero after 10 ms, therefore the signal afterwards is not presented. As in the case of CIGS, a clear and broad band edge absorption is observed. Figure 3.11b to 3.11d show the results of corresponding power dependency measurements. The absorption signal increases linearly

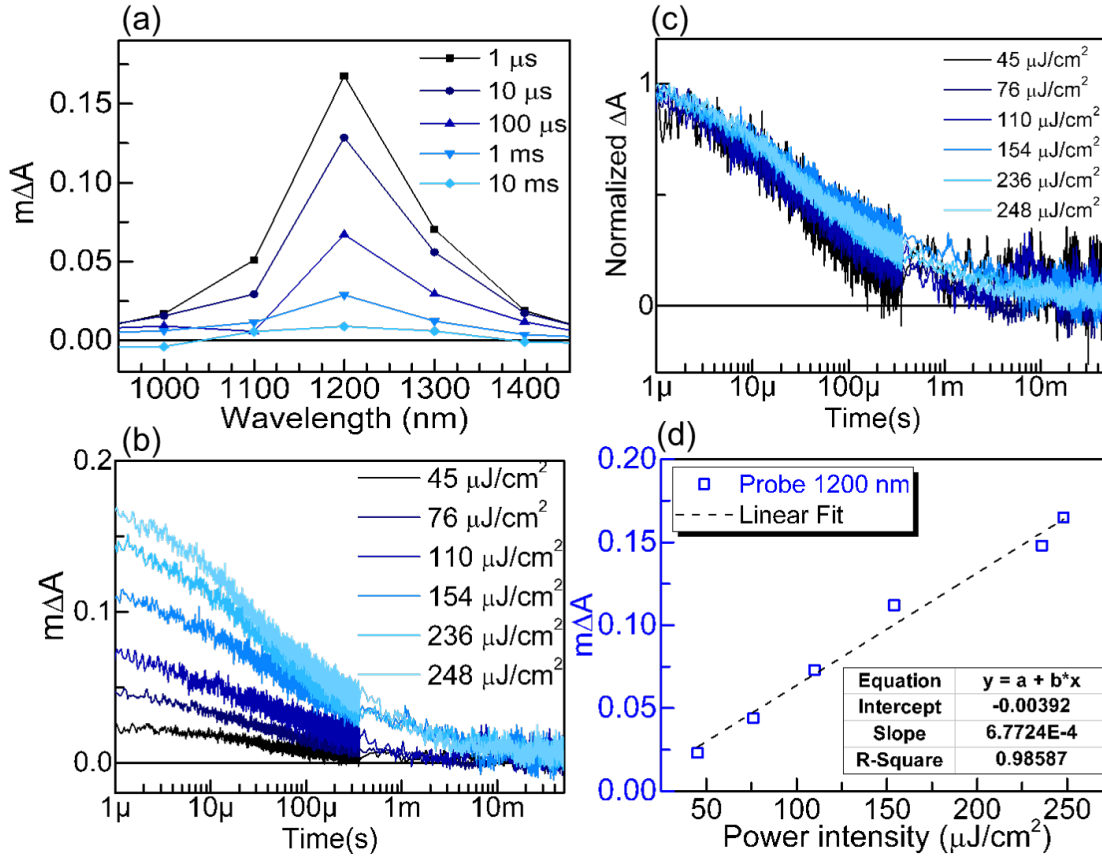


Figure 3.11: Slow transient absorption spectra of a CIS thin film sample recorded at 1 μs , 10 μs , 100 μs , 1 ms and 10 ms after excitation of a CIS thin film sample using 355 nm laser. The fluence is 248 $\mu\text{J}/\text{cm}^2$, equivalent to $4.4 \cdot 10^{14}$ photons/ cm^2 absorbed (b) The TA decay kinetics probed at 1200 nm with fluences from 45 to 248 $\mu\text{J}/\text{cm}^2$. (c) Shows the corresponding kinetic trace normalized at 1 μs and (d) shows the highest ΔA amplitude as a function of fluence.

with increasing intensity but the normalized kinetics remain unchanged. Also, the decay kinetics fit well with a stretched exponential function, with a stretching constant of 0.1 (Appendix Figure A.6). As discussed previously in the CIGS section, this absorption feature is proposed to result from the presence of localized charges.

3.3.3 Summary of charge carrier dynamics in CIGS and CIS

- **Picosecond-nanosecond timescale**

In both CIGS and CIS materials, a dominant photobleach with a peak close to its band edge is observed. This chalcogenide material exhibits a high dielectric constant (~ 13.6)[38], which results in an efficient and rapid charge separation process. In addition,

the effective mass of an electron is smaller than the one of a hole[39]. For a direct bandgap semiconductor, the TA amplitude is proposed to be inversely proportional to the effective mass of the associated charge carriers[40], the photobleach TA feature observed at ultrafast timescales is most likely attributed to the ground state bleach of free electrons. Furthermore, the decay kinetics of the photobleach signal differ significantly depending on where the charge carriers are generated. The closer the charge carriers are generated towards the back surface, the shorter-lived they are, and their decay kinetics also exhibit a much more stretched exponential behaviour. The time in which the signal amplitude decays to 50% of its initial value ($t_{50\%}$) within the investigated CIGS material varies between 140 ps to 650 ps and within CIS between 70 ps to 580 ps (from the back region to the front region). As the grain size and the GGI ratio is homogeneous throughout the entire film in both cases, the reason for observing such different time constants within one film is likely to be from MoSe_2 residuals that potentially act as recombination centers, the defects formed during the peeling-off procedure, and the surface oxidation at the air-exposed back region, resulting in more charge carriers recombining there. However, till this point, it is not possible to identify what defects specifically contributed to this effect.

• Microsecond-second timescale

In CIGS and CIS, a clear and structured absorption with a maximum at the band edge is observed in microsecond-second timescale. Though a long-lived structured absorption is commonly associated with charge carriers being trapped in defect states, in this study it is not clear whether the defects are directly involved in the absorption process or not. For example, if the defect states are not directly involved but instead building up an electric field after accumulation of trapped charges, this electric field will affect the band edge absorption. In literature, band edge absorption is discussed in the context of Stark [41][42][43] and Franz-Keldysh effects[44] which both are seen as an electroabsorption signal at the bandedge. Here, despite the fact that the bandedge absorption in the microsecond-second timescale aligns well with the feature in the 1st derivative of the UV-VIS absorptance spectrum, more experiments need to be conducted in the future to figure out the origins of this type of defects.

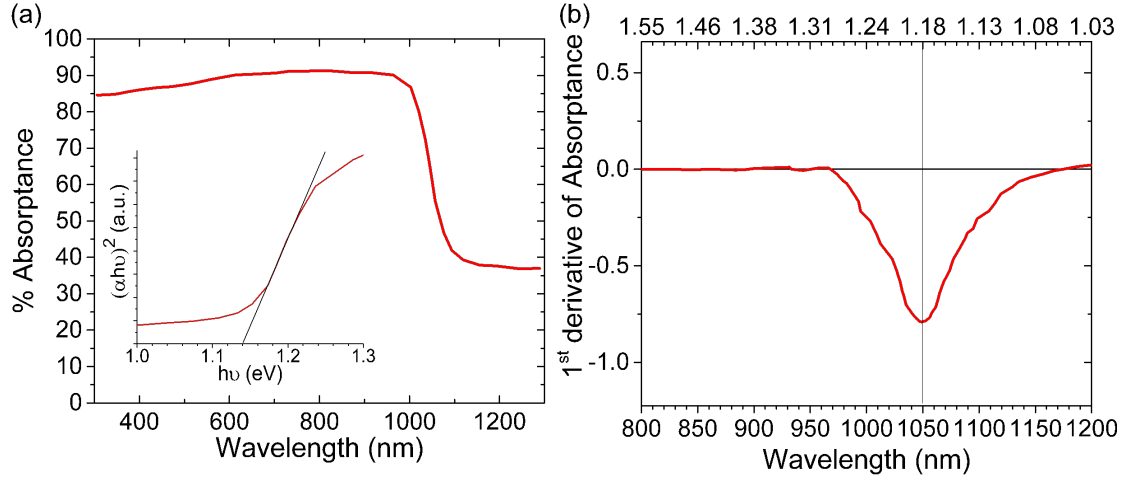


Figure 3.12: Steady state UV-VIS results of a Sb_2Se_3 thin film sample. (a) Absorptance spectra. (b) The corresponding 1^{st} derivative result of UV-VIS absorbance. *Note that this UV-VIS measurement was carried out by Dr. Rajiv Ramanujam Prabhakar from University of Zurich.*

3.3.4 Sb_2Se_3

Figure 3.12a, b shows the steady-state absorption spectrum and the corresponding 1^{st} derivative of a Sb_2Se_3 polycrystalline thin film, respectively. From the Tauc plot and the result of 1^{st} derivative of the UV-VIS absorption spectrum, the bandgap of the Sb_2Se_3 thin film sample is estimated to be 1.12–1.18 eV, which agrees well with previous literature[45]. To further investigate the charge carrier dynamics in Sb_2Se_3 thin films, a 700 nm wavelength (~ 1.77 eV) was chosen for the excitation due to being larger than the bandgap of Sb_2Se_3 and therefore all the photons are presumed to be fully absorbed. The penetration depth of a 700 nm laser pulse is estimated to be ~ 200 nm. Figure 3.13 shows the TA spectra of a Sb_2Se_3 thin film sample recorded from 0.5 ps to 6 ns following an excitation wavelength of 700 nm. First of all, it is clear that the spectra evolve over time, indicating different TA species being observed. At 0.5 ps, a photobleach with a peak at approximately 960 nm is dominant in the whole spectrum. The prominent photobleach signal red-shifts to ~ 980 nm within 2 ps likely due to charge carrier relaxation. However, this photobleach signal recovers fast and turns into an absorption signal with a peak at ~ 980 nm at 100 ps. This absorption signal grows within several nanoseconds and remains constant until the end of the measurement. The 980 nm photobleach signal (PB1) is assigned to a ground state bleach, as it appears relatively close to the band edge (at the

lower end of the 1st derivative of the UV-VIS absorptance spectrum). On the other hand, it is suspected that the long-lived absorption signal (PA1) results from the trapped charge carriers[46][47].

By analysing the charge carrier kinetics, more details of the charge carrier dynamics can be revealed. Figure 3.14 illustrates the normalized 980 nm TA kinetics (maximum photobleach position) under a range of fluences ($17.8 \mu\text{J}/\text{cm}^2$ to $131 \mu\text{J}/\text{cm}^2$). Probing at 980 nm allows a direct observation of both free and trapped charge carriers. It is clear that the decay kinetics are insensitive to varying fluences, suggesting that the free charges do not undergo radiative or Auger recombination. Instead, it suggests that the depopulation of free charge carriers is predominantly occurring by charge trapping, because the fluences do not affect the distribution of defect states.

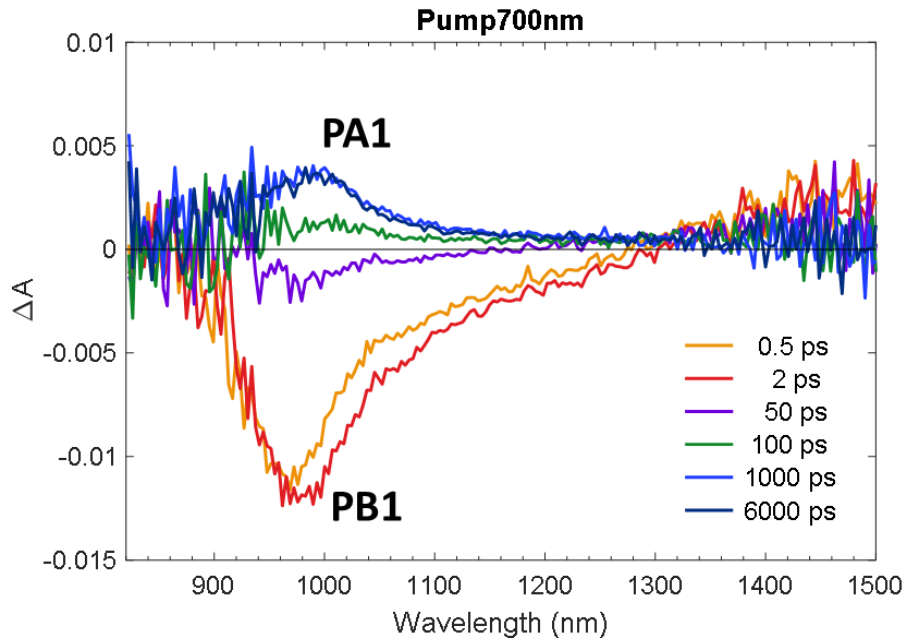


Figure 3.13: Transient absorption spectra recorded at 0.5 ps, 2 ps, 50 ps, 100 ps, 1 ns and 6 ns of a Sb_2Se_3 thin film following an excitation wavelength of 700 nm. The fluence is $131 \mu\text{J}/\text{cm}^2$, equivalent to 4.7×10^{14} photon/ cm^2 being absorbed. Photobleach is denoted as PB, whilst photoabsorption is denoted as PA.

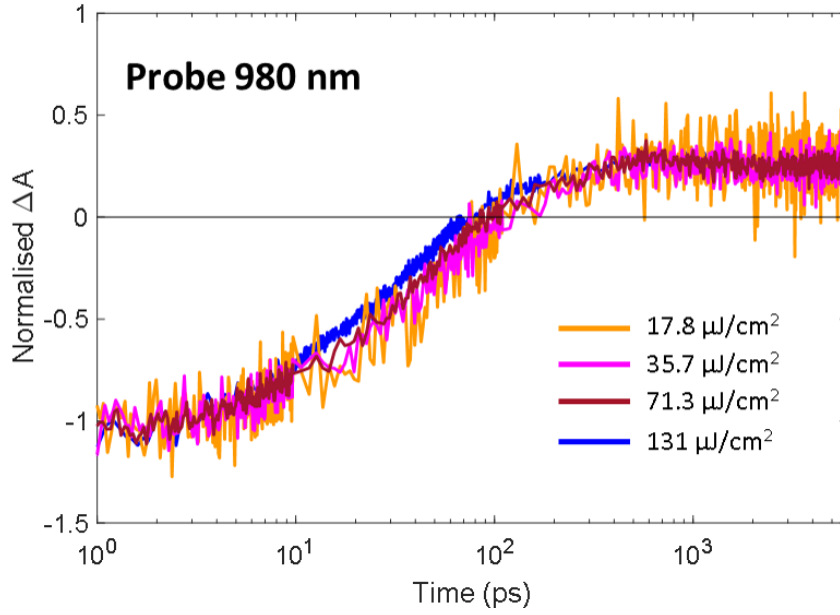


Figure 3.14: Normalized TA kinetics at 980 nm (the photobleach maximum) of Figure 3.13 using a range of power intensities between $17.8 \mu\text{J}/\text{cm}^2$ to $131 \mu\text{J}/\text{cm}^2$. $t_{50\%} = 15 \text{ ps}$

Since the 980 nm photobleach is comprised of both free and trapped charge carrier dynamics, to obtain the decay time constant of free charge carriers and the rise time constant of the trapped charge carriers requires more in-depth analysis such as global analysis. Due to the scope of this chapter, instead of performing a global analysis, the time in which the signal amplitude decays to 50% of its initial value before turning zero ($t_{50\%}$) is extracted as an estimation of the free charge carrier lifetime. As a result, a $t_{50\%}$ of 15 ps is obtained, which is close to the results from previous literature ($\sim 23 \text{ ps}$)[46]. Unfortunately, the lifetime of trapped charge carriers can only be extracted if a global analysis is performed.

A μs -s TA measurement is performed and a prominent absorption is detected from 1 μs until 0.1s, as shown in Figure 3.15a. This absorption has the same peak (1050 nm) as in the 1st derivative of the UV-VIS absorbance spectrum (Figure 3.12b), however, the absorption range appears to be broader than the UV-VIS one. It is suspected that this μs absorption results from the same species that induced the absorption in the nanosecond timescale due to the following reasons. The ns and μs absorption signal both range from 900 nm to 1300 nm, and both absorption peak positions are located at the bandedge. However, the types of defects are not distinguishable from this result.

Further comparing it to the absorption signal detected in the picosecond-nanosecond

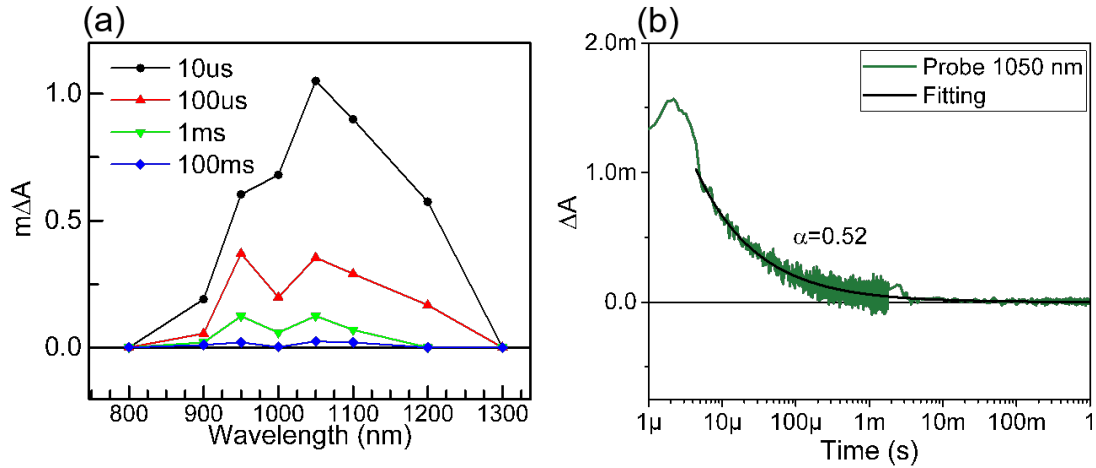


Figure 3.15: (a) Transient absorption spectra recorded at 10 μ s, 100 μ s, 1 ms and 10 ms of a Sb₂Se₃ thin film sample following an excitation wavelength of 355 nm. The fluence is 0.33 mJ/cm², equivalent to 5.9×10^{14} cm⁻² photons absorbed. (b) The TA decay kinetics probed at 1050 nm. The measurement was taken under N₂ atmosphere in the DR-TAS system.

timescale, though both spectra show an absorption range from 900 nm to 1300 nm, the peak of the absorption in the picosecond-nanosecond timescale is 50 nm blue-shifted and is 4 times larger than the absorption at 1200 nm. A long-lived absorption signal is commonly linked to trapped charge carriers, and the defects can be either directly involved in the absorption process or not, as discussed previously in Chapter 3.3.3. Furthermore, the decay kinetics can be fitted well with a power law function ($y = a * x^{-\alpha}$) with the power component (α) equals to 0.52, as shown in Figure 3.15b. As the power component is smaller than 1, it suggests a trap-limited recombination, further supporting the assignment of charges trapped in the defect states.

3.3.5 Summary of charge carrier dynamics in Sb₂Se₃

• Picosecond-nanosecond timescale

For the Sb₂Se₃ material, a photobleach with its peak close to the bandedge is observed already at 0.5 ps, however, this photobleach quickly evolves into an absorption signal for which the amplitude remains constant until the end of the measurement. The $t_{50\%}$ of this photobleach signal is estimated to be 15 ps, which corresponds to the lifetime of free charge carriers.

- **Microsecond-second timescale**

A prominent absorption signal with a peak at bandedge is observed in the microsecond-second timescale. This long-lived absorption signal is proposed to originate from the same species which induce the absorption in the nanosecond timescale. The decay kinetics probed at the bandedge is fitted well with a power law function, indicating the existence of trapped charges in the microsecond-second timescale.

3.3.6 Comparison between CIGS/CIS and Sb_2Se_3

- **Picosecond-second timescale**

Comparing the $t_{50\%}$ of all three materials, it can be seen that the Sb_2Se_3 exhibits the lowest value. The CIGS and CIS materials have overall higher charge carrier lifetimes even in the defective back region, indicating that Sb_2Se_3 is more defective than CIGS or CIS. In all three samples, the decay kinetics of the prominent photobleach is insensitive to the fluence, considering the fact that the injection level is higher than the doping level in all three cases, suggesting that the reduction of the photobleach is mainly caused by SRH recombination rather than radiative or Auger recombination.

Last, it is important to note that in the Sb_2Se_3 case, the photobleach turns into a positive absorption after approximately 100 ps. This is not observed in the CIGS or CIS cases, in which the photobleach lasts till the end of the measurement (6 ns). A detailed discussion on the origin of this absorption signal and the possible difference between the CIGS, CIS and Sb_2Se_3 materials are given below.

- **Microsecond-second timescale**

With the assignment of the absorption signal to the charge carriers trapped in defect states, an explanation for why this absorption signal appears much earlier in the Sb_2Se_3 case (absorption signal detected after 100 ps) than in the CIGS/CIS case (absorption signal only detected from $1\mu\text{s}$ onwards) is provided here. The peak position and range of this long-lived absorption is identical with those of the photobleach signal at the early timescale. Hence, these two signals counter each other and how fast the absorption appears depends highly on the amount of free charge carriers being trapped. If the ratio of trapped charge carriers to free charge carriers is $\gg 1$, the band edge absorption would

appear earlier than in the case of a lower ratio. In the Sb_2Se_3 case, assuming equal attenuation coefficients of trapped and free charge carriers, the ratio of deeply trapped charge carriers to free charge carriers is estimated to be 25 % (Figure 3.14). In both CIGS/CIS cases, no absorption signal is observed in TA measurements in picosecond-nanosecond timescale regardless of excitation energy and fluence. This suggests that the amount of trapped charges is significantly lower in CIGS/CIS than in Sb_2Se_3 .

3.4 Conclusion

The study in this chapter reveals a long-lived absorption signal in CIGS/CIS material that has never been found before. Though the nature of this absorption needs further investigation, it is likely that it associates with the deep defect states that trapped charges for long time (second timescale). It is also interesting to see that the long-lived absorption signal is more significant in Sb_2Se_3 than CIGS/CIS material, which coincides with a much faster charge carrier lifetime in Sb_2Se_3 . This suggests that this long-lived absorption signal may serve as an indicator for detecting the quality of the material.

In addition, this chapter provides a solid foundation not only for the studies presented in the next two chapters but potentially for any future relevant work. It reveals the methods to obtain TA signal in CIGS/CIGS/ Sb_2Se_3 with decent signal-to-noise ratio and the fluence required to achieve this. Furthermore, this study also gives reasonable assignment for each TA signal observed in a near-IR wavelength range along with the appropriate data analysis in all three materials.

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Chapter 4

Transient absorption studies on electron dynamics along the Ga-gradient in CIGS solar cells

4.1 Abstract

An engineered Ga-gradient profile across the CIGS thin film along with an alkali atom post-deposition treatment improves device efficiency significantly. However, one of the key indications for a Ga-gradient high efficiency cell: the minority carrier mobility in the bulk and towards the back contact, is not well established. In this chapter, the competition between recombination and drift of minority carriers (electrons) after photoexcitation in a state-of-the-art CIGS solar cell with a Ga-gradient profile and NaF+RbF PDT treatments will be investigated by means of ultrafast transient absorption spectroscopy. A proposed kinetic model and experiments fully decouple carrier transport and recombination behaviour in this complex Ga-graded device structure. The results reveal that the recombination times differ significantly depending on the GGI ratio, ranging from ~ 100 ps for $\text{GGI} > 0.6$ (close to the Mo back contact) to 19.1 ns for $\text{GGI}=0.2$. Furthermore, minority carriers excited at the high GGI region drift-diffuse within 2 ns to an engineered energy notch around $2.7 \mu\text{m}$ into the film, corresponding to a mobility of $16.3 \pm 4.0 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

4.2 Introduction

Engineering the compositional profile of solar cells to achieve good device performance is employed in a wide range of commercialized and emerging photovoltaics such as Si [1], CdTe[2], CIGS[3], and perovskite[4] solar cells. State-of-the-art CIGS solar cells make use of a bandgap engineering approach, varying the $[\text{Ga}]/([\text{Ga}]+[\text{In}])$ ratio (GGI ratio) across the absorber film. The introduction of Ga into the CuInSe_2 lattice can widen the band gap from 1 eV[5][6] up to 1.68 eV[7] in pure CuGaSe_2 . A double Ga-gradient profile (*Ga-rich/Ga-poor/Ga-rich*), which the GGI ratio is designed to increase towards both front and back contacts and leave a low GGI region in between, is commonly implemented in high-efficiency CIGS solar cells[3][8][9]. As introduced in detail in Chapter 1.4.3, such design has been shown to suppress recombination losses associated with smaller CIGS grain sizes near the Mo back contact and with interfacial recombination at the CIGS/Mo junction[9], thereby significantly increasing device open-circuit voltage V_{OC} [10][11][12].

Optimisation of the CIGS film thickness, composition and the Ga-gradient profile has largely been carried out by monitoring improvements in device efficiency, with only

limited knowledge of the underlying minority carrier dynamics driving electrons to the electron collecting contact. In particular, minority carrier mobility and drift-diffusion times in high-efficiency CIGS solar cells are important parameters to quantify in order to understand performance losses in state-of-the-art devices. There have been several studies focusing on CIS and CIGS materials measuring mobility by a variety of techniques, but large variations in calculated mobilities are found, as listed in Table 4.1. Furthermore, as it is experimentally difficult to access in the presence of a composition gradient, only few studies investigated Ga-graded CIGS. Weiss et al. determined a lower limit of $8.3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for the minority carrier mobility of a single back-graded CIGS via both simulations and TRPL spectroscopy[13]. Kuciauskas et al. carried out time-resolved photoluminescence (TRPL) studies on a Ga gradient device and estimated a minority carrier mobility of 55-230 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ in the SCR at the CdS/CIGS interface [14], but did not address electron transport across the Ga-gradient towards the back contact region.

Herein, by using broadband TAS on picosecond to nanosecond timescales, both electron transport and recombination processes are probed. This broadband ultrafast TAS study focuses on monitoring minority carrier dynamics across the entire Ga-graded CIGS film (from the high GGI region near the Mo back contact to the low GGI energy notch (band gap minimum) in the SCR) in efficient solar cells, studied after removal of the Mo back contact. By tuning the wavelength of monochromatic excitation pulses to selectively excite different spatial depths of the Ga-gradient CIGS film, it is possible to calculate minority carrier mobilities outside the SCR and to monitor the kinetics of the competing charge recombination losses. Furthermore, a kinetic model is proposed that takes into account the dynamic competition between transport and recombination, allowing to decouple both processes and obtain the electron mobility across the CIGS film in the presence of a Ga-gradient. Experiment results reveal that the charge carrier lifetime reduced significantly with increasing GGI ratio of the detected region, and no charge transport is detected from the region where CIGS shows small grains. The resultant insights on electron mobility and recombination in optimized high-efficiency solar cells will be especially useful in guiding further optimisation of device performance by addressing the back surface field near the Mo contact.

Table 4.1: Electron/hole mobility of CIGS at room temperature measured by the Hall effect, Admittance spectroscopy, Time of Flight, Terahertz, Time-resolved photoluminescence (TR-PL), and transient absorption spectroscopies (TAS)

Measurement technique	Material	Sample type	Ga gradient	Mobility (cm^2/Vs)	Mobility of	Reference
Hall	n-CIS	Thin film	x	1–80	e^-	[15][16][17][18]
	n-CIS	Single crystal	x	~ 1000	e^-	[19][20][21][22]
	p-CIS	Thin film	x	0.2–80	h^+	[16],[17],[23]
	p-CIS	Single crystal	x	60–360	h^+	[19],[22],[24]
	p-CIGS	Thin film	x	160–310	h^+	[25]
Admittance Spectroscopy	p-CIGS	Thin film	x	3–22	h^+	[26],[27]
Terahertz	p-CIS	Thin film	x	1000	e^-	[28]
Time of Flight	p-CIGS	Thin film	x	0.02–0.05	e^-	[29]
				0.02–0.7	h^+	[30]
TR-PL	p-CIS	Thin film	x	32–45	e^-	[13]
	p-CIGS	Thin film	✓	55–230	e^-	[14]
				lower limit: 8.3	e^-	[13]
TAS	p-CIGS	Thin film	✓	16.3	e^-	This study

4.3 Experimental methods

In this chapter, TAS in picosecond–nanosecond timescale is utilized as the main tool to investigate electron dynamics along the Ga gradient in a high efficiency CIGS device. Other techniques such as steady-state UV-VIS, PL, SIMS, and J-V measurement are also utilized for examining the steady-state optical, material and device properties of the CIGS device. Details of each instrument set-up and fundamental principles are described in Chapter 2.

The CIGS device studied in this chapter is subjected to **Ga gradient implementation and RbF+NaF PDT**. The fabrication methods of the whole CIGS device can be found in Chapter 2.2.1. The CIGS device structure is illustrated previously in Figure 2.12a. And as described in Chapter 2.3, to measure the CIGS device in a transmission mode in TAS, the CIGS sample is prepared by peeling of the Mo back contact from the rest of the CIGS stacks, as shown in Figure 2.12b.

4.4 Results and Discussions

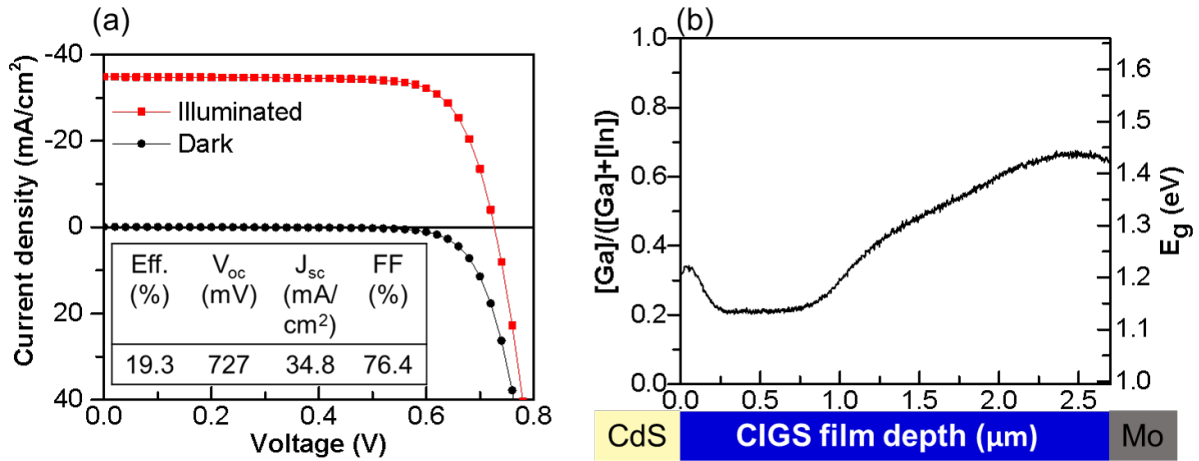


Figure 4.1: Cu(In,Ga)Se₂ solar cell properties. a) J-V curve of CIGS device measured under simulated sunlight (100 mW cm⁻², 1 sun). b) Compositional depth profile from the secondary ion mass spectroscopy (SIMS) measurements of the CIGS film, showing the varying GGI ratio throughout the CIGS film and the corresponding calculated band gap energy, E_g.

The study presented in this chapter was carried out on a CIGS solar cell with a device efficiency >19% as shown in Figure 4.1a. In this device, the ratio of indium and gallium

is adjusted through the course of CIGS film evaporation leading to a characteristic Ga-gradient profile[31][32][33]. The Ga gradient profile was extracted from a depth profile secondary ion mass spectrometry (SIMS) measurement, and the result is shown in Figure 4.1b. From this composition profile the optical band gap, E_g , can be approximated with Equation 4.1.

$$E_g(x) = E_g(CIS)(1 - x) + E_g(CGS)x - bx(1 - x) \quad (4.1)$$

$E_{g,CIS}$ and $E_{g,CGS}$ is the direct band gap of pure CuInSe₂ (~ 1 eV) and CuGaSe₂ (~ 1.68 eV) respectively, x is the GGI ratio, and b is the measured bowing coefficient[34][35][36]. For the materials studied in this thesis, the bowing coefficient, b , has been characterised by means of reflectance and transmittance, and the calculated value is around 0.03[37]. Resulting values of E_g as a function of film depth are also shown in Figure 4.1b alongside the GGI ratio. It is apparent that the CIGS bandgap first drops from 1.22 eV (GGI ratio of 0.33–0.34) at the CIGS/CdS interface to a bandgap minimum of 1.13 eV (GGI ratio of 0.2) 300 nm into the layer. The bandgap remains at 1.13 eV until approximately 800 nm and increases all the way to 1.44 eV at the Mo back contact (corresponding to a GGI ratio of 0.66–0.67). Note that in this thesis the bandgap minimum region is termed the "energy notch".

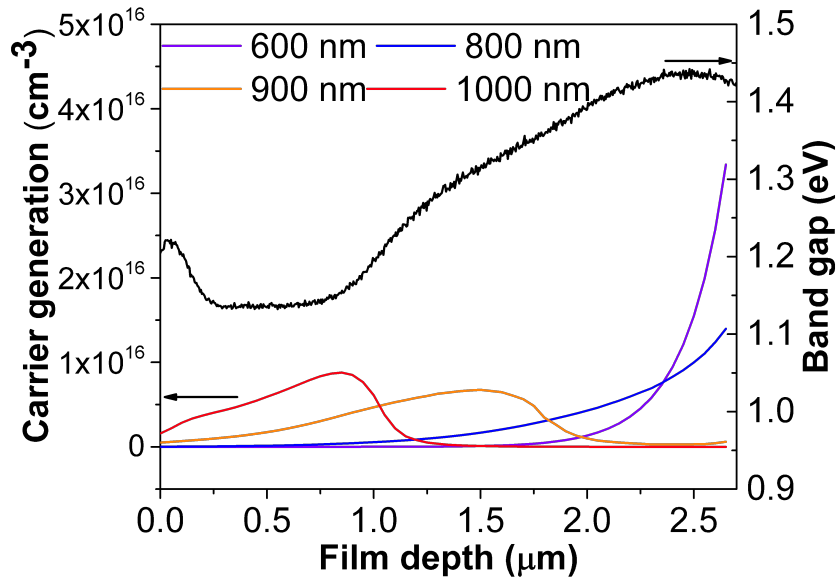


Figure 4.2: Simulated carrier generation profile in a Ga-gradient CIGS film following excitation wavelengths of 600 nm, 800 nm, 900 nm and 1000 nm from the back side. Along with the carrier concentration profile, the band gap profile from the SIMS measurements in Figure 4.1b is shown.

To further observe charge carrier dynamics in different GGI regions of the CIGS, a transmission TAS study using varying excitation energies (600 – 1000 nm) was performed. Figure 4.2 illustrates the charge carrier generation profile in such Ga-graded CIGS absorber after 600, 800, 900 and 1000 nm excitation energies from the back side. As illustrated, employing different excitation energies results in charge carriers generated from different GGI regions. For example, exciting with 1000 nm (1.24 eV) charge carriers are predominantly excited in the energy notch (between 0 μm – 1.2 μm from the CdS/CIGS interface) whereas exciting with 600 nm laser, charge carriers are generated in the high bandgap region within 200 nm from the back interface.

Figure 4.3 shows the corresponding time-resolved absorption study on the CIGS TAS sample using 600, 800, 900 and 1000 nm excitation wavelengths from the back side. In Figure 4.3a, a negative ΔA signal with a minimum at 1025 nm (1.21 eV) appears shortly after excitation with 1000 nm laser light (i.e.: within 1 ps). This signal essentially maintains its spectral signature during the entire time window of the measurement (from 1 ps to 6 ns), with only a modest decay in signal amplitude and a slight red-shift to a peak position of 1030 nm (1.20 eV). The energy of the photobleach (1.20 eV) coincides with the 1st derivative of the steady-state absorptance spectrum (see Appendix Figure B.1) and can hence be attributed to a band edge photobleach. Furthermore, a ~ 70 meV Stokes-shift between the steady-state emissions relative to the absorption feature is also observed (see Appendix Figure B.1). This is analogous to the results of the non Ga-graded CIGS sample studied in Chapter 3. The presence of a 70 meV Stoke shift indicates stimulated emission does not contribute significantly to the transient absorption signal. In Figures 4.3b-d, laser pulses with increasingly higher photon energies (900 nm, 800 nm and 600 nm) were applied. 1 ps after excitation, bleach signals centred at 936 nm (1.32 eV), 892 nm (1.39 eV) and 875 nm (1.42 eV) were observed, respectively. These signals are in agreement with the calculated band gap energies in the respective excitation volumes. For example, the bandgap close to the back interface is calculated to be between 1.42 eV and 1.44 eV (Figure 4.1b). With time, a decay of these initial signals was observed in concurrence with a rise of a 1025 nm bleach signal. The 1025 nm kinetics corresponds to the band gap energy (1.21 eV) at the energy notch. By 6 ns, the initial bleach signals are fully decayed (Figure 4.3c and 4.3d) and solely the 1025 nm bleach is observed for all excitation wavelengths. The rise of the 1025 nm bleach signal is thus a direct probe of the

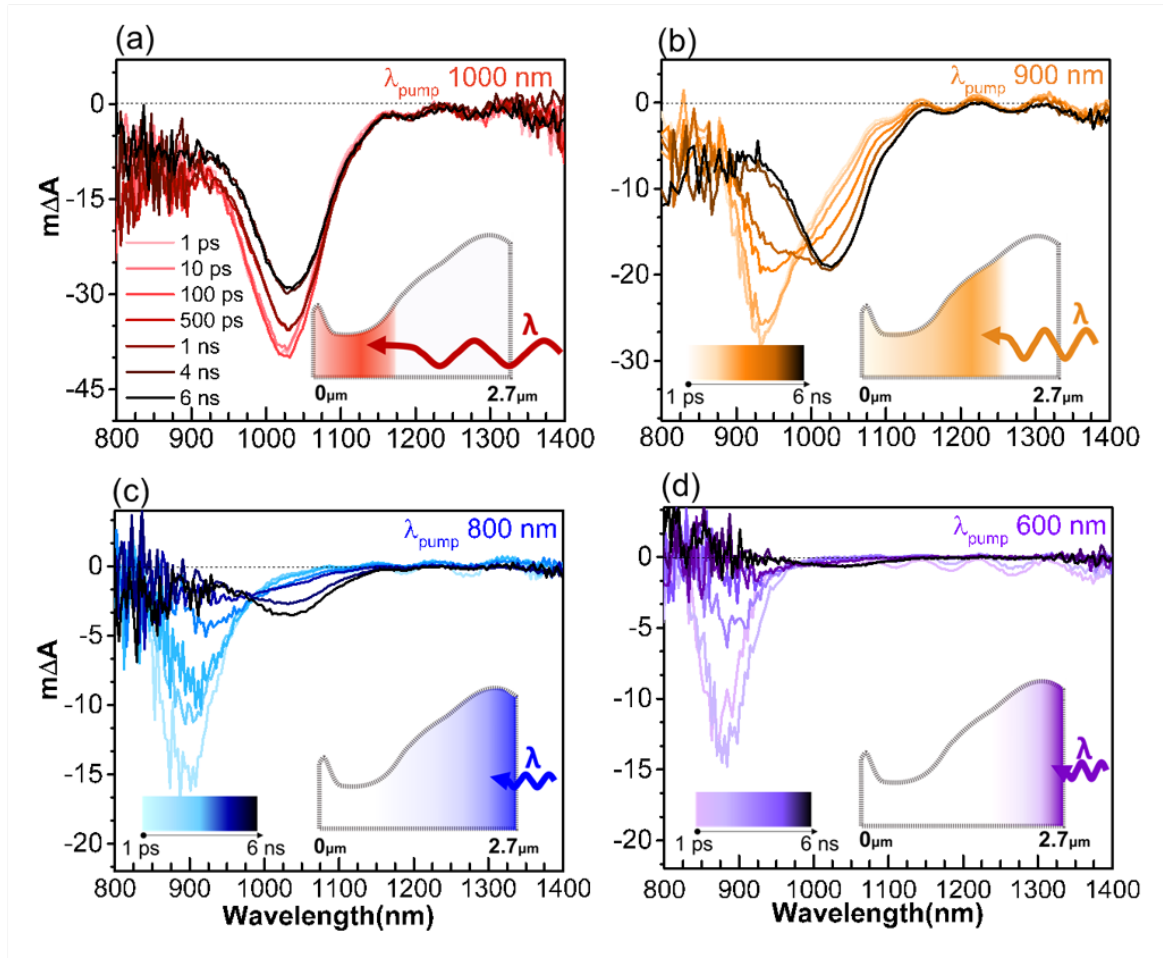


Figure 4.3: Ultrafast transient absorption spectra recorded 1 ps, 10 ps, 100 ps, 500 ps, 1 ns, 4 ns and 6 ns after excitation of a Ga-gradient CIGS sample using excitation wavelengths a) 1000 nm, b) 900 nm, c) 800 nm, and d) 600 nm from the back side. The light penetration depth of light impinging on the back side and the resultant excitation volume in the CIGS film are indicated in the inset in each spectrum. For (b), and (c), the fluence is 15.3 and 17.4 $\mu\text{J}/\text{cm}^2$ respectively, equivalent to 7×10^{13} photon/ cm^2 absorbed. The photon/ cm^2 absorbed is normalised to 7×10^{13} photon/ cm^2 absorbed for (a), and (d).

kinetics of minority charge carrier transport from the higher bandgap excitation region to the low bandgap notch region, with the amplitude of the emerging 1025 nm bleach being a measure of the efficiency of this transport process. Note that a series of TA experiment following 355 nm and 700 nm excitation from the front side also shows that the bleach signal red-shifted to 1025 nm by 6 ns (see Appendix Figure B.2). It should also be noted that for 900 nm excitation, the decay of the initial photobleach at 936 nm is coincident with a rise of the photobleach at 1025 nm. However for 800 nm and 600 nm excitation, a significant fraction of the initial photobleach decays faster and prior to growth of the

1025 nm photobleach.

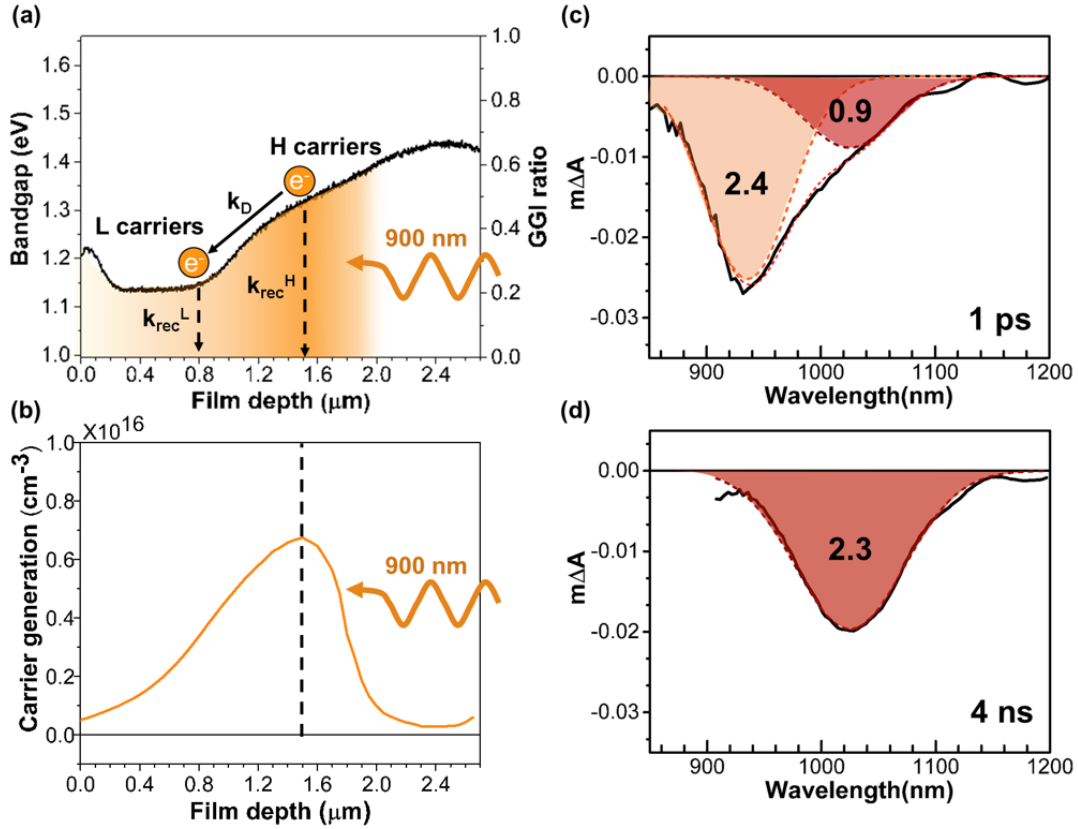


Figure 4.4: (a) The schematic of the proposed drift-diffusion model for electrons in a Ga-graded CIGS absorber excited with 900 nm excitation wavelength from the back side. k_{rec}^L and k_{rec}^H denote the decay constants of recombination of electrons at the energy notch (named as L) and in the regions of high bandgap/GGI ratio (named as H). This schematic is based on SIMS data shown in Figure 4.1b. (b) Charge carrier generation profile following 900 nm excitation wavelength from the back side. (c), (d) Integrated TAS spectra taken from Figure 4.3b at 1 ps and 4 ns, respectively. At 1 ps, the integrated area of the 936 nm and the 1025 nm signals correlate to the electrons excited in GGI=0.5 region and in the energy notch. The corresponding integrated area of the 936 nm and 1025 nm peaks are -2.4 and -0.9 respectively. At 4 ns, the 1025 nm peak dominates the TAS spectrum, with an integrated area of -2.3. $R^2 > 0.99$ for (c) and (d)

Figure 4.4a illustrates a kinetic model that is employed to explain and quantify the charge carrier dynamics in the Ga-graded CIGS absorbers studied herein. Note that this model does not include consideration of the fast initial photobleach decay observed following excitation adjacent to the back (Mo) interface, which will be discussed further below. Electrons generated at high GGI regions (denoted as “H carriers” in this thesis), are expected to undergo two competitive processes: 1) recombination and 2) drift-diffusion to the energy notch region. Kinetics for these two processes are given by equation 4.2 and 4.3,

$$\frac{dH}{dt} = -(k_D + k_{rec}^H)[H] \quad (4.2)$$

$$H(t) = [H]_0 \times e^{-(k_D + k_{rec}^H)t} \quad (4.3)$$

with k_{rec}^H and k_D representing the decay constants of recombination and drift processes, respectively, and $[H]_0$ the initial concentration of excited carriers in the high GGI region. The number of electrons $[H](t)$, that drift to the energy notch, impacts the dynamics of carriers, $[L](t)$, in the energy notch region as given by equation 4.4, and 4.5.

$$\frac{dL}{dt} = -k_{rec}^L[L] + k_D[H] \quad (4.4)$$

$$L(t) = ([L]_0 + \frac{k_D}{k_D + k_{rec}^H - k_{rec}^L}[H]_0)exp(-k_{rec}^L t) - \frac{k_D}{k_D + k_{rec}^H - k_{rec}^L}[H]_0 exp(-(k_D + k_{rec}^H)t) \quad (4.5)$$

Equation 4.5 is the solution to the differential Equation 4.4 containing all necessary parameters to understand kinetics in a Ga-graded CIGS crystal. It enables to extract electron mobilities across the Ga-graded layer and understand GGI-dependent recombination in state-of-the-art CIGS devices. In the following a straightforward step-by-step approach to extract all parameters from this equation is presented.

- *Electron dynamics in the energy notch (GGI=0.2) region*

As the spectra in Figure 4.3a shows, excitation with 1000 nm laser light excites carriers in the energy notch. As no photo-generated charge carriers were extracted, the decay of the bleach signal was mainly from **recombination**. The decay constant of minority charge carrier is set as k_{rec}^L , and the corresponding time constant is $\tau_{rec}^L = 1/k_{rec}^L$. Further, τ_{rec}^L is obtained by fitting a mono-exponential function to the 1025 nm kinetics, as shown in Figure 4.5. As a result, $\tau_{rec}^L = 19.1$ ns .

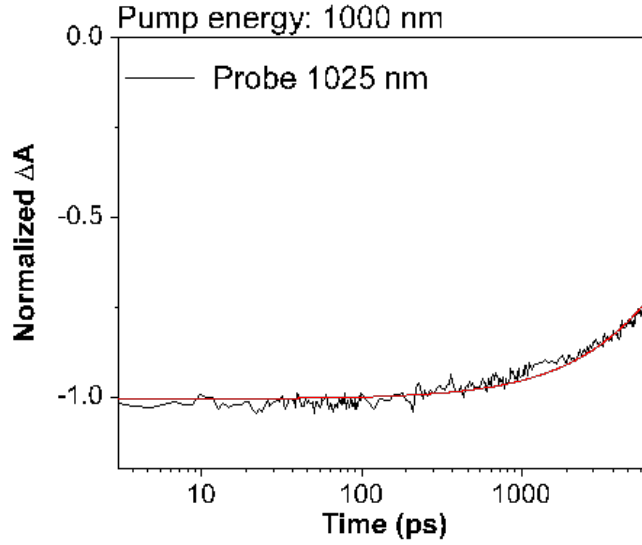


Figure 4.5: Normalized TA decay kinetics probed at 1025 nm following 1000 nm excitation wavelength from the back side. A mono-exponential function was employed for data fitting. The red line represents the fitting result.

- *Electron dynamics in $GGI=0.2-0.5$ region: the competition between drift and recombination*

Looking at the 1 ps spectrum of 900 nm excitation wavelength case (Figure 4.3b), the bleach peaks at 936 nm (~ 1.32 eV) but unlike the Gaussian-shaped bleach signal when exciting the energy notch region with 1000 nm excitation wavelength (Figure 4.3a), the 1 ps spectrum in Figure 4.3b shows a tail towards lower energies. It is postulated that this tail comes from charge carriers generated in the energy notch volume by the 900 nm excitation wavelength as the charge carrier generation profile suggests. Figure 4.4b reveals that upon 900 nm excitation, the largest proportion of electrons are generated at $1.5 \mu\text{m}$ depth position. According to the SIMS result (Figure 4.1b), the $1.5 \mu\text{m}$ depth position corresponds to an energy bandgap of 1.32 eV, which dovetails with the 936 nm peak in the 1 ps TAS spectrum. On the other hand, the amount of electrons generated in the energy notch ($0.8 \mu\text{m}$ depth) is still too considerable to be ignored. These electrons in the energy notch therefore result in the long tail in the 1 ps TAS spectrum. Consequently, by deconvoluting the 1 ps spectrum as Gaussian peaks centred at 936 nm and 1025 nm peaks and integrating the areas underneath, the amount of charge carriers generated in the $GGI=0.5$ region and in the energy notch respectively were estimated, as shown in

Figure 4.4c. With increasing time delay, the 936 nm signal decays whilst the 1025 nm signal grows in and reaches a plateau at approximately 4 ns which is shown in Figure 4.4d. The proportion of electrons drifting to the energy notch can therefore be estimated with the integrated areas. The ratio of electrons drifting to the energy notch compared to the number of electrons excited in the high GGI region initially is estimated to be 58%. Since this proportion is the outcome of the two processes, drift and recombination, competing in the Ga graded system, the relation of k_D and k_{rec}^H can be acquired accordingly via Equation 4.6 and 4.7. As a result, $k_{rec}^H = (10/14) k_D$ was obtained.

$$\frac{k_D}{k_D + k_{rec}^H} = \frac{A_{1025nm,4ns} - A_{1025nm,1ps}}{A_{936nm,1ps}} = \frac{14}{24} = 58\% \quad (4.6)$$

$$k_{rec}^H = \frac{10}{14} k_D \quad (4.7)$$

To further obtain k_D , Equation 4.5 was employed as a fitting function for the measurement data of 1025 nm kinetics. Since now the relation of k_D and k_{rec}^H is obtained, k_{rec}^H in Equation 4.5 can therefore be replaced by $10/14 k_D$, leaving only one variable: k_D in the equation. Equation 4.5 can therefore be re-written, as shown in Equation 4.8. After plugging-in all the known parameters, as listed in Table 4.2, the fitting result is then obtained and shown in Figure 4.6. The obtained time constants of drift and recombination processes are 1998 ps (τ_D) and 2797 s (τ_{rec}^H) respectively.

$$L(t) = ([L]_0 + \frac{k_D}{(\frac{24}{14})k_D - k_{rec}^L} [H]_0) \exp(-k_{rec}^L t) - \frac{k_D}{(\frac{24}{14})k_D - k_{rec}^L} [H]_0 \exp(-((\frac{24}{14})k_D)t) \quad (4.8)$$

The TAS kinetics probed at 936 nm and 1025 nm were extracted and are shown in Figure 4.6. It is obvious that the decay of the 936 nm kinetics and the rise of the 1025 nm kinetics share the same time constant, $k' = k_{rec}^H + k_D = (1/1164)s^{-1}$, which further validates the kinetic model established here. The time constant of the drift-diffusion process, τ_D , can be employed to calculate the electron mobility in the Ga-graded CIGS absorbers using Equation 4.9,

$$\mu = \frac{(\Delta x)^2}{\Delta \phi \Delta t} = \frac{(\Delta x)^2}{\Delta \phi \tau_D} \quad (4.9)$$

with Δx being the carrier travel distance, $\Delta \phi$ the corresponding potential change, and Δt the carrier travel time. A minority carrier mobility of $16.3 \pm 4.0 \text{ cm}^2 V^{-1} s^{-1}$ in the large grain region (where GGI = 0.2 to 0.5) is calculated.

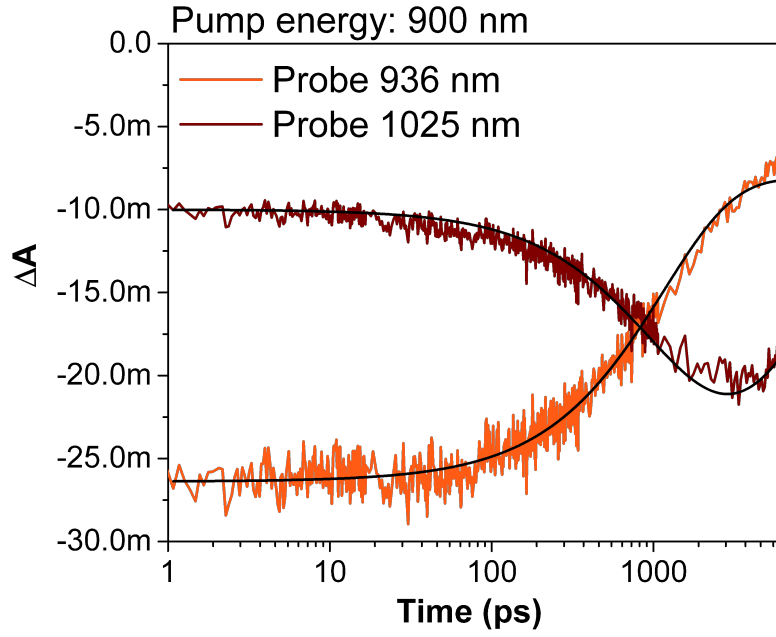


Figure 4.6: TA decay kinetics probed at 936 nm and 1025 nm following 900 nm excitation. The black lines represent the fitting results. For both decay kinetics, the fitting time constant (k') is $(1/1164) \text{ s}^{-1}$.

Table 4.2: The plug-in parameters for the fitting of the 1025 nm signal in the 900 nm excitation case and the fitting results.

Plug-in parameters			Results	
L_0	$1/(k_{rec}^L),$	H_0	$1/(k_D),$	$1/(k_{rec}^H),$
	unit: ps		unit: ps	unit: ps
-0.01	19,100	-0.026	1998	2797

Table 4.3: Carrier location, travel distance, potential change, travel time and mobility retrieved from fs-TAS measurement on CIGS sample with 900 nm excitation from the back side.

Pump Energy	Carriers location		Travel distance ($\Delta\mathbf{x}$)	Potential Change ($\Delta\phi$)	Travel time (Δt)	Mobility (μ)
	Unit: $\mu\mathbf{m}$					
	1 ps	6 ns	Unit: $\mu\mathbf{m}$	Unit: eV	Unit: ns	Unit: $cm^2V^{-1}s^{-1}$
900 nm	1.5 ± 0.075	0.8 ± 0.04	0.7 ± 0.085	0.15 ± 0.0075	1.998 ± 0.02	16.3 ± 4.0

Reported electron mobilities of poly-crystalline CIGS and CIS vary five orders of magnitude ranging from 0.02 to $1000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, as summarised in Table 4.1. Comparing the different experimental techniques, it is apparent that Time of Flight (TOF) measurements tend to measure mobility values on the lower edge of the above mentioned range (typically $0.02\text{--}0.06 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$)[29]. In contrast, Tera-Hertz measurements, provided an electron mobility of $1000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in a stoichiometric CIS thin film[28], which is similar to the mobility for a CIS single crystal. This indicates that Tera-Hertz measurements probe primarily to intragrain mobilities. Therefore, it gives a relatively high value compared to other methods, as it neglects the grain boundary effects in the poly-crystalline CIGS. On the other hand, a mobility of $16.3 \pm 4.0 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in the large grain region (where $\text{GGI} = 0.2\text{--}0.5$) is obtained from this work, which is in good agreement with electron mobilities obtained from Hall measurements in n-type CIS thin films ($1\text{--}80 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$)[15][16][17][18] and from transient photoluminescence (TR-PL) studies for p-type CIS ($32\text{--}45 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for CIS[13]) and CIGS (lower limit of electron mobilities in a Ga-graded CIGS: $8.3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [13]) thin films.

- *Electron dynamics in $\text{GGI} > 0.6$ region*

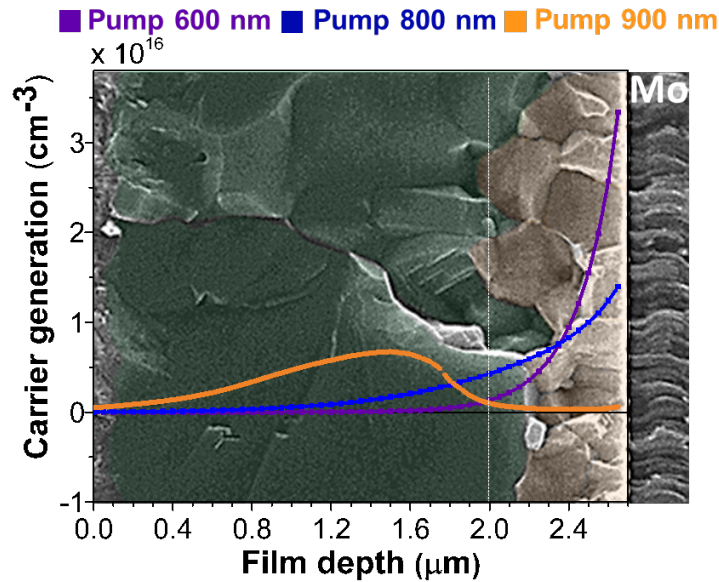


Figure 4.7: Simulated minority charge carrier concentration profile in the Ga-graded CIGS absorber after 600 nm, 800 nm and 900 nm excitation from the back side. The SEM cross-section image demonstrates the morphology of the Ga graded CIGS absorber utilized for TAS measurements in this work.

Now turn to consideration of the dynamics of electrons generated close to the back side, and in particular to the fast decay of the initial photobleach noted above. In Figure 4.7, a cross-section SEM image of the Ga-graded CIGS is presented. Large grains of CIGS on the order of $>2\ \mu\text{m}$ dominate the device structure but at the interface with the Mo back contact the grain size is significantly smaller, on the order of $0.5\ \mu\text{m}$ (brownish shaded area). From the fitting results (overlaid curves in Figure 4.7), with 600 nm excitation wavelength impinging on the sample from the back side, generates charge carriers mostly in the high bandgap (i.e. high GGI) regions where small grains dominate. With 800 nm excitation wavelength, the charge generation profile was more evenly distributed and extended further into the regions with bigger grains. In the following paragraphs, for the simplicity of description, the high GGI regions with big grains are abbreviated as “H-BG” and those with small grains as “H-SG”.

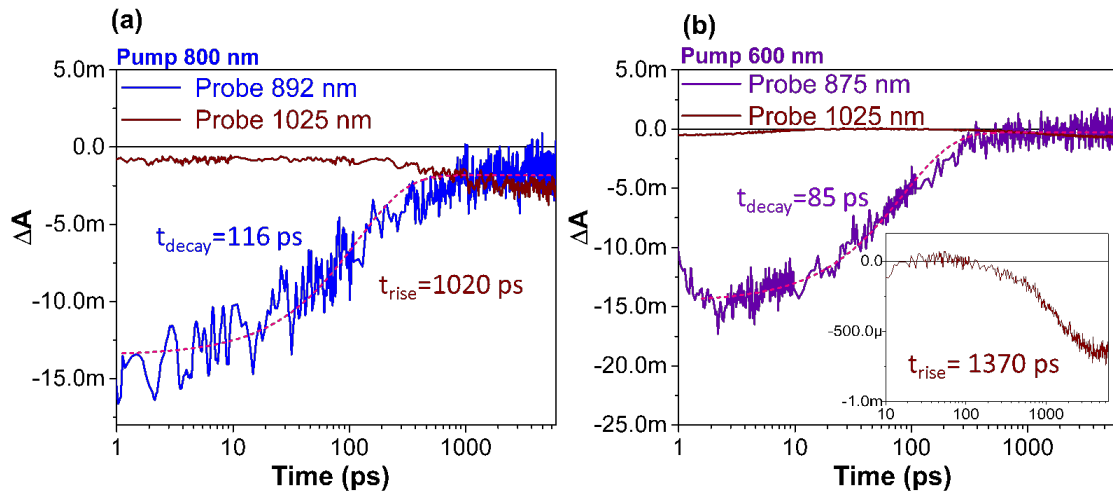


Figure 4.8: (a) The TA kinetics probed at 892 nm and 1025 nm following 800 nm excitation wavelength from the back side. (b) The TA kinetics probed at 875 nm and 1025 nm following 600 nm excitation wavelength from back side. The red short dash lines represent the fitting results.

Figures 4.8a, b illustrate the transient absorption kinetics after 800 nm and 600 nm excitation. The 892 nm (Figure 4.8a) and 875 nm (Figure 4.8b) signals correspond to the initial (1 ps) photobleach peak positions in the TAS spectra (Figure 4.3 c,d), and therefore track the populations of carriers generated in the H-SG region. As discussed above, the 1025 nm probe kinetics correspond to carriers in the energy notch region. As can be seen in Figures 4.8a,b, the decay time constant of 892 nm/ 875 nm signal is significantly faster

than the rise time constant of the 1025 nm signal, with only small residual decays at 892 and 875 nm on the timescale of the 1025 nm rise. This indicates that the fast decays observed at 892 and 875 nm are primarily associated with fast charge recombination to ground, rather than charge transport to the notch region. Following consideration of the SEM image discussed above, it appears most likely that this fast decay represents ‘H-SG’ charge carrier recombination in small CIGS grains, and the slower 1025 nm rise signal from H-BG charges generated in the larger grains.

To quantify the amount of H-BG and H-SG charges generated initially, first the 800 nm excitation case is considered: the 1 ps TA spectrum was fitted with two peaks: 1) 892 nm, which corresponds to the H-SG charges, and 2) 936 nm, which corresponds to the H-BG charges, as shown in Figure 4.9a. The fitting result showed that only 29% of the charges generated are H-BG charges. In the 600 nm excitation case, the ratio of H-BG/H-SG charges is only 5%, as shown in Figure 4.9b. The 1025 nm signal rise amplitude in the 800 nm excitation case is larger than in the 600 nm excitation case, consistent with this analysis of a varying ratio of H-BG to H-SG carriers in different excitation volumes.

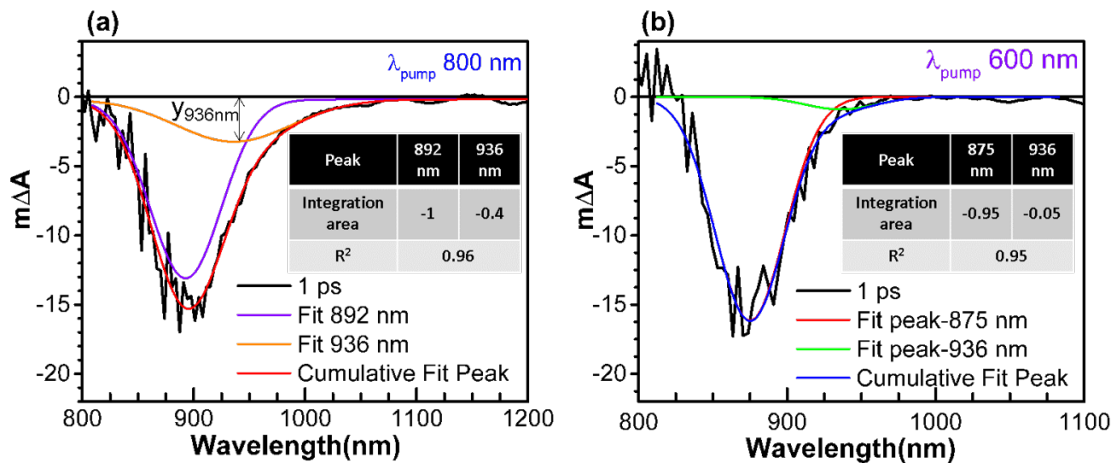


Figure 4.9: Integrated TAS spectra of (a) 800 nm and (b) 600 nm excitation taken from Figure 4.3c,d at 1 ps. In the 800 nm excitation case, the integrated area of the 892 nm and the 936 nm signals correlate to the H-SG electrons and H-BG electrons, respectively. The corresponding integrated area of the 892 nm and 936 nm peaks are -1 and -0.4. In the 600 nm excitation case, the integrated area of the 875 nm and the 936 nm signals correlate to the H-SG electrons and H-BG electrons respectively. The corresponding integrated area of the 875 nm and 936 nm peaks are -0.95 and -0.05.

From the 900 nm excitation case, the charge transport ratio $\frac{k_D}{k_D + k_{rec}^H}$ is equal to $\frac{14}{24}$, therefore, the 1025 nm yield in 800 nm and 600 nm excitation case can be calculated via Equation 4.10. In 800 nm excitation case, with 936 nm signal amplitude being -3 mΔA, the resulting yield of 1025 nm signal is calculated to be -1.75 mΔA. This is consistent with the experimental data, which the yield of 1025 nm signal is -1.85 mΔA, as shown in Figure 4.10a. In 600 nm excitation case, with 936 nm signal amplitude being -1 mΔA, the resulting yield of 1025 nm signal is estimated to be -0.58 mΔA, which is also comparable with the experimental result (-0.65 mΔA), as shown in Figure 4.10b.

$$Yield_{1025nm} = y_{936nm} * \frac{k_D}{k_D + k_{rec}^H} \quad (4.10)$$

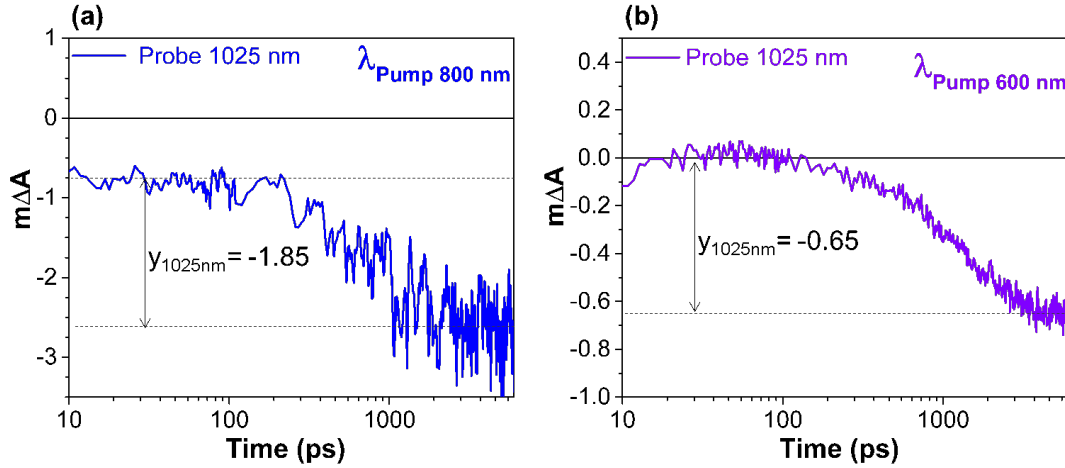


Figure 4.10: TA kinetics probed at 1025 nm following (a) 800 nm and (b) 600 nm excitation. The yield of 1025 nm signal is -1.85 mΔA for 800 nm excitation case and -0.65 mΔA for 600 nm excitation case.

Note that in this study, a series of fluence dependence TA measurement following 800 nm, 900 nm, and 1000 nm laser pulse from the back side was performed (see Appendix Figure B.3, B.4, and B.5). The results show that all the charge carriers decay kinetics regardless of the wavelength of the laser pulse are insensitive to fluence, which is not surprised as the same phenomenon is observed for non Ga-graded CIGS (data presented and discussed in Chapter 3).

It can be concluded from this work that the number of electrons drifting to the notch region decreases significantly for excitation nearer to the Mo back contact. This can

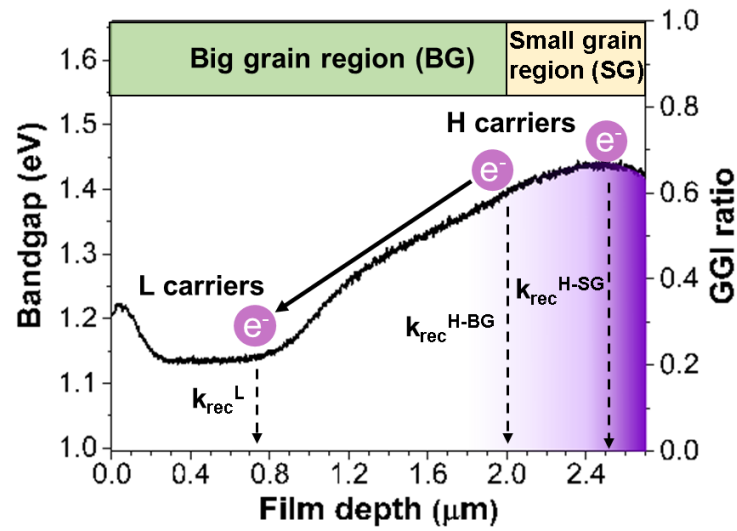


Figure 4.11: Illustration of minority charge carrier dynamics inside the Ga graded CIGS absorber after 600 nm excitation wavelength from the back side. k_{rec}^L , k_{rec}^{H-LG} and k_{rec}^{H-SG} denote the charge recombination processes at the energy notch (region L), in the high bandgap regions exhibiting large grains (named as H-BG) and small grains (named as H-SG) respectively.

be attributed to much faster carrier recombination at the region where the GGI ratio exceeds 0.5 and small grains are predominant (see Appendix Figure B.6 for TA decay kinetics probed at band gap positions following excitation energies from 355 nm to 1000 nm from the back side), as shown in Figure 4.11. This is consistent with previous literature regarding the impact of different GGI ratios on the grain size, the corresponding recombination, and the overall device performance. In 2019, Spindler et al. summarized the electronic defects of CIS and CGS studied by photoluminescence, admittance, and photocurrent spectroscopies in previous studies and showed that deep recombination centres exist when the GGI ratio exceeds 0.5[38]. In fact, the grain size itself is also influenced by the GGI ratio: it has been shown that Ga atoms have a low diffusivity and tend to accumulate at CIGS/Mo interface where they restrain grain growth[39]. Fan et al. designed four different Ga gradient profiles and found that a separated layer consisting of small grains was formed close to CIGS/Mo interface in all four samples[40]. Lundberg et al. observed that the grain size of CIGS decreases with shorter deposition time, and a smaller grain size correlates with a decrease in cell performance which was attributed to increased grain boundary recombination[41]. In addition to a higher GGI ratio leading to a faster charge recombination, in this case, the air exposed small grain surface is likely affecting

the recombination times measured. As discussed in Chapter 3, the charge carrier lifetime in the region unaffected by the surface oxidation is approximately 4–5 times longer than those affected by the surface oxidation. Note that even if the charge carrier lifetime of the H-SG charges is 5 times longer (without surface oxidation), it is still 2-3 times shorter than the rise time constant of the 1025 nm signal. As a result, the charge transport from the small grains to the energy notch would still be unlikely. Though it would be desirable for future studies of the small grain region, to prepare the samples in an inert environment and encapsulate thereafter, it should be noted that the measurements of the SG region are still relevant to understanding device performance. Especially in devices and modules with pinholes and other fabrication defects, those regions will likely be prone to undergo surface oxidation which eventually will result in recombination rates as fast as measured in this work (~ 100 ps). Such fast recombination at the back contact most likely decreases device efficiency. A correlation between device efficiency and competing charge carrier dynamics in devices with different alkali atom PDTs will be discussed in Chapter 5.

4.5 Conclusion

To conclude, the challenge of experimentally accessing the minority charge carrier dynamics in Ga-graded CIGS devices is addressed herein by transient absorption spectroscopy. In this study, the behaviours of recombination and transport kinetics in state-of-the-art NaF+RbF treated Ga-graded CIGS devices were successfully decoupled and an electron mobility of $16.3 (\pm 4.0) \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (for GGI=0.2–0.5) is obtained. Moreover, charge carrier recombination is found to be not only depends on the GGI ratio within a large grain (i.e. ~ 3 ns in GGI=0.5 versus ~ 19 ns in GGI=0.2), but is highly dependent also on the morphology. When grain size is rather small (i.e. $0.5 \mu\text{m}$) then recombination times decrease to values significantly lower than 1 ns (i.e. ~ 100 ps in this study to ~ 400 ps estimated for the device). The device model established in this work and the corresponding kinetic time constants provide important insight to guide future CIGS device design especially at the back region where recombination is predominant due to a higher GGI ratio and smaller grain sizes. This work shows that transient absorption spectroscopy is a powerful tool for immediate observation of minority carrier dynamics, often difficult to track with other techniques.

4.6 Publications

The results of this chapter is also utilized for the manuscript in the publication:

Chang, Y.-H. et al. Insights from transient absorption spectroscopy into electron dynamics along the Ga-gradient in CIGS solar cells. (2020).

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Chapter 5

Effects of incorporated alkali atoms (Na and Rb) on minority carrier kinetics in Ga-graded CIGS solar cells

5.1 Abstract

An engineered Ga-gradient profile in the bulk along with an alkali atom postdeposition treatment (PDT) is essential for high efficiency CIGS solar cells. Although numerous studies have aimed at unravelling the effect of alkali atom incorporation in CIGS solar cells, the influence of alkali atoms (especially of Na and Rb) on minority charge carrier dynamics in the regions of different $[Ga]/([Ga] + [In])$ (GGI) ratios is still under investigation. Here, a transient absorption spectroscopy (TAS) study focused on the differences in carrier dynamics originating from varying PDTs is presented. The device with NaF PDT shows a 2.3 – 2.5 -fold extension in electron lifetime and 1.3 times as fast electron transport across the Ga-gradient of the CIGS absorber compared to the untreated sample. Comparing electron dynamics in the RbF+NaF PDT sample to the NaF PDT sample, it can be seen that Rb incorporation clearly improves electron lifetime in CIGS exhibiting a GGI ratio < 0.5 . In the region where $GGI > 0.6$ and the grain size < 500 nm, the improvement is insignificant and no electron transport was detectable from this region towards the energy notch, independent of PDT. Moreover, a long-lived absorption signal (up to 0.01 s) which is considered to be charge trapping process at CIGS defects is detected in the μ s-s timescale TAS measurements conducted herein. The signal amplitude does not change with PDTs but with the GGI ratio. In the context of previous studies on alkali atom passivation, the results of this study propose that Na atoms effectively passivate recombination centres in grain interiors and at grain boundaries in the CIGS of GGI ratio ranging from 0.2 – 0.67. On the other hand, Rb passivation works exclusively in low GGI domains ($GGI < 0.5$).

5.2 Introduction

Alkali atom incorporation in CIGS absorber fabrication has long been considered to be essential for achieving high device efficiency[1][2]. While earlier works benefited from diffusion of Na^+ ions from soda lime glass into the CIGS absorber, nowadays a post deposition treatment with a range of alkali fluorides offers better reproducibility in device fabrication and can be implemented in devices with flexible substrates where the absence of soda lime glass (and hence Na^+ ions) leads to relatively poor device performances. In this chapter, the effect of Na and Rb incorporation into Ga-graded CIGS absorbers on minority carrier dynamics will be discussed. A detailed literature review on NaF PDT

and RbF+NaF PDT on CIGS solar cells are given previously in Chapter 1.4.4. Hence, in the following paragraphs, only the literature discussing the impact of NaF and RbF PDT from a kinetic point of view will be introduced in detail.

Among all the alkali atom PDTs, the effect of Na PDT has been studied most intensively. It is generally observed that the V_{OC} and FF increase with Na incorporation[3][4][5][6], which is correlated with the increased p-type characteristic[3][5][7][8] and/or the passivation of non-radiative recombination centres at grain boundaries[9][10][11][12][13]. Transient optical studies also showed a correlation of increased charge carrier lifetime with optimal Na atoms incorporation. Eid et al. utilized ultrafast pump-probe reflectance spectroscopy to study Ga-graded CIGS devices with different thicknesses of NaF (incorporated prior to selenization) and found a 1.5-fold increase in minority carrier lifetime in samples with higher Na concentrations which was correlated with higher device performance[6][14]. However, owing to the GGI profile changing significantly with different Na concentrations in their experiments, whether Na atoms passivate grain interiors (GIs) and grain boundaries (GBs) cannot be elucidated. Lee et al. detected a ~ 5 fold prolonged charge carrier lifetime on CIGS (GGI=0.14) grown on soda-lime glass compared to reference films grown on borosilicate glass, indicating the addition of Na atoms prohibits the formation of defect states at CdS/CIGS junction and hence increases carrier lifetime[15]. Though the study did not address the correlation between defect states and GBs, a smaller grain size was observed in the borosilicate CIGS device. Using time-resolved photoluminescence spectroscopy, Jarzembowski et al. showed that the rear surface recombination velocity in a GGI=0.4 CIGS thin film with NaF PDT is reduced 3-fold compared to the one without any PDT[16], indicating Na atoms can effectively passivate defects at Mo/CIGS interface.

Following this large body of research on NaF PDTs, recent studies have focused on a combined NaF+RbF PDT. Rb atoms were found to easily replace the position of Na atoms at GBs and cause Na migration into the grain[17][18]. At CdS/CIGS junction, a thin layer of RbInSe₂ was found to form[19], resulting in a beneficial band bending and thus reduced interface recombination[20][21]. Rb incorporation is also proposed to reduce non-radiative recombination centres in the space charge region[22][23]. Furthermore, several studies observed charge carrier lifetime in Ga-graded CIGS absorbers to increase by a factor of 4 after RbF PDT[22][24][25]. However, these studies revealed the influence of Rb in only the first 1 μm from the CdS/CIGS interface which typically exhibits GGI ratios <0.5 and

the effect of Rb in different GGI regions of typically Ga-graded CIGS absorber layers has not yet been studied.

Here, a TAS study on ps-ns and μ s-s time scales investigating the impact of Na and Rb on minority carrier dynamics in CIGS absorbers spanning a range of GGI ratios typically employed in high-efficiency CIGS solar cells is performed. The kinetic model established in Chapter 4 allows to decouple the charge carrier recombination from minority carrier drift across the conduction band edge gradient in Ga-graded CIGS absorbers. This kinetic model is utilized here to understand the effect of NaF and NaF+RbF PDTs on the kinetics of minority carriers in Ga-graded CIGS solar cells comparing alkali treated devices to equivalent devices without a PDT (labelled as ‘No PDT’ in this chapter).

5.3 Experimental methods

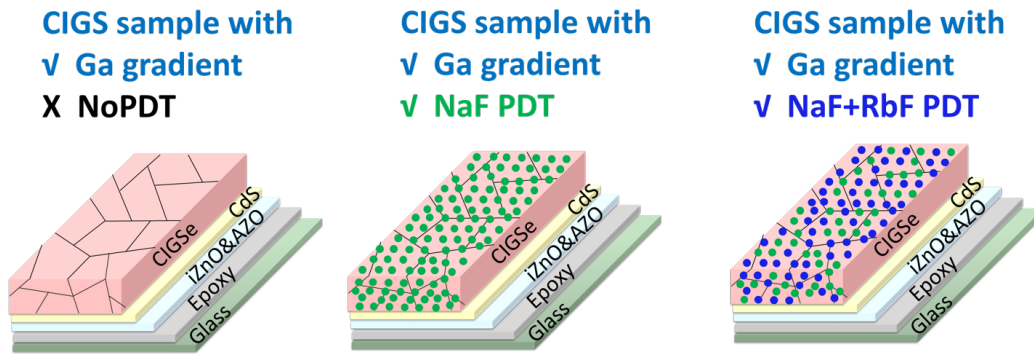


Figure 5.1: Schematic of the Ga gradient CIGS samples (No PDT, NaF PDT, and NaF+RbF PDT) utilized for transient absorption measurements

In this chapter, Ga-graded CIGS devices with 3 different post deposition processing conditions (No PDT, NaF PDT and NaF+RbF) are investigated primarily using transient absorption spectroscopy. In addition, other techniques such as steady-state UV-VIS, PL, SIMS, and J-V measurement are also utilized for examining the steady-state optical, material and device properties of the CIGS device. Details of each instrument set-up and fundamental principles are described in Chapter 2.

The fabrication methods of the whole CIGS device can be found in Chapter 2.2.1. The CIGS device structure is illustrated previously in Figure 2.12a. And as described in Chapter 2.3, to measure the CIGS device in a transmission mode in TAS, the CIGS sample is prepared by peeling of the Mo back contact from the rest of the CIGS stack.

Figure 5.1 illustrates the three CIGS samples peeled off from the Mo back contact for TAS study. The first sample is the pristine CIGS device without any PDT treatment. The second and the third sample is subject to NaF PDT and RbF+NaF PDT, respectively.

5.4 Results

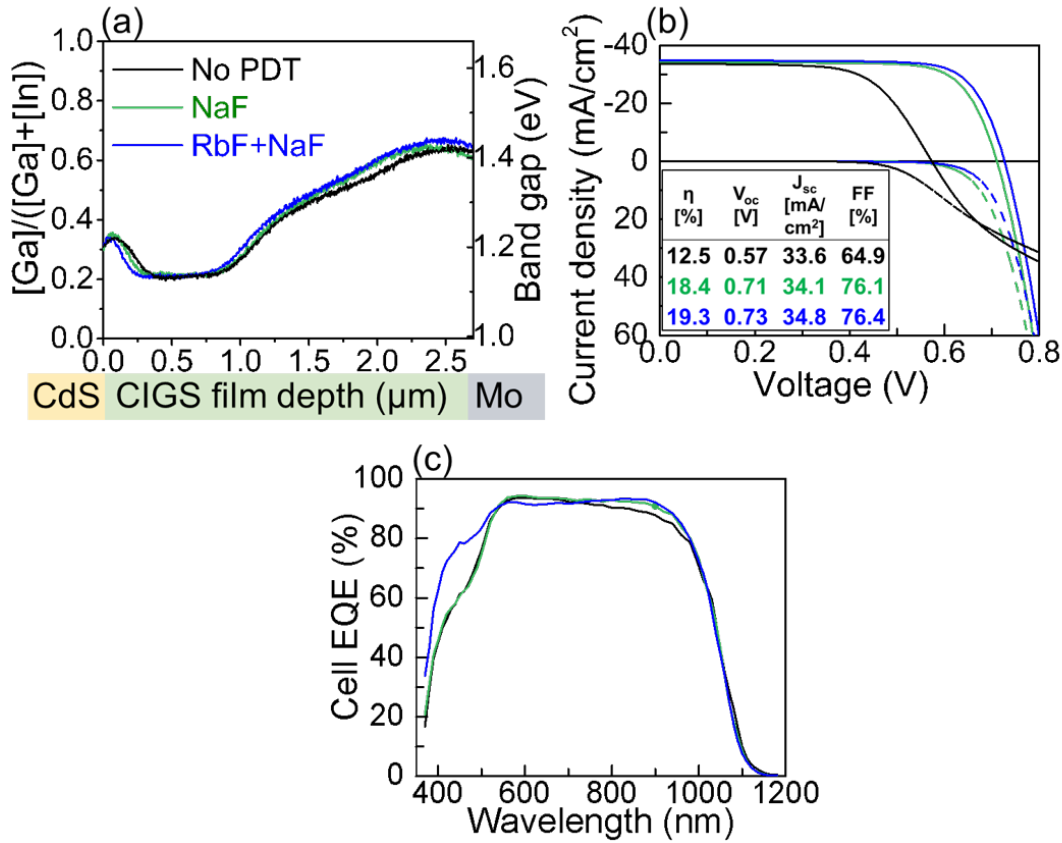


Figure 5.2: Device characteristics of Ga-gradient CIGS solar cells without any PDT, termed ‘No PDT’ (black), with NaF PDT (green) and RbF+NaF PDT (blue), respectively. a) Secondary ion mass spectroscopy measurements, illustrating the increasing $[\text{Ga}]/([\text{Ga}]+[\text{In}])$ (GGI) ratio along CIGS absorber towards CdS and Mo sides (with especially high GGI ratios towards the Mo side) leaving a region with minimum GGI ratio in between in all three devices (termed energy notch). As the GGI ratio is directly proportional to the energy bandgap, the region with minimum GGI is therefore the energy notch of the cell. b) J-V characteristics conducted under simulated sunlight (100 mW cm^{-2} , 1 sun), and c) external quantum efficiency (EQE).

In this study, all three samples have a typical CIGS device structure and an identically engineered Ga-gradient across each of the CIGS absorber layers as shown in Figure 5.2a. Figure 5.2b show the J-V characteristics of No PDT, NaF PDT and RbF+NaF

PDT CIGS devices. It is evident that efficiency enhancement in devices with alkali PDT results largely from a significant improvement in V_{OC} (25% and 28% increase after NaF PDT and NaF+RbF PDT, respectively). Figure 5.2c shows external quantum efficiency (EQE) spectra. Device characteristic spectral EQE response in two wavelength intervals is observed: i) $\sim 800\text{--}1000\text{ nm}$ and ii) $\sim 400\text{--}550\text{ nm}$. The photocurrent and EQE improvements in the $400\text{--}500\text{ nm}$ range are due to a 50 nm thinner CdS layer employed in the RbF+NaF PDT device[26][27][28]. To understand the lower EQE response in the $800\text{--}1000\text{ nm}$ region, and the V_{OC} loss in the No PDT device, a transient absorption study investigating charge carrier dynamics on ps-ns time scales (Figure 5.3) is performed.

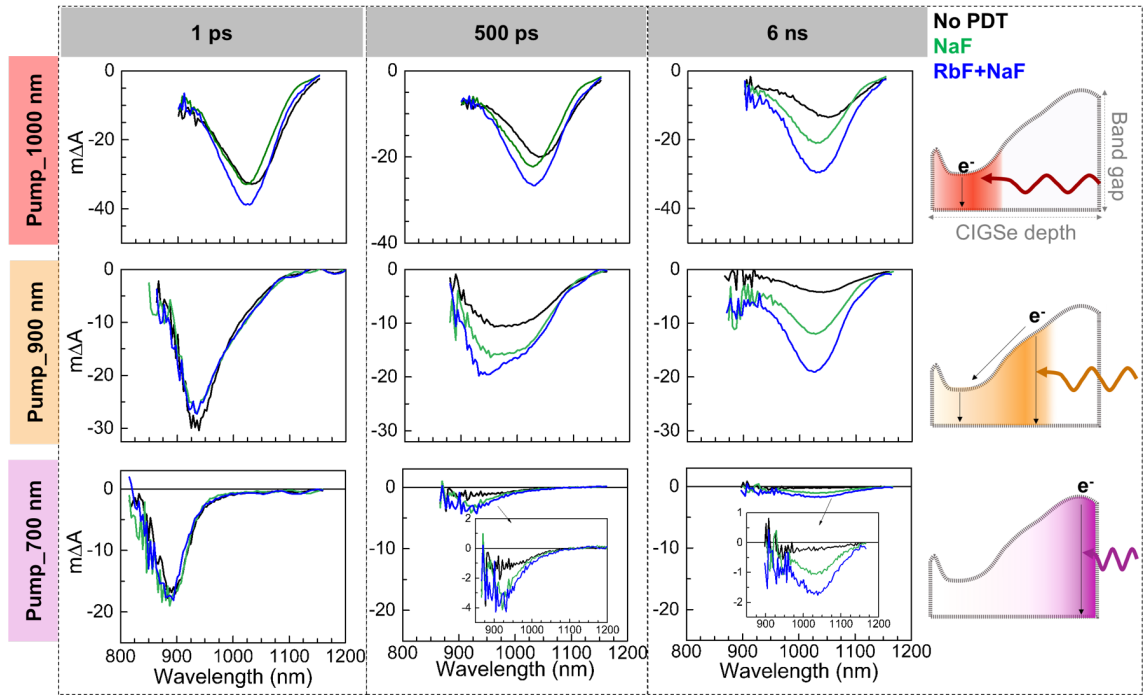


Figure 5.3: Picosecond to nanosecond transient absorption study showing spectral snapshots at 1 ps, 500 ps and 6 ns after excitation (follow columns) with 1000 nm, 900 nm, and 700 nm laser light (follow rows) of No PDT (black traces), NaF PDT (green), and RbF+NaF PDT (blue) samples). As indicated in the schematic on the right hand side, samples were excited from the peeled-off Mo side in different excitation volumes (shaded areas based on carrier generation profiles in Appendix Figure C.1) leading to several processes for the photogenerated charge carriers (as indicated by the arrows). The laser excitation density utilized is equivalent to 7×10^{13} photons/cm² absorbed.

1000 nm, 900 nm and 700 nm excitation wavelengths are selected to track charge carriers from different GGI regions across the CIGS film. The schematic in the last column of Figure 5.3 shows the excitation volumes for each pump energy based on the charge carrier generation profiles in Appendix Figure C.1. In Chapter 4, a correlation between the 1 ps peak position of the photobleach in the Ga-graded RbF+NaF and the excitation volume where each pump wavelength is absorbed strongest is established. This correlation seems to hold for all 3 samples investigated herein. Following are the photobleach peak positions observed at 1 ps in the 1000 nm, 900 nm, and 700 nm excitation cases: i) in the energy notch (at ~ 1025 nm or 1.21 eV, GGI = 0.2 indicated by the intense red shading in Figure 5.3a (sketch)) for excitation with 1000 nm, ii) half-way on the Ga-gradient towards the Mo side (at 935 nm or 1.33 eV, GGI = 0.5, intense orange shading) for excitation with 900 nm and iii) close to the (removed) Mo back contact (885 nm or 1.40 eV, GGI = 0.66, intense pink shading) for excitation with 700 nm laser light. Note that in the 900 nm excitation case the usually Gaussian-shaped curves show a tail extending towards 1100 nm because of the extended absorption and charge carrier generation profile as shown in Appendix Figure C.1.

Comparison of the 1 ps spectra of all 3 samples (with and without PDTs), shows no significant difference in spectral shape or intensity (for same number of photons excited), as one would expect based on the identical GGI profiles (Figure 5.2a). Note that in the 1000 nm excitation case, a slightly more redshifted photobleach peak position in the No PDT sample (1040 nm) compared to the PDT samples (1025 nm) is observed whereas steady-state PL is slightly blue-shifted by 26 meV as seen in Appendix Figure C.2. While a more dedicated study to this phenomenon would surely be needed, one explanation to consider would likely be a slight change in carrier concentration and statistical carrier distribution near the valence band edge upon PDT. This hypothesis would be consistent with the observed increase in p-type character upon alkali atom PDT treatment[7][18][25][29].

To understand the 500 ps and 6 ns spectra in Figure 5.3, the kinetic model established in Chapter 4 tracking minority carrier drift-diffusion in Ga-graded CIGS absorbers is exploited. As shown in Figure 5.4a, this kinetic model is based on four decay constants predicting minority carrier movement in the Ga-graded CIGS absorber layer which is divided into three excitation volumes probed with 1000 nm, 900 nm and 700 nm, yielding decay constants k_{rec}^L for electrons decaying in the energy notch (GGI=0.2) , k_{rec}^{H-BG} and

k_D for recombination and drift in large grains with GGI gradient varying from 0.5 to 0.2 and k_{rec}^{H-SG} for electrons decaying in small grains with $GGI > 0.6$ (see SEM image in Appendix Figure C.3).

In the energy notch region no significant changes in the signal size and the photobleach peak position are observed till ~ 500 ps in both PDT samples. Only when the signal starts decaying significantly a shift in peak position from 1025 nm to 1030 nm is also observed. As no photocurrent is extracted in this case, the only decay process of charge carriers generated in the energy notch region is due to recombination. Fitting the kinetics of the decay at the respective peak position (1025 nm for PDT and 1040 nm for No PDT samples) with a single exponential function (Figure 5.4b, full circles), recombination times, $\tau_{rec}^L = 5.3$ ns, 13.2 ns, and 19.1 ns for No PDT, NaF PDT, and RbF+NaF PDT samples, respectively, is obtained.

Now discuss charge carrier dynamics in the excitation volume excited by 900 nm laser pulse. This volume is denoted as "H-BG" indicative of the increasing GGI ratio from 0.2 to 0.5 and predominantly large/big grain size of CIGS. In Figure 5.3 (second row) a notable red-shift in the photobleach signal in all three samples is observed: while the initial photobleach peak position coincides with the initially excited volume with the respective band gap and GGI ratio, by 6 ns, the photobleach peak is red-shifted to 1025 nm for the PDT samples and 1040 nm for the No PDT sample, which is identical to the peak position in the energy notch as discussed above. In addition, at 6 ns, it can be seen that the spectral intensities for all 3 samples are almost identical as in the case of excitation with 1000 nm with the signal size of the photobleach in the RbF+NaF PDT sample being ~ 4 times larger than in the No PDT sample. Earlier in Chapter 4, the red-shifted photobleach was assigned to a drift-diffusion process of electrons from their initial excitation volume to the energy notch region, and a kinetic model was established to decouple the kinetics competition between recombination process (with recombination time constant $\tau_{rec}^{H-BG} = 1/k_{rec}^{H-BG}$) and drift process (with drift time constant $\tau_D = 1/k_D$), as illustrated in Figure 5.4a. This kinetic model is utilized here to obtain the τ_D and τ_{rec}^{H-BG} of NoPDT and NaF PDT samples, following the method demonstrated previously in Chapter 4 (see Appendix Figure C.4 for the fitting results). Figure 5.4c shows the fitting results for each sample, yielding recombination time constants $\tau_{rec}^{H-BG} = 620$ ps, 1430 ps, and 2797 ps and transfer times $\tau_D = 3980$ ps, 2950 ps, and 1998 ps for No PDT,

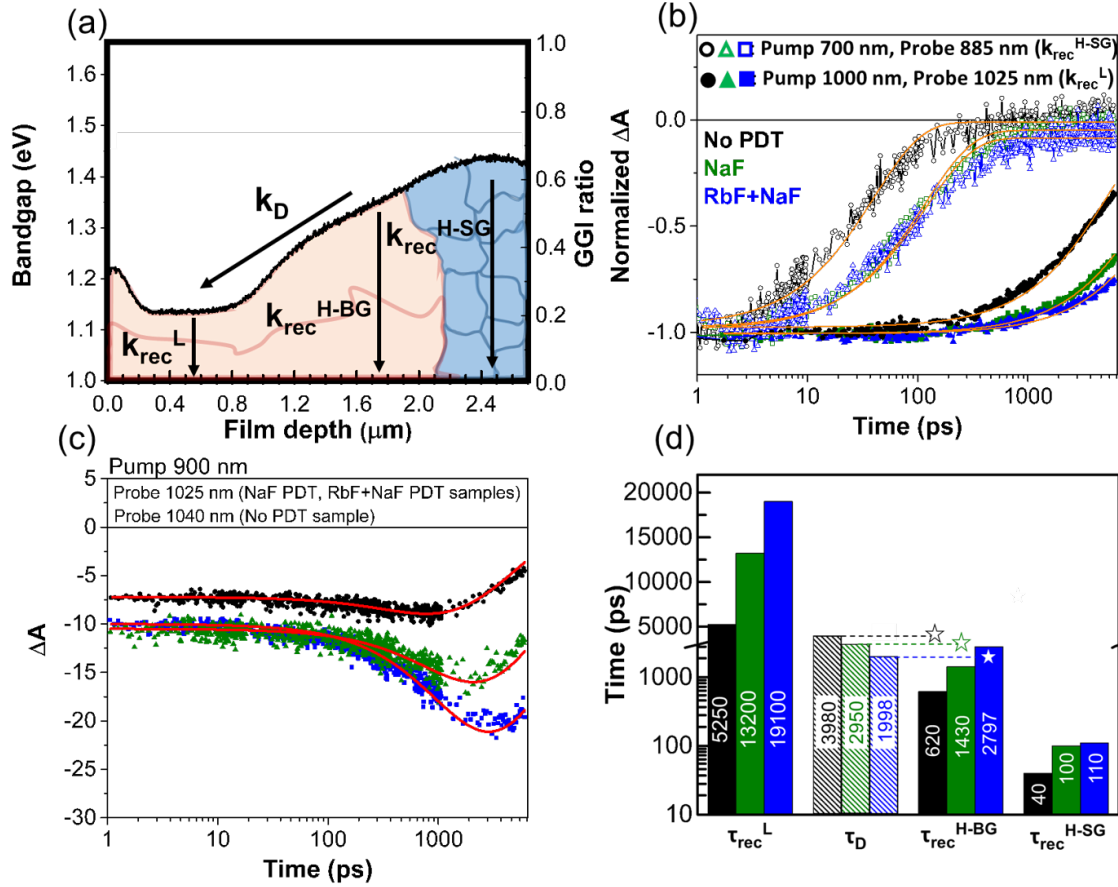


Figure 5.4: (a) Schematic of the proposed drift-diffusion model in a Ga-graded CIGS system. The GGI ratio and the corresponding energy bandgap is based on the SIMS result of RbF+NaF PDT sample in Figure 1a. k_{rec}^L , k_{rec}^{H-BG} and k_{rec}^{H-SG} denote the decay constants for charge recombination in the energy notch (names as L), in the high bandgap regions exhibiting large grains (named as H-BG) and small grains (named as H-SG) respectively. Studies of transient absorption decay kinetics with b) 700 nm laser excitation probed at 885 nm wavelength and 1000 nm laser excitation probed at 1025 nm wavelength respectively, c) 900 nm laser excitation probed at 1025 nm (in NaF PDT and RbF+NaF PDT samples)/ 1040 nm wavelength (in No PDT sample). The red thin lines showed the fitting results. The laser excitation density utilized is equivalent to 7×10^{13} photons/cm² absorbed (d) Histogram showing time constants of the TAS signals decayed at the energy notch (τ_{rec}^L), in the H-BG (τ_{rec}^{H-BG}), and the H-SG (τ_{rec}^{H-SG}) regions and the corresponding drift time constant (τ_D) of charge carriers. The stars indicate the competition between charge recombination and drift.

NaF PDT, and RbF+NaF PDT samples, respectively.

Further, carrier dynamics in the volume excited by 700 nm laser excitation, which is denoted as “H-SG” indicative of the high GGI ratio ($\text{GGI} > 0.6$) and small CIGS grain size, is discussed. In Figure 5.3 (3^{rd} row), a rapid photobleach decay in all 3 samples (more than half of its original amplitude decays by 500 ps) is observed. From the 880 nm probe kinetics (Figure 5.4b) fitted with a single exponential function, recombination time constants in the air-exposed small grain region of $\tau_{\text{rec}}^{\text{H-SG}} = 40$ ps, 100 ps, and 110 ps for No PDT, NaF PDT, and RbF+NaF PDT samples, respectively, is observed. It is noted that the small signal centred at 1025 nm in RbF+NaF PDT and NaF PDT samples or at 1040 nm in the No PDT sample results from charge carriers generated in the large grain (H-BG) region (see absorption tail of 700 nm light in Appendix Figure C.1). The fast recombination rates on the order of ~ 100 ps prevent charge carriers generated in this region to drift towards the energy notch region. The resulting four time constants ($\tau_{\text{rec}}^{\text{L}}$, $\tau_{\text{rec}}^{\text{H-BG}}$, τ_D , and $\tau_{\text{rec}}^{\text{H-SG}}$) for all 3 samples were plotted in comparison in Figure 5.4d and are discussed below.

5.5 Discussions

• *Comparison of NaF PDT versus No PDT*

From the results, it is clear that the incorporation of Na atoms improves the charge carrier lifetime by a factor of 2.3 – 2.5 across the entire CIGS absorber layer with GGI ratios varying between 0.2 – 0.67. This improvement is effective in large grain and in small grain CIGS, suggesting a homogenous passivation of recombination centres throughout the CIGS layer (inclusive of GIs and GBs). Furthermore, a 1.3 fold increase in electron mobility in the NaF treated sample calculated from the electron drift time constant in the large grain region ($8.2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in the No PDT, $11.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in the NaF treated sample) is obtained. Since the increase in electron lifetime in the small grain region with a higher grain boundary surface area is not proportionally larger compared to the lifetime enhancement in the energy notch region and because the electron mobility is obtained in the large grain volume of the CIGS film, all suggest a homogenous defect passivation throughout the CIGS film in its GIs and at the GBs.

Na has been suggested to reduce compensating donor defects such as the Se vacancy (V_{Se}) or the In on Cu anti-site (In_{Cu}) in the GIs and GBs leading to the observed increase

in p-type character in CIGS[30][31]. Siebentritt et al. calculated Urbach energies in CIGS devices that were fabricated analogous to the samples herein and found a reduced density of tail states in samples with NaF PDT[23]. Interestingly, a 15 meV blue shift in the peak positions of the photobleach in the energy notch region in the NaF and NaF+RbF treated samples (1025 nm in PDT samples versus 1040 nm in No PDT) is observed despite an identical GGI ratio in all 3 samples in this region. This would support both of the above-mentioned observations though in this study it is not distinguishable whether Na atoms passivate a specific shallow defect state or a distribution of tail states in CIGS.

• *Comparison of RbF+NaF PDT versus NaF PDT*

As shown in Figure 5.4d, compared to a NaF PDT, the combined NaF+RbF PDT increases charge carrier lifetime 1.4-fold in the energy notch and ~ 2.0 -fold in the bandgap-graded H-BG region. On the other hand, in the small grain, high GGI (H-SG) region, RbF barely affects electron lifetime (only 1.1- fold increase). Electron transport in the H-BG region across the conduction band gradient is ~ 1.5 times faster in the NaF+RbF treated sample compared to the NaF equivalent.

Taguchi et al. showed the formation of a surface RbInSe₂ layer on CIS and CIGS but could not detect a separated phase on CGSe surfaces[19]. Furthermore, Ishizuka et al. demonstrated no significant improvement in device performance in a CGSe device with RbF PDT compared to one without[32]. The results in this chapter show a negligible effect of Rb in the H-SG volume and support those observations, suggesting that no surface passivation layer is formed on CIGS surfaces with GGI ratios exceeding 0.6. Neither, do significant evidence for passivation of defects in GIs by Rb within these small grains is obtained. As a result, all 3 samples show fast recombination in the small grains such that all photogenerated electrons are lost to recombination without any left to drift to the energy notch region. Neither NaF nor a combined NaF+RbF PDT offer effective passivation in this H-SG region. It remains to determine if the ultrafast recombination is a result of surface or/and bulk recombination and how the high GGI ratio (>0.6) impacts the formation of additional bulk and/or surface defect states.

A μ s-s transient absorption study (see Appendix Figure C.6 and C.7) is conducted and the results show a long-lived positive absorption signal (up to 10 ms) in all three samples. As discussed in Chapter 3, this positive signal is related to the absorption caused by charge carriers trapped in the deep defect states. The amplitude of the absorption signal

is observed to be the same among the three samples but decreases towards lower GGI. This finding agrees well with a faster recombination in regions of higher GGI ratio due to the presence of more deep defects that are not passivated by either of the PDTs studied herein.

While the smallest impact of Rb on carrier dynamics is observed in the small grain and high GGI region (H-SG), the largest improvement is visible in the H-BG volume where drift ($\tau_D = 1998$ ps) outcompetes recombination ($\tau_{rec}^{H-BG} = 2797$ ps, $k_{rec}^{H-BG}/k_D = 0.7$) in the NaF+RbF treated sample, whilst the other two samples both show faster recombination ($k_{rec}^{H-BG}/k_D = 2.1$ and 6.4 for NaF and No PDT, respectively). This kinetic competition between recombination and drift of minority carriers photogenerated in the H-BG volume (indicated with stars in Figure 5.4d) controls the yield of minority carriers in the energy notch, where carriers are most long-lived and detrimental to photocurrent and photovoltage generation. This result obtained from the H-BG region is in good agreement with the trend in EQE (Figure 5.2c), showing an enhanced EQE in the 750 nm – 1000 nm range in NaF and NaF+RbF devices. The resulting higher mobility and slower recombination rates in RbF+NaF PDT samples (compared to NaF PDT) can be the result of further tail state or shallow defect state passivation analogous to the NaF PDT as discussed above.

Siebentritt et al. reported that RbF PDT could further reduce the density of tail states which were already somewhat smaller than in the untreated devices[23]. And while Taguchi et al. attributed the improved device performance to the formation of a surface RbInSe_2 layer[19] at CdS/CIGS interface, other works find Rb to passivate recombination centres in the space charge region[22][24][25]. From the results of this study, clear improvements in electron lifetime not only are observed in the energy notch region (within the space charge region) but also in the $\text{GGI}=0.2\text{--}0.5$ big grain region. Though it is not able to distinguish whether the passivation is on the defects in GIs or at GBs from the results of this study, previous atom probe topography studies have shown Rb is mostly accumulated at GBs[17][18], suggesting it is more likely that Rb atoms passivate defects at GBs.

It should also be noted that the charge carrier lifetime detected in the TA experiments (non-radiative decay) here are much shorter compared to those measured by time-resolved PL (radiative)[24][25]. However, this phenomenon has been observed in most of

the CIGS TA studies[6][15][33][34]. For example, Chen et al. obtained a non-radiative recombination lifetime of ~ 750 ps on a 12.35% CIGS device via transient reflectivity spectroscopy[34]. Whilst the radiative recombination lifetime (time-resolved PL decay time) is expected to be 10 ns for a CIGS device with similar efficiency[35]. If considering the ~ 13 fold difference between TA decay time and time-resolved PL decay time observed in Chen's study, the radiative recombination lifetime in the energy notch region of the RbF+NaF PDT CIGS sample investigated in this study would be 247 ns, which is consistent with the values reported in literature[24][25][22].

5.6 Conclusion

In this chapter, Ga-graded CIGS devices with 3 different post deposition processing conditions (No PDT, NaF PDT and NaF+RbF) using transient absorption spectroscopy are investigated. The kinetic model established previously in Chapter 4 divides each of these CIGS films in 3 main volume slabs namely the energy notch region ($\text{GGI} = 0.2$), bandgap graded region ($\text{GGI} = 0.2 - 0.5$ (H-BG)) and a region with $\text{GGI} > 0.6$ and predominantly smaller grain size. Comparing recombination kinetics of NaF treated and pristine CIGS, it is found that the minority carrier lifetime is increased 2.3 – 2.5-fold in all 3 regions, indicating a homogeneous passivation of recombination centres throughout the CIGS layer (in both grain interior and in grain boundaries) after NaF PDT. Further, comparing RbF+NaF PDT to the NaF PDT sample, the minority carrier lifetime in the energy notch ($\text{GGI} = 0.2$) and big grain region ($\text{GGI} = 0.2 - 0.5$) increases another 1.4-fold and 2.0-fold, respectively, whereas in the small grain region ($\text{GGI} > 0.6$) the improvement is negligible (1.1-fold). These results suggest that the passivation of recombination centres after RbF PDT is rather ineffective in the $\text{GGI} > 0.6$ small grain region, indicating that the effectiveness of Rb passivation depends on the GGI ratio and works the best in the $\text{GGI} < 0.5$ domain. Furthermore, a kinetic competition between electron recombination and transfer to the energy notch in the H-BG region that determines the yield of electrons in the energy notch where they are most long-lived determining the photocurrent and photovoltage generation is found. The effective passivation in the big grain region by the PDTs significantly increases electron mobility and explains the observations of higher EQEs in the 750 nm – 1000 nm range and an increased open-circuit voltage in the

PDT CIGS devices. Last, a positive long-lived absorption signal, which is linked to the presence of charge carriers trapped in the deep defects, is found in both PDT and untreated samples with a stronger signal in the high GGI small grain volume slab. Though it needs further studies to investigate which type of deep defects give rise to this positive absorption signal on the ms timescale, it can be concluded that the alkali PDTs studied herein do not passivate these effectively.

5.7 Publications

The results of this chapter is also utilized for the manuscript in the publication:

Chang, Y.-H. et al. Impact of RbF and NaF postdeposition treatments on charge carrier transport and recombination in Ga-graded CIGS solar cells. (2020).

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Chapter 6

Concluding remarks

6.1 Concluding remarks

The aim of this thesis is to unravel minority charge carrier kinetics in Ga-graded and alkali treated CIGS solar cells. To achieve this, transient absorption spectroscopy is utilized as the main tool, allowing to investigate non-radiative processes such as charge carrier trapping and drifting of minority charge carriers over a broad timescale (picosecond-nanosecond and microsecond-second) in a such complex structure.

In Chapter 3, minority charge carrier dynamics of a GGI=0.4 CIGS thin film (without Ga gradient and alkali PDT), a CIS thin film, and a Sb_2Se_3 thin film are investigated. In all three materials, a photobleach which clearly follows the 1st derivative of the UV-VIS absorptance is observed in the picosecond-nanosecond timescale, is assigned to the ground state bleach. The time constant of this ground state bleach decay is calculated to be 650 ps, 580 ps, and 15 ps for CIGS, CIS, and Sb_2Se_3 , respectively. It should be noted that in CIGS and CIS samples, the decay time constant of an air-exposed region is 4-5-fold smaller than the epoxy-covered region. This may be due to MoSe_2 residuals and/or surface oxidation that act as recombination centers. In microsecond-second timescale, a prominent bandedge absorption is observed in all three samples. This long-lived absorption is assigned to the presence of trapped charge carriers, though the type of defects cannot be specified. In the Sb_2Se_3 thin film, a higher amplitude of the absorption signal per photons/ cm^2 is obtained compared to the CIGS and CIS samples, indicating a more defective film quality of the Sb_2Se_3 sample.

In Chapter 4, minority carrier dynamics of a 19.3% efficient CIGS solar cell with an implemented Ga gradient (GGI ranges from 0.2–0.67) and $\text{RbF}+\text{NaF}$ PDT is investigated. A kinetic model established here divides such CIGS films into 3 main volume slabs namely the energy notch region (GGI =0.2), bandgap graded region (GGI 0.2 to 0.5 (H-BG)) and a layer with GGI>0.6 and predominantly smaller grain size. Moreover, it allows to decouple the recombination and drift kinetics in the H-BG region of the device, and a corresponding electron mobility of $16.3 (\pm 4.0) \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ is obtained. Further, it is found that the minority carrier lifetime decreases from 19 ns in the energy notch region (grain size $>2\mu\text{m}$) to 100 ps (400 ps estimated for the sample without detachment of the Mo back contact) in the H-SG region (grain size $< 0.5 \mu\text{m}$). This indicates that the minority carrier lifetime in the CIGS film depends on both the GGI ratio and the crystalline grain size.

In Chapter 5, minority carrier dynamics of three CIGS devices with an identical Ga gradient profile but three different alkali PDTs (without any alkali treatment, NaF PDT, and RbF+NaF PDT) are investigated. Making use of the kinetic model established in Chapter 4, the time constant of recombination in every region (energy notch, H-BG, and H-SG) and drift in the H-BG region of each sample is obtained and compared, respectively. It is found that the minority carrier lifetime of the Na treated sample is increased by a similar degree compared to the one without any alkali treatment in all 3 regions, indicating a homogeneous passivation of recombination centres throughout the CIGS layer (in both grain interior and at grain boundaries) after NaF PDT. On the other hand, comparing the RbF+NaF treated device to the NaF treated one, the minority carrier lifetime increases more profoundly in the energy notch and the H-BG region, whereas in the H-SG region the improvement is negligible. These results suggest that the passivation of recombination centres after RbF post deposition treatment is more effective in the low GGI ($\text{GGI} < 0.5$) region.

Nevertheless, it can be concluded that both Na and Rb atoms passivate the big grain region (including the energy notch and the H-BG region) effectively, which leads to not only a higher minority carrier lifetime but also a faster minority carrier mobility. Consequently, a higher amount of minority carriers drift to the front region and being collected, which explains the observations of higher EQEs in the 750 nm – 1000 nm range and an increased open-circuit voltage in the PDT-treated CIGS devices. Last, a positive long-lived absorption signal, which is assigned to the presence of trapped charge carriers, is found in all three samples with a stronger signal in the H-SG region. Though further research is needed to investigate which type of defects give rise to this positive absorption signal on the ms timescale, it can be concluded that both Na and Rb atoms do not passivate these effectively.

6.2 Future work

Though the results of this thesis unravel some pieces of the puzzle in the field of CIGS, many questions are still waiting to be answered.

- ***For CIGS***

1. **Origins of the positive absorption signal existing in the microsecond-second timescale needs further investigation.** This long-lived positive bandedge absorption appears in every CIGS sample investigated in this study, though it is speculated to result from trapped charge carriers, further evidences are surely needed. A comparison between CIGS with single crystalline and poly-crystalline structures would be worthwhile investigating. This is due to a single crystalline CIGS is proposed to have less defects (less grain boundaries) than a poly-crystalline one. Further, conducting applied potential transient absorption experiments will also help to understand how transient optical signals change with external bias.

2. **The air-exposed region due to the detachment of Mo back contact.** In this study, it is found that the charge carrier recombines much faster in the air-exposed back region than in the encapsulated front region. Though it may be contributed by MoSe₂ and/or the surface oxidation due to air exposure, it is not possible to distinguish which poses a major impact. Therefore, designing experiments that perform the peeling-off procedure in a glove box and encapsulate the detached region with epoxy immediately may elucidate the main cause.

3. **Rb atoms passivation on the GGI>0.6 small grain region.** From this study, no significant improvement is detected in the small grain region comparing RbF+NaF PDT and NaF PDT samples. However, it cannot be derived from this study why Rb atoms do not passivate recombination centers in the small grain region. As the small grained region is associated with the high GGI ratio, the chemical compositions of the CIGS region might be a determining factor for the effectiveness of Rb atoms passivation. A detailed DFT calculation implementing these findings might provide further insights.

- ***For Sb_2Se_3***

Note that the investigation of Sb_2Se_3 material is only a small side topic for this thesis, hence, the corresponding results presented in this thesis are basic. For sure, much in-depth research is needed to draw a clear picture on charge carrier dynamics in this material.

1. Deconvolution of the ground state bleach and the positive absorption associated with trapped charge carriers observed in the picosecond-second timescale. From the results of this study, the ground state bleach signal and the positive absorption signal are superimposed on one another. Therefore, to obtain a recombination and charge trapping time constant with high accuracy, a detailed kinetic model or global analysis is needed.

Appendix

Appendix A

Supporting figures for Chapter 3

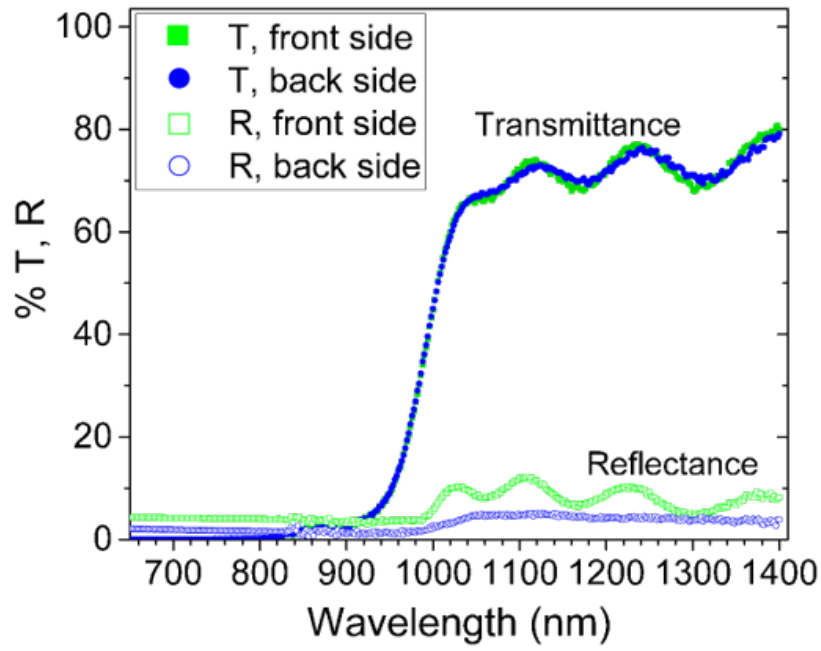


Figure A.1: Transmittance (T) and Reflectance (R) spectra of a GGI = 0.4 CIGS thin film upon excitation from the front and back side.

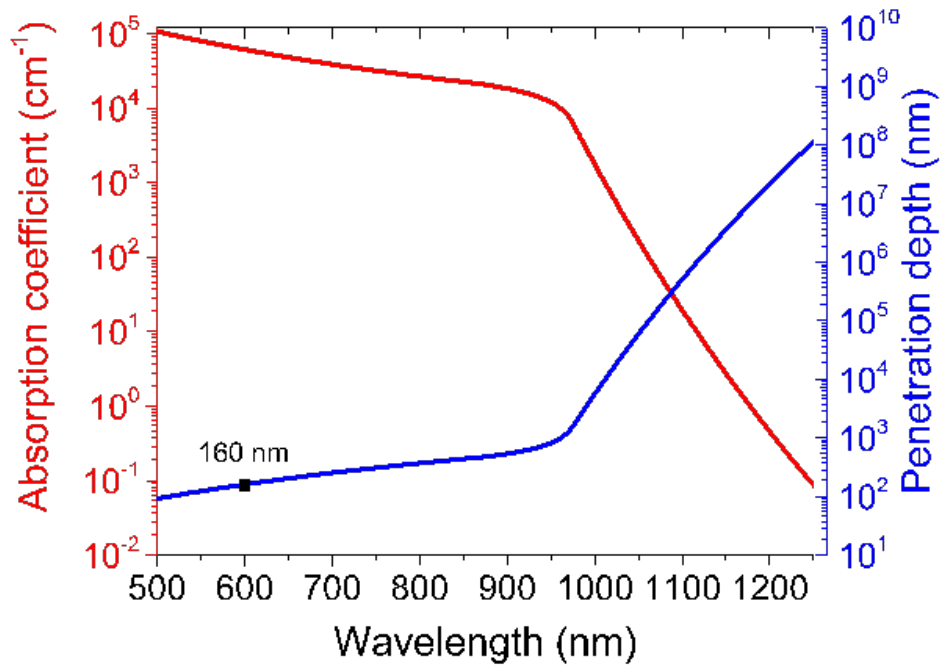


Figure A.2: Absorption coefficient and penetration depth of a GGI = 0.4 CIGS thin film

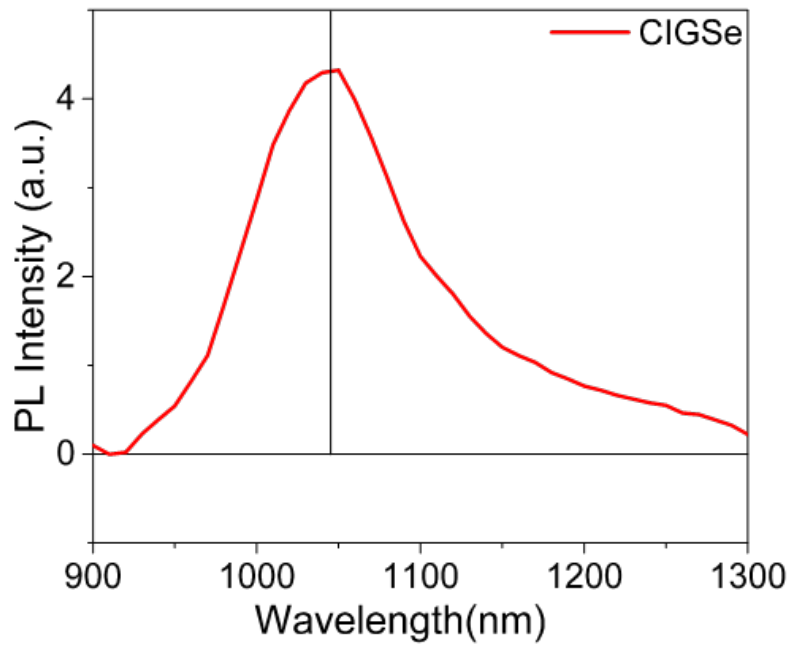


Figure A.3: PL spectrum of a GGI = 0.4 CIGS thin film following 1 sun white light illumination from the front side.

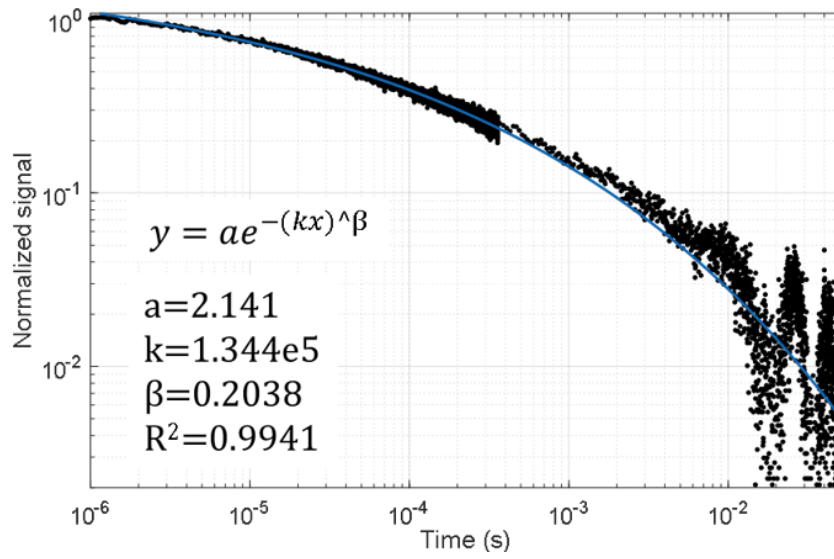


Figure A.4: Stretched exponential fitting ($y = ae^{-(kx)^\beta}$, k : decay constant, β : stretching component) of normalized TA kinetics probed at 1000 nm of a GGI = 0.4 CIGS thin film (Normalized TA curve of $248 \mu\text{J}/\text{cm}^2$ in Figure 3.5c) in 355 nm excitation case.

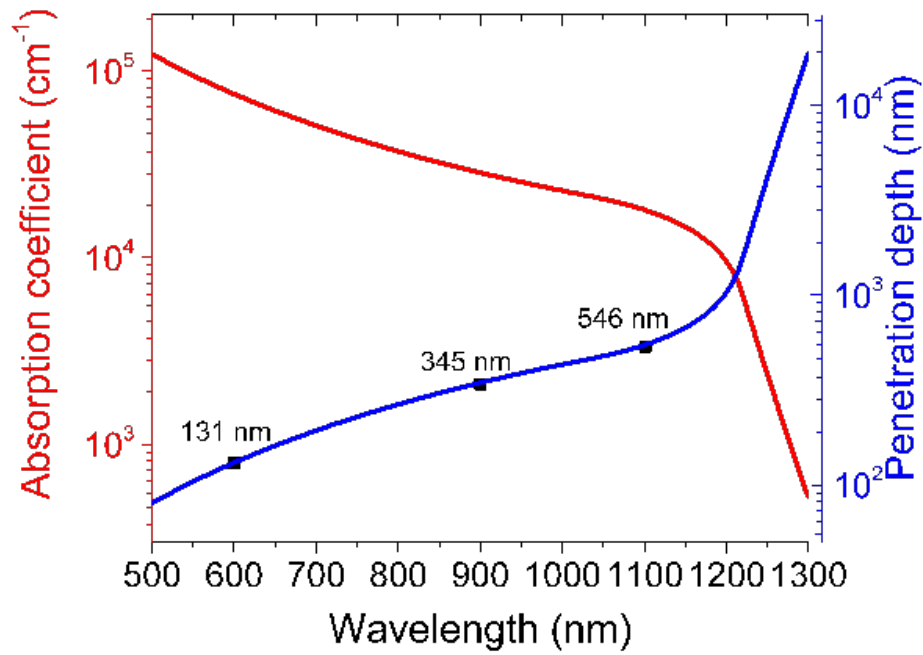


Figure A.5: Absorption coefficient and penetration depth of CIS thin film.

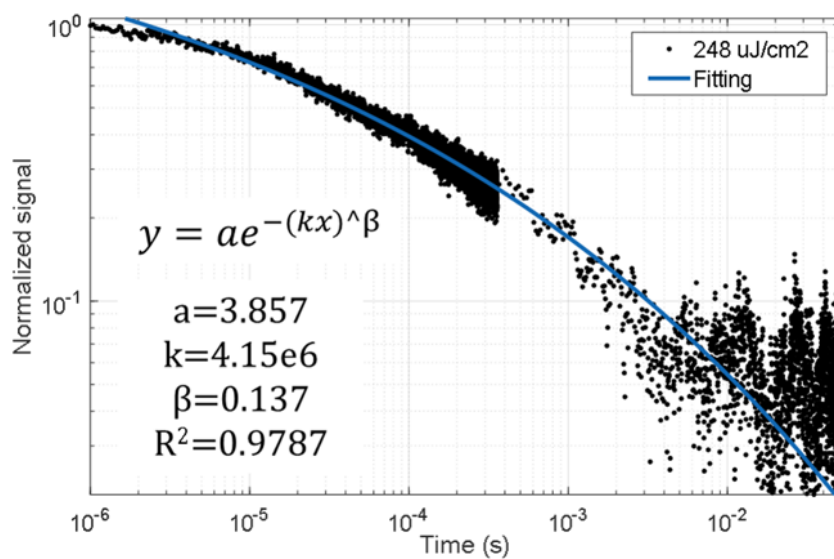


Figure A.6: Stretched exponential fitting ($y = ae^{-(kx)^\beta}$, k : decay constant, β : stretching component) of normalized TA kinetics probed at 1200 nm of CIS thin film (Normalized TA curve of 248 $\mu\text{J}/\text{cm}^2$ in Figure 3.11c) following 355 nm excitation.

Appendix B

Supporting figures for Chapter 4

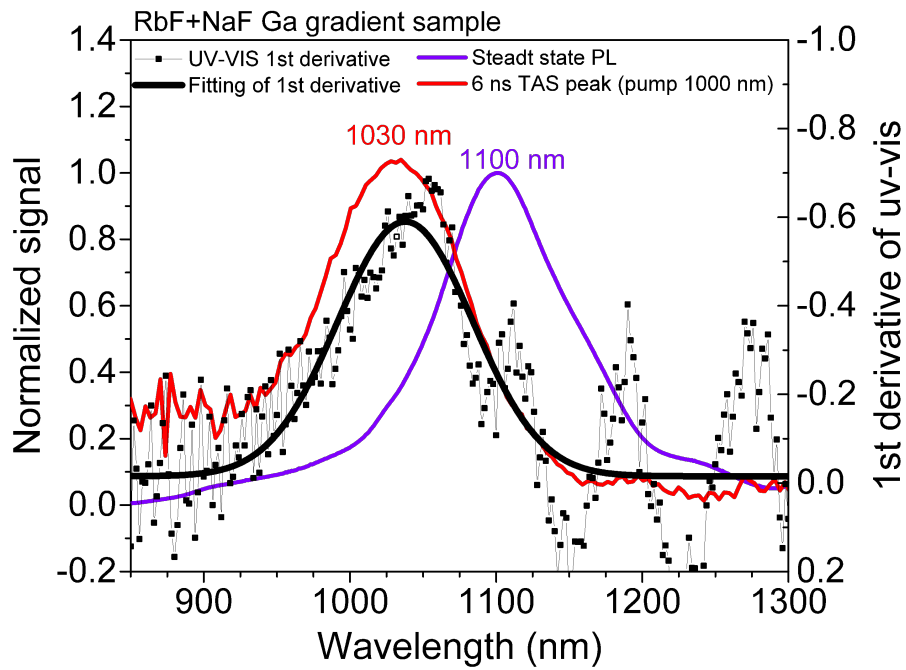


Figure B.1: Comparison of the peak positions from 6 ns TAS peak (pump 1000 nm case), UV-VIS 1st derivative of absorptance, and steady state PL in RbF+NaF Ga gradient CIGS sample

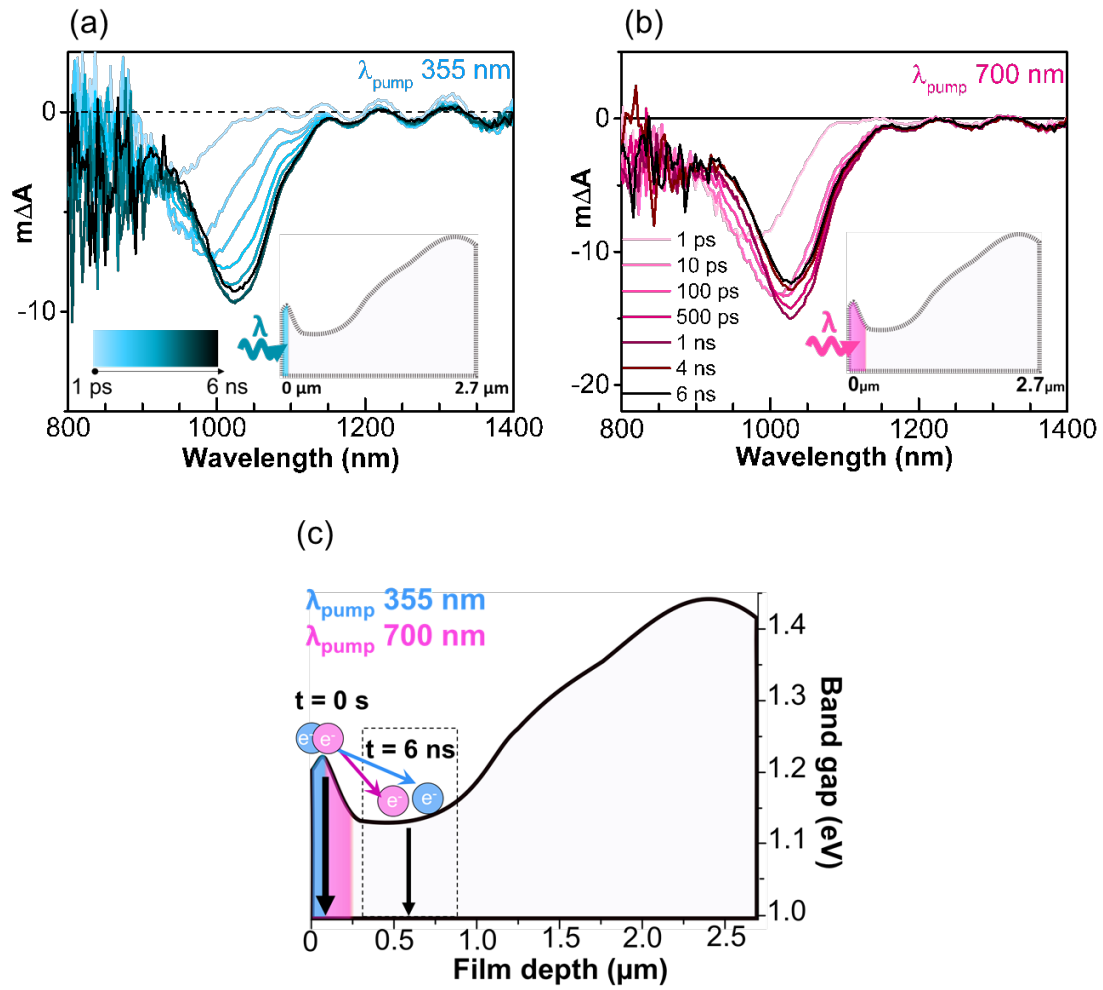


Figure B.2: Transient absorption measurement results for (a) 355 nm (b) 700 nm excitation wavelength from the front side. Laser fluence: $6 \mu\text{J}/\text{cm}^2$. c) Schematic of carriers moving position after excitation in the time window from 0 s to 6 ns.

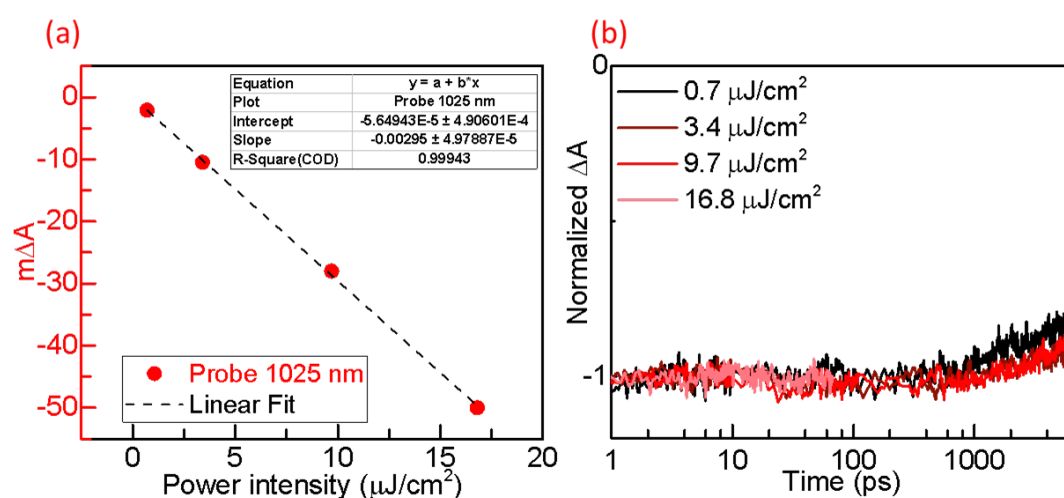


Figure B.3: Fluence-scaled TA decay kinetics probed at 1025 nm following 1000 nm excitation wavelength with 0.7, 3.4, 9.7 and 16.8 $\mu\text{J}/\text{cm}^2$ fluence. (a) shows the amplitude of ΔA as a function of fluence. (b) show the normalized kinetic trace probed at 1025 nm. 1 $\mu\text{J}/\text{cm}^2$ equals to $4 \cdot 10^{12}$ photons/ cm^2 absorbed.

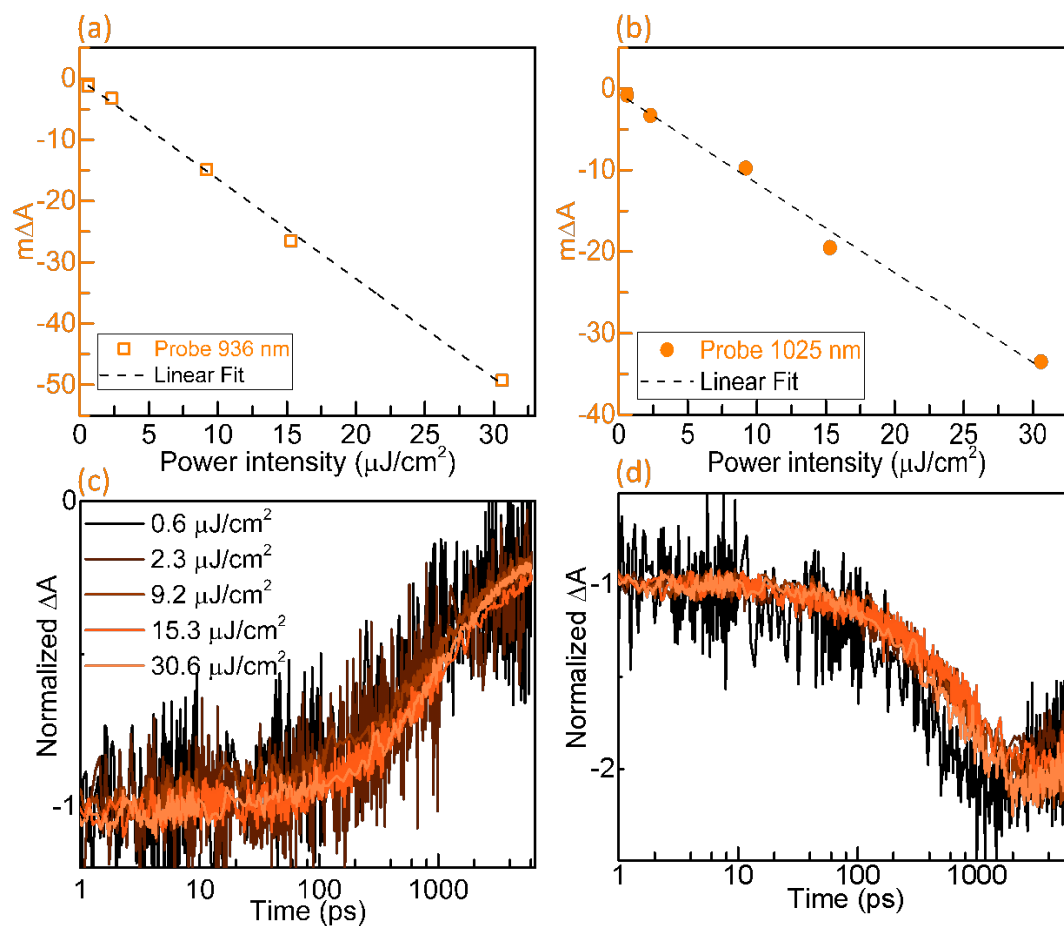


Figure B.4: Fluence-scaled study on TA decay kinetics probed at (a) 936 nm and (b) 1025 nm following 900 nm excitation wavelength with 0.6, 2.3, 9.2, 15.3, and 30.6 $\mu\text{J}/\text{cm}^2$ fluence. (a) and (b) show the amplitude of ΔA as a function of fluence of 930 nm and 1025 nm probe, respectively. (c) and (d) show the normalized kinetic trace probed at 936 nm and 1025 nm, respectively. 1 $\mu\text{J}/\text{cm}^2$ equals to 4×10^{12} photons/ cm^2 absorbed.

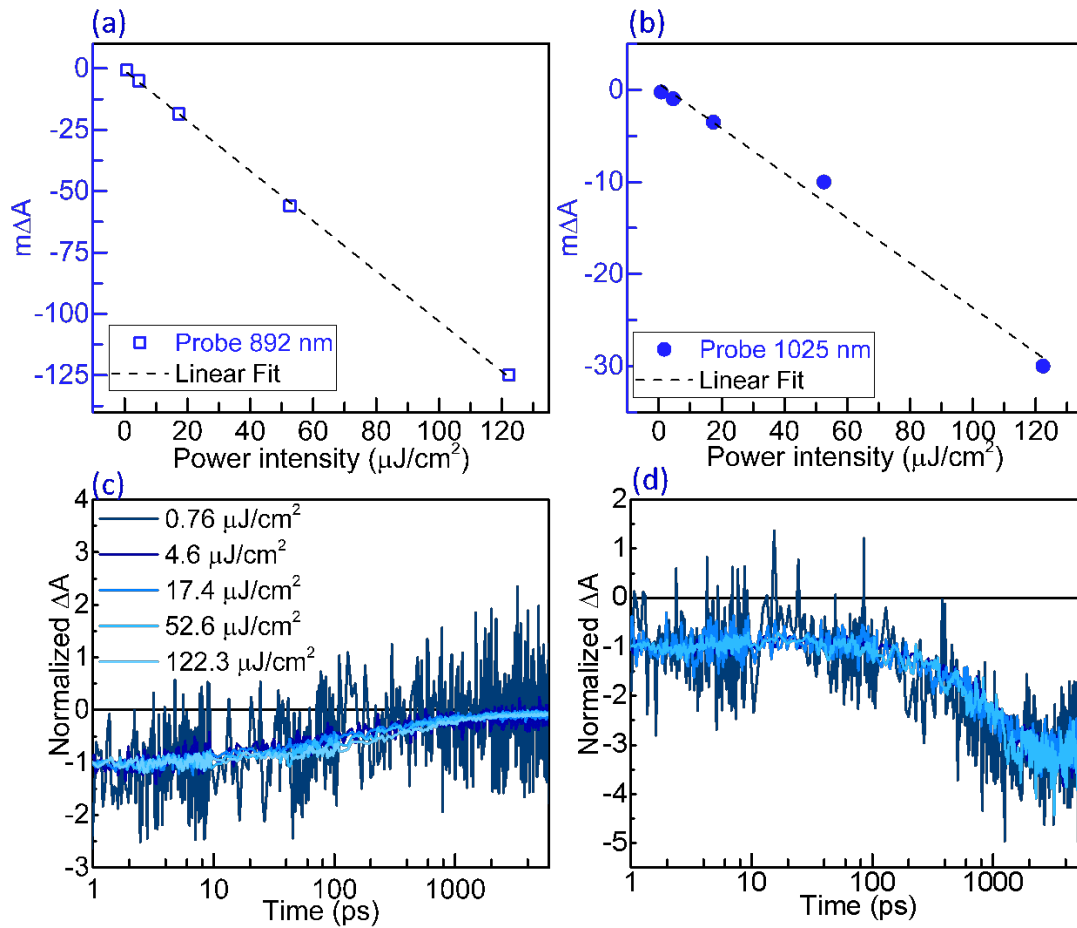


Figure B.5: Fluence-scaled study on TA decay kinetics probed at (a) 892 nm and (b) 1025 nm following 800 nm excitation wavelength with 0.76, 4.6, 17.4, 52.6, and 122.3 $\mu\text{J}/\text{cm}^2$ fluence. (a) and (b) show the amplitude of ΔA as a function of fluence of 892 nm and 1025 nm probe, respectively. (c) and (d) show the normalized kinetic trace probed at 892 nm and 1025 nm, respectively. 1 $\mu\text{J}/\text{cm}^2$ equals to 4×10^{12} photons/ cm^2 absorbed.

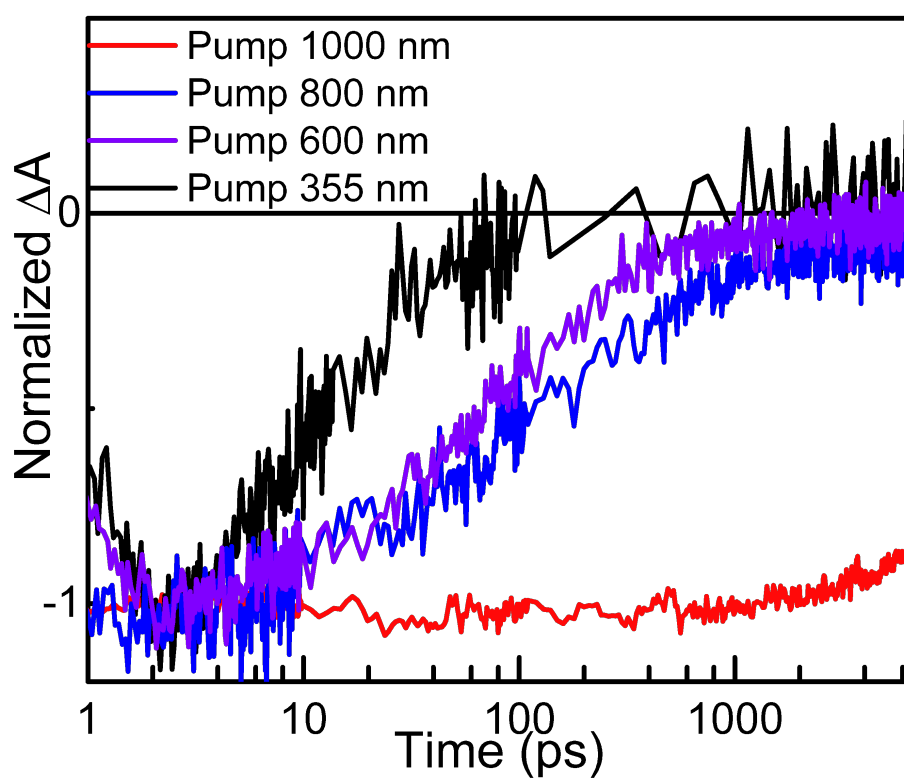


Figure B.6: Normalized transient absorption kinetics probed at 1025 nm for 1000 nm laser pulse (colour red), 892 nm for 800 nm laser pulse (colour blue), 875 nm for 600 nm laser pulse (colour purple), and 870 nm for 355 nm laser pulse (colour black) from the back side.

Appendix C

Supporting figures for Chapter 5

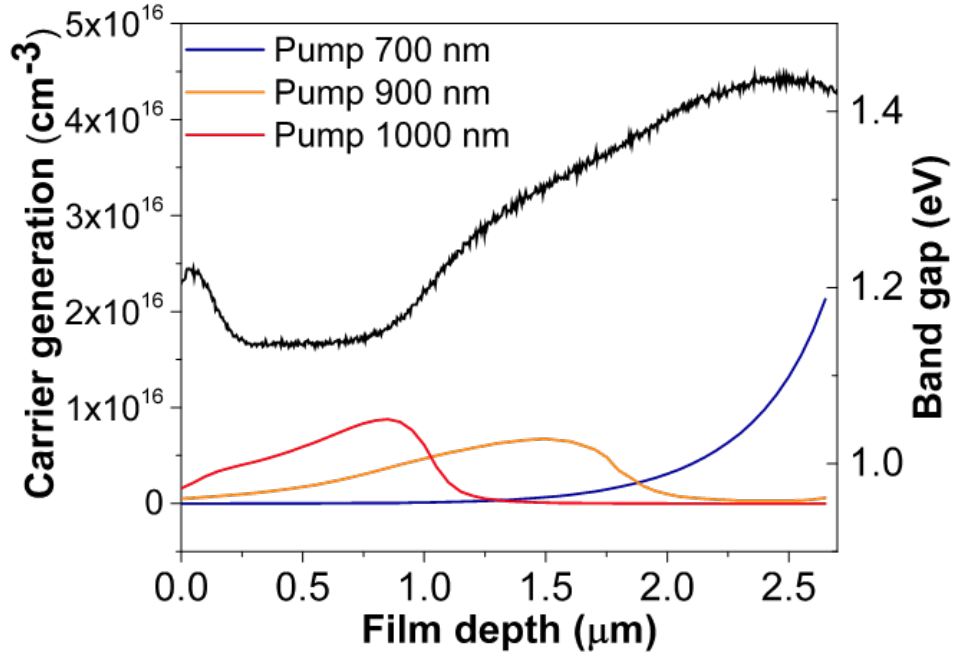


Figure C.1: Charge carrier generation in a Ga-graded CIGS absorber following 700 nm, 900 nm and 1000 nm excitation from the peeled-off Mo side. The bandgap profile is based on the SIMS result of RbF+NaF PDT sample, as shown in Figure 5.2a.

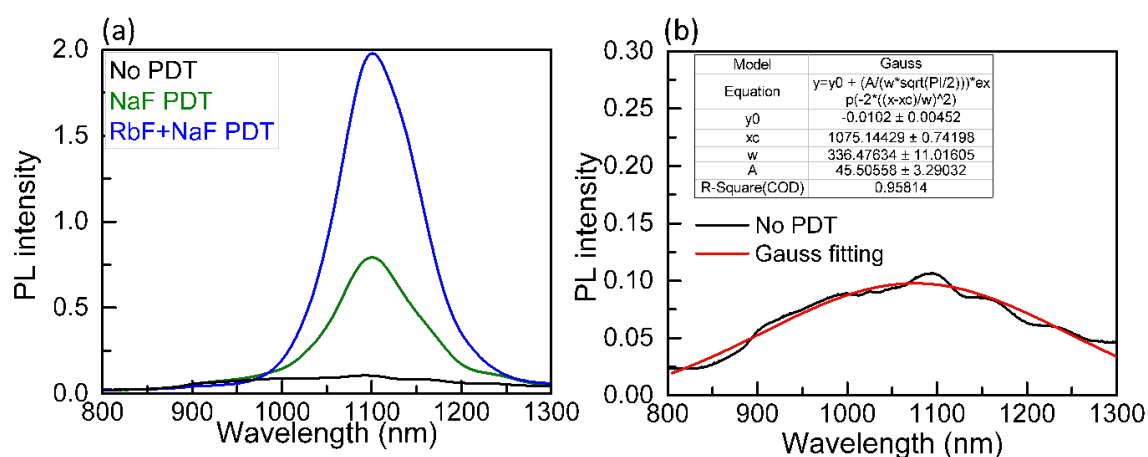


Figure C.2: (a) steady state PL measurements of No PDT, NaF and RbF+NaF PDT samples, respectively. (b) Gauss fitting of PL spectrum of the No PDT sample. For the two PDT samples, the peak positions are at 1100 nm, whilst for No PDT sample the peak position is at 1075 nm.

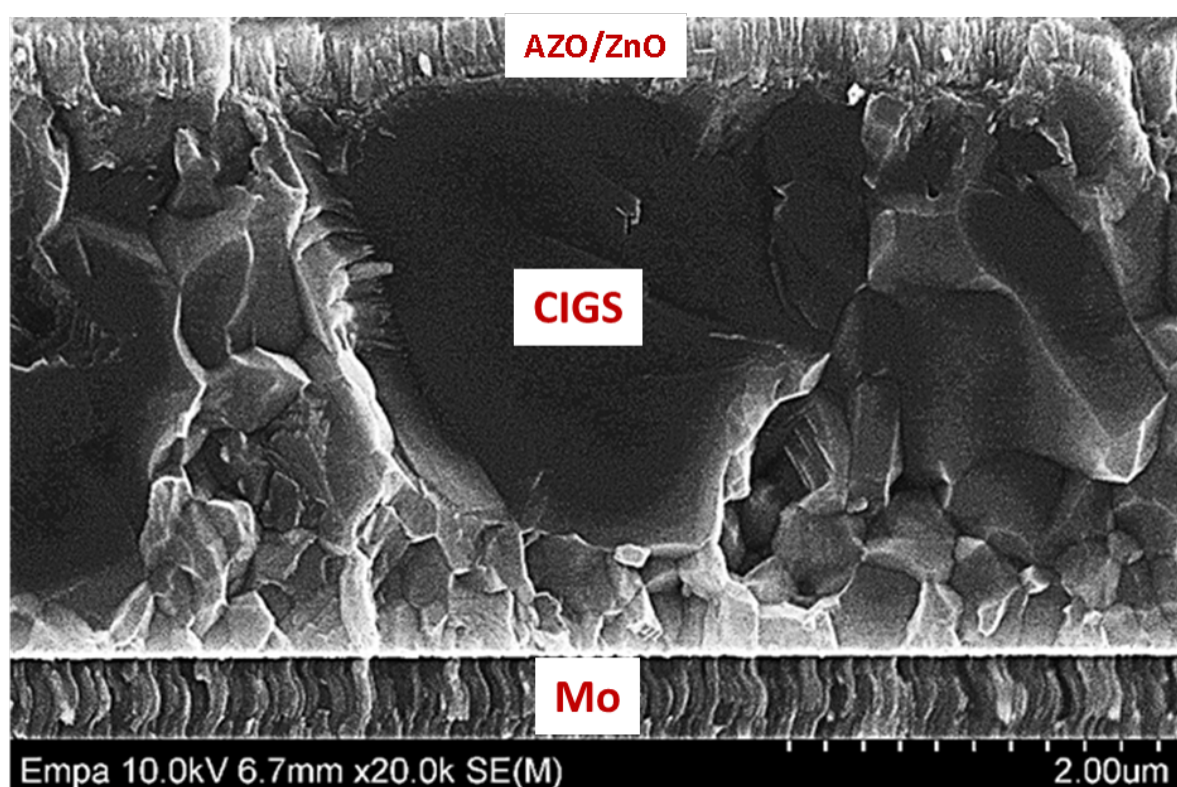


Figure C.3: SEM cross section of the Ga-graded NaF+RbF-treated CIGS device investigated in this study

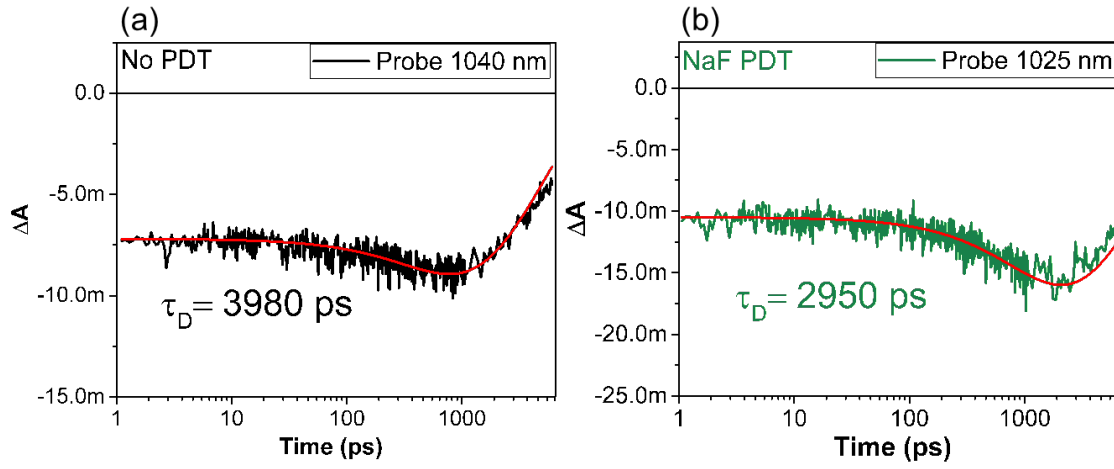


Figure C.4: As demonstrated in detail in Chapter 4, Equation 4.5 can be utilized to fit the decay constants k_D and k_{rec}^H of the 1040 nm (for No PDT sample)/ 1025 nm (for NaF PDT sample) kinetics. Inputting the parameters listed in Table C.1 into Equation 4.5, the fitting results of the (a) 1040 nm kinetics of the No PDT samples and (b) 1025 nm in the NaF PDT sample are shown as red lines, respectively.

Table C.1: Plug-in parameters for Equation 4.5 of No PDT and NaF PDT samples. H_0 and L_0 are the initial amplitudes of the 939 nm/943 nm and 1025 nm/ 1040 nm signals of the No PDT and NaF PDT samples. k_{rec}^L is the decay constant obtained in the case of 1000 nm excitation.

$\frac{k_D}{k_D + k_{rec}^H}$ is estimated with the TAS integrated areas, as shown in Figure C.5

Sample	Plug-in parameters			
	L_0	$1/(k_{rec}^L)$, unit: ps	H_0	$k_D/(k_D + k_{rec}^H)$
No PDT	-0.0072	5,250	-0.029	7.6/23.2
NaF PDT	-0.0105	13,200	-0.026	3.5/26

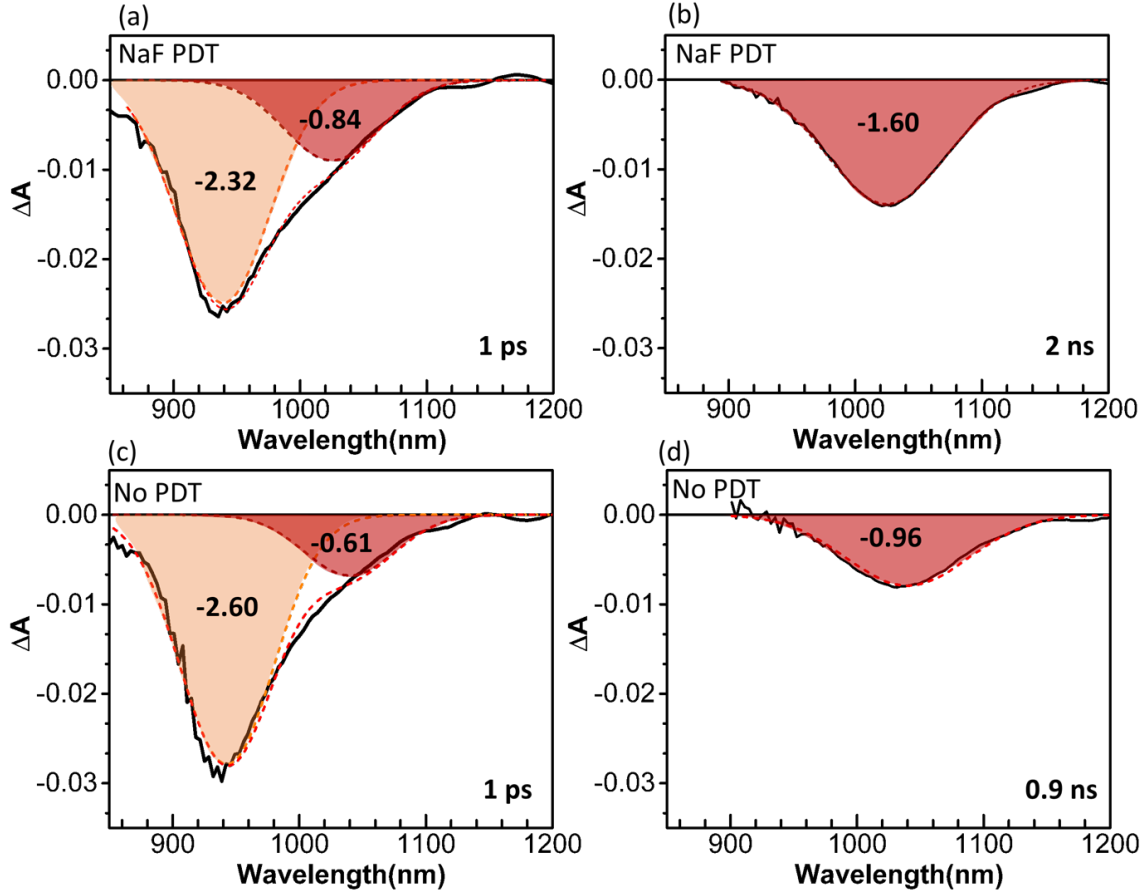


Figure C.5: Integrated TAS spectra taken from Figure 5.3 (900 nm excitation) in the main text of NaF PDT sample probed at (a) 1 ps and (b) 2 ns, respectively. At 1 ps, the integrated area of the 939 nm and the 1025 nm signals correlate to the electrons excited in $GGI \leq 0.5$ region and in the energy notch. The corresponding integrated areas of the 939 nm and 1025 nm peaks are -2.32 and -0.84 respectively. At 2 ns, the 1025 nm peak dominates the TAS spectrum, with an integrated area of -1.60. (c) and (d) show the integrated TAS of No PDT sample probed at 1 ps and 1 ns, respectively. At 1 ps, the integrated area of the 943 nm and the 1040 nm signals correlate to the electrons excited in $GGI \leq 0.5$ region and in the energy notch. The corresponding integrated area of the 943 nm and 1040 nm peaks are -2.60 and -0.61 respectively. At 0.9 ns, the 1040 nm peak dominates the TAS spectrum, with an integrated area of -0.96.

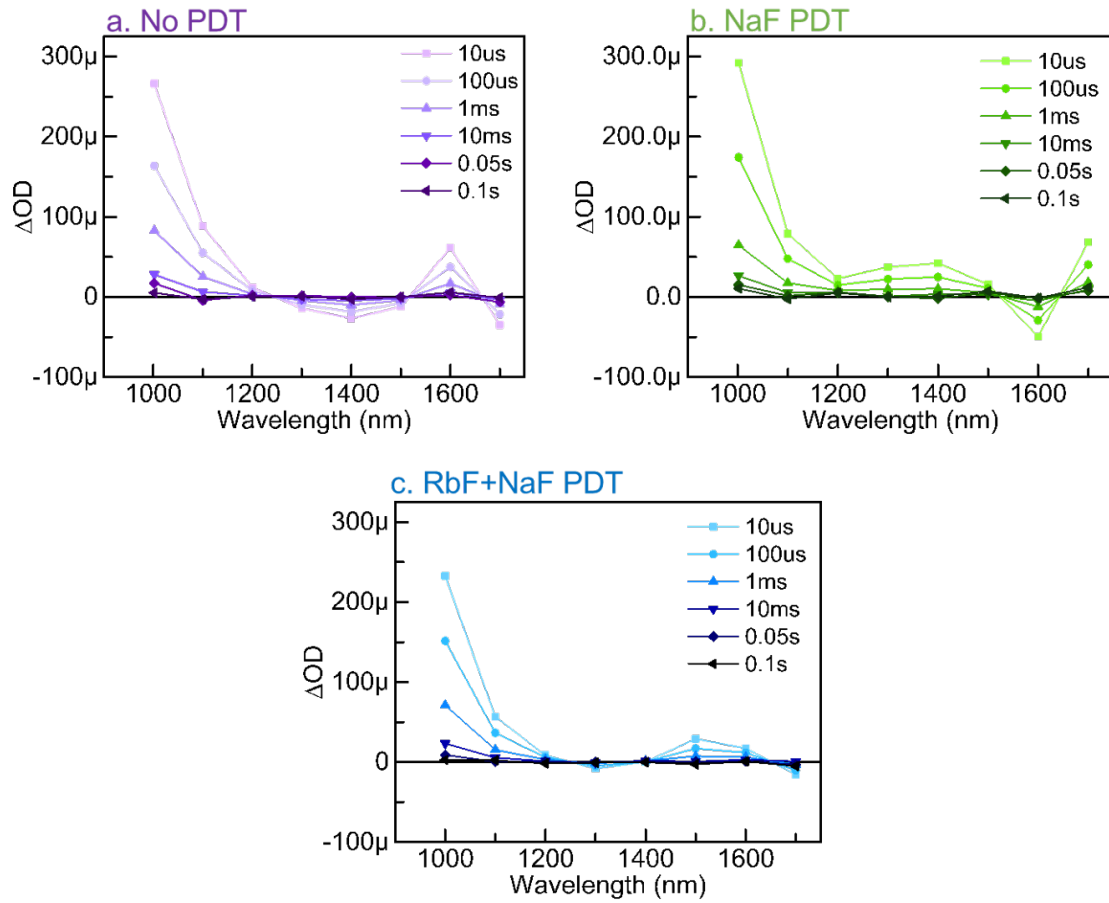


Figure C.6: Microsecond - second transient absorption study on the CIGS cell. Excitation from the peeled-off Mo side with 355 nm laser light excitation. Laser excitation density: 0.36 mJ/cm². An absorption signal is observed in all three samples in the near-band gap position.

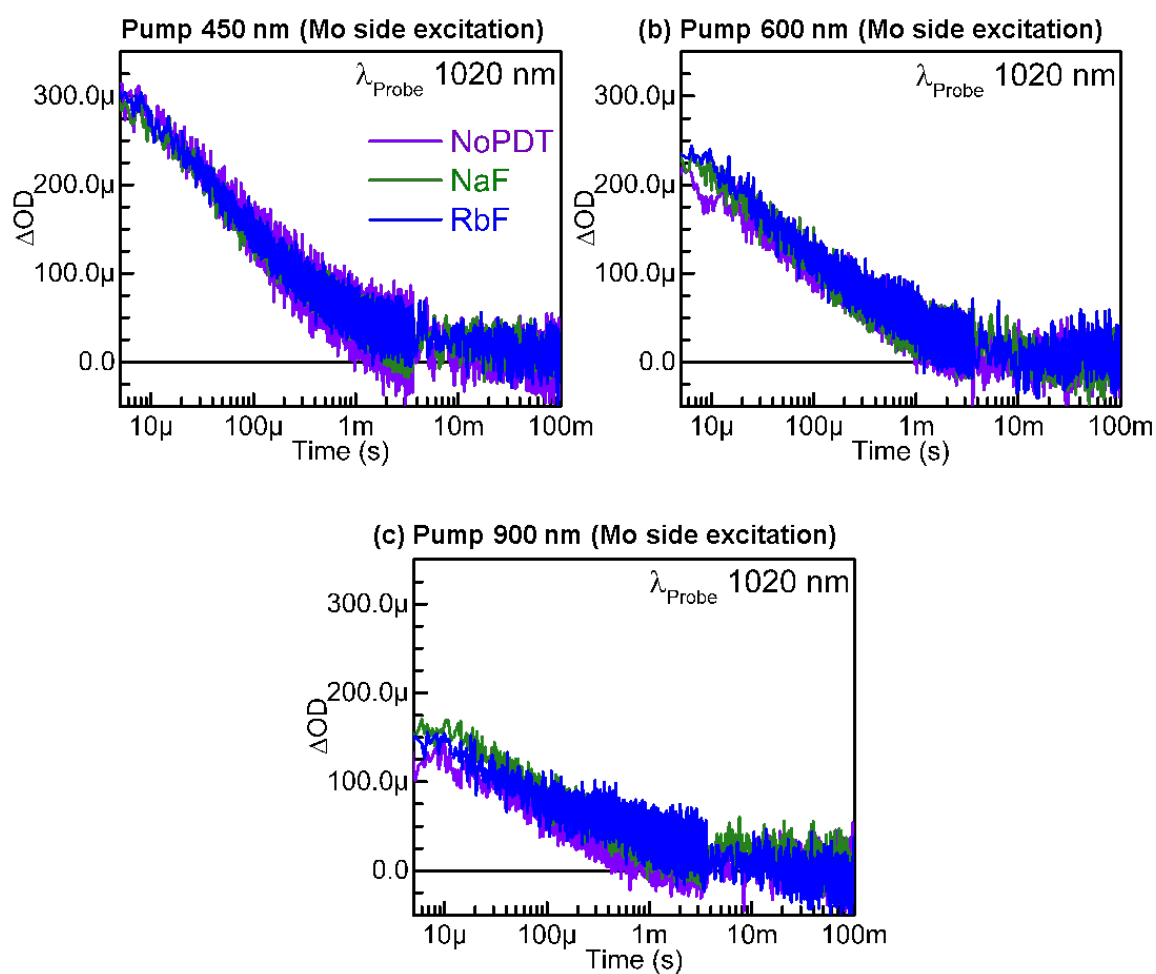


Figure C.7: Microsecond - second transient absorption kinetics probed at 1020nm from peeled-off Mo side following (a) 450 nm, (b) 600 nm, and (c) 900 nm laser light excitation on No PDT (purple line), NaF (green line) , RbF+NaF (blue line) samples with $9E14$ photons/cm² input.

Appendix D

Permissions summary for third party copyright works

Page No.	Type of work:	Name of work	Source of work	Copyright holder and contact	permission requested on	I have permission yes/no	Permission note
30	figure	Figure 1.2 (a) Primary energy demand in the UK from 2008 to 2035 (projection)[6] and (b) electrical generating capacity by main renewable sources between 2000 to 2018	(a) Updated energy and emissions projections: 2018 - GOV.UK (b) Digest of UK Energy Statistics (DUKES) 2019 - GOV.UK	UK Government	07/10/2020	yes	the Open Government Licence v3.0
36	figure	Figure 1.4 Absorption coefficient of c-Si, a-Si, GaAs, CdTe, and ClGSe solar cells.	Stefan G. Haass, Alkali Treatment of Solution Processed Kesterite Solar Cells. PhDthesis, 2017	The author, ETH Zurich	07/10/2020	yes	Creative Commons Attribution-NonCommercial 4.0 International (CC BY-NC 4.0)
37	(a) figure (b) image (website)	Figure 1.5: (a) Solar spectrum: BB 6000 K – 6000 K black body spectrum, AM 0: spectrum calculated based on irradiation outside of the earth's atmosphere. AM 1.5D: spectrum calculated based on sunlight irradiation considering absorption of earth atmosphere only, AM 1.5G: similar as AM 1.5D spectrum but with consideration of light scattering. This figure is adapted with permission from reference [15]. (b) Shockley-Queisser limit (S-Q limit, shown as the black line) as a function of bandgap of current record-efficiency cells. Two grey lines refer to the 75 % and 50 % of S-Q limit. This figure is reproduced from reference [16] and [17] with permissions from the owner and AAAS	(a) Sven Rühle. Tabulated values of the Shockley-Queisser limit for single junction solar cells. Solar Energy, 130:139–147, jun 2016. (b) https://www.lmpv.nl/SQ/ A. Polman, M. Knight, E. G. Gamett, B. Ehrler, and W. C. Sinke, Science 352, 307 (2016). DOI: 10.1126/science.aad4424.	(a) Elsevier (b) AAAS	07/10/2020	yes	(a) License-4923740223672 (b) Permission granted by the author and the publisher
43	figure	Figure 1.10: Schematic of a particle (with energy E) tunneling through a potential barrier V. This figure is reproduced with permission from reference [19].	https://commons.wikimedia.org/w/index.php?curid=11921166		07/10/2020	yes	Creative Commons Attribution-Share Alike 3.0 Unported
46	figure	Figure 1.12 Schematic of zincblende and chalcopyrite structures.	Stefan G. Haass, Alkali Treatment of Solution Processed Kesterite Solar Cells. PhDthesis, 2017	The author, ETH Zurich	07/10/2020	yes	Creative Commons Attribution-NonCommercial 4.0 International (CC BY-NC 4.0)

Table D.1: Permissions summary for third party copyright works - 1.

Page No.	Type of work:	Name of work	Source of work	Copyright holder and contact	permission requested	I have permission yes /no	Permission note
47	figure	Figure 1.13 Comparison of the band alignment (VBM in blue, CBM in red) obtained by slab calculations of CuInSe ₂ and CuGaSe ₂	Beckaert et al. Native point defects in CuIn _{1-x} Ga _x Se ₂ : Hybrid density functional calculations predict the origin of p- and n-type conductivity Physical Chemistry Chemical Physics, 16(40):22299–22308, sep 2014.	ROYAL SOCIETY OF CHEMISTRY	07/10/2020	yes	LICENSE NUMBER:1068459-2
48	figure	Figure 1.14 Illustration of the defect levels (including intrinsic defects and deep defects) in CuInSe ₂ and CuGaSe ₂ system.	Spindler et al. Electronic defects in Cu(In,Ga)Se ₂ : Towards a comprehensive model Physical Review Materials, 3:90302, 2019.	N/A	07/10/2020	yes	Creative Commons Attribution 4.0 International License
55	figure	Figure 1.17:(a) CIGS device structure utilized for EQE simulation model. Thicknesses of layers from top to bottom are (in nm): 250, 60, 70, 1600 and 320. (b) Comparisons of simulation EQE results with the EQE measurement data (shown in dashed lines) and 1-R (shown in solid lines) data. The areas with different color indicate the light absorption by each material. This figure is reproduced with permissions from reference [107].	N. Rezaei, O. Isabella, Z. Vroon, and M. Zeman, "Quenching Mo optical losses in CIGS solar cells by a point contacted dual-layer dielectric spacer: a 3-D optical study," Opt. Express 26, A39-A53 (2018).	OSA Publishing	07/10/2020	yes	Gold Open Access Publishing Journal
56	figure	Figure 1.18 (a) Optical efficiency versus electrical efficiency with respect to SQ limit of different record solar cells. (b) Loss analysis on a 19.7 % CIGS device (blue triangle with light grey square in (a)). The analysis was performed by combining the simulated results of EQE and device performance.	Takuya Kato 2017 Jpn. J. Appl. Phys. 56 04CA02	The Japan Society of Applied Physics	07/10/2020	yes	Permission granted by the publisher by email
57	figure	Figure 1.19 (a) Steady state optical signals (transmittance, reflectance, and absorbance) of a SLG/Epoxy/CIGS (GGI = 0.29, CGI = 0.82, Eg = 1.198 eV) obtained from UV-VIS measurements. The continuous lines and dash lines correspond to CIGS with and without wet Br polishing, respectively. (b) Schematic of the light absorption affected by light scattering, reflection, and light trapping within layers owing to different scale of surface roughness of the CIGS layer.	Carron et al. Refractive indices of layers and optical simulations of Cu(In,Ga)Se ₂ solar cells Science and Technology of Advanced Materials, 19(1):396–410, dec 2018.	National Institute for Materials Science in partnership with Taylor & Francis	07/10/2020	yes	Creative Commons Attribution License

Table D.2: Permissions summary for third party copyright works - 2.

Page No.	Type of work:	Name of work	Source of work	Copyright holder and contact	permission requested	I have permission yes/no	Permission note
58	figure	Figure 1.20 Tauc plot of a CIS thin film (thickness: 1.3 μm). Figures reproduced with permissions from reference [106].	Müller et al. Composition, structure and optical properties of sputtered thin films of CuInSe ₂ . Thin Solid Films, 496(2):364–370, 2006.	Elsevier	07/10/2020	yes	LICENSE NUMBER: 4923720670742
59	figure	Figure 1.21: (a) Room temperature PL spectra of a CIGS cell and an as-deposited CIGS thin film. The GGI ratio is 0.41 for both the cell and the film. Figures reproduced with permissions from reference [109]. (b) Room temperature PL spectra of two CIGS devices (device efficiency of A and B is 15.3% and 13.0%, respectively) of 1.21 bandgap energies. Figures reproduced with permissions from reference [110].	(a) Shirakata et al. Time-resolved photoluminescence in Cu(In,Ga)Se ₂ thin films and solar cells. Thin Solid Films, 515(15 SPEC. ISS.):6151–6154, may 2007 (b) Chantana et al. Investigation of Cu(In,Ga)Se ₂ absorber by time-resolved photoluminescence for improvement of its photovoltaic performance. Solar Energy Materials and Solar Cells, 130:567–572, 2014.	(a) Elsevier (b) Elsevier	07/10/2020	yes	(a) LICENSE NUMBER: 4923720049448 (b) LICENSE NUMBER: 4923720402559
60	figure	Figure 1.22: Time-resolved PL of a polycrystalline CIGS thin film corresponding to 18–19.4% devices. The red coloured line indicates a single exponential fitting of the TRPL data. Figures reproduced with permissions from reference [115].	Metzger et al. Cu (In,Ga) Se ₂ solar cells. Applied Physics Letters, 93(2):022110, jul2008.	AIP Publishing LLC.	07/10/2020	yes	LICENSE NUMBER: 4923710942771
61	figure	Figure 1.23: (a) Transient absorption map of a $E_g = 1.24\text{ eV}$ CIGS thin film. (b) Transient absorption spectra of (a) recorded at 0.2, 1, 10, 100, 500, 1000, 2000 ps. The CIGS thin film is excited following 1000 nm excitation wavelength. Figures reproduced with permissions from reference [121].	Okano et al. Individual identification of free hole electron dynamics in CuIn _{1-x} Ga _x Se ₂ thin films by simultaneous monitoring of two optical transitions. Appl. Phys. Lett., 106(10):181903–113725, 2015.	AIP Publishing LLC.	07/10/2020	yes	LICENSE NUMBER: 4923710541880

Table D.3: Permissions summary for third party copyright works - 3.

Page No.	Type of work	Name of work	Source of work	Copyright holder and contact	permission requested	I have permission yes /no	Permission note
62	figure	Figure 1.24: Schematic of electron dynamics of ClGS following excitation with 400 nm and 800 nm excitation energies. Yellow circles indicate VCu defects and red correspond to charge carrier trapped by defects at the surface and in the bulk, respectively. (b) Normalized ΔT (transmittance) signals as a function of time of the ClGS thin film following 400 nm and 800 nm excitation. Figures reproduced with permissions from reference [124].	Lee et al. Ultrafast Photocarrier Dynamics in 83BBLIOGRAPHY Dynamics at the p-n Junction in Cu(In,Ga)Se ₂ Solar Cell with Various Zn(O,S) Buffer Layers Measured by Optical Pump-Terahertz Probe Spectroscopy. ACS Applied Energy Materials, 1(2):522–530, feb 2018	Copyright © 2018 American Chemical Society	07/10/2020	yes	Permission granted at no charge
63	figure	Figure 1.25: Crystal structure of Sb ₂ Se ₃ . Se and Sb atoms are represented by yellow and brown balls, respectively. This figure is reproduced with permission from reference [125].	Kai Zeng, Ding-Jiang Xue, and Jiang Tang, Antimony selenide thin-film solar cells. Semiconductor Science and Technology, 31(6):063001, jun 2016	IOP Publishing, Ltd	07/10/2020	yes	LICENSE NUMBER: 1068448-1
64	figure	Figure 1.26: (a) Total and partial density of states (DOS), (b) energy band diagram in first Brillouin zone, and (c) the S-Q limit of Sb ₂ Se ₃ . This figure is reproduced with permission from reference [127].	A review of Sb ₂ Se ₃ photovoltaic absorber materials and thin-film solar cells. Solar Energy, 201:227–246, may 2020	Elsevier	07/10/2020	yes	LICENSE NUMBER: 4923691323764
65	figure	Figure 1.27: The device structure of the current-state-of-the-art thin film Sb ₂ Se ₃ solar cell. This figure is reproduced with permission from reference [128].	Wen, X., Chen, C., Lu, S. et al. Vapor transport deposition of antimony selenide thin film solar cells with 7.6% efficiency. Nat Commun 9, 2179 (2018).	Springer Nature	07/10/2020	yes	Creative Commons Attribution 4.0 International License
66	figure	Figure 1.28: Band alignment of a wide range of transparent electrode (TE), window/buffer, hole transport layer (HTL), and back contacts (BCs) in Sb ₂ Se ₃ solar cells. This figure is reproduced with permission from reference [127]	A review of Sb ₂ Se ₃ photovoltaic absorber materials and thin-film solar cells. Solar Energy, 201:227–246, may 2020	Elsevier	07/10/2020	yes	LICENSE NUMBER: 492369006620

Table D.4: Permissions summary for third party copyright works - 4.

Page No.	Type of work:	Name of work	Source of work	Copyright holder and contact	permission requested	I have permission yes /no	Permission note
91	figure	Figure 2.5 Schematic representation of (a) deposition setup and (b) a three-stage deposition process of CIGS thin films.	(a) Avancini et al., Impact of compositional grading and overall Cudefficiency on the near-infrared response in Cu(In,Ga)Se ₂ solar cells.Progress inPhotovoltaics: Research and Applications, 25(3):233–241, mar 2017. (b) Emrico Avancini, Investigation of Elemental Distribution, Microstructure and Optoelectronic Properties of Cu(In,Ga)Se ₂ Thin Films for Solar Cells.PhD thesis, apr2019.	(a) The Authors. Progress in Photovoltaics: Research and Applications published by John Wiley & Sons Ltd (b) The author. ETH Zurich	07/10/2020	yes	(a) Creative Commons Attribution-NonCommercial License (CC BY-NC 4.0) (b) In Copyright - Non-Commercial Use Permitted
93	figure	Figure 2.6 Principles a TOF-SIMS system. Reproduced with permission from reference	http://simslab.rice.edu/surface-analysis-lab/teaching-activities-resources/time-of-flight-secondary-ion-mass-spectrometry/	Website owner	07/10/2020	Yes	Permission granted by the author
93	figure	Figure 2.7 SIMS depth profiles signals from Na, K, Rb, and Cu in the CIGS absorbers treated by NaF PDT, NaF and KF PDT, and NaF and RbF PDT. Reproduced with permission from reference \cite{Avancini2017cm}	Avancini et al., Effects of Rubidium Fluoride and Potassium Fluoride PostdepositionTreatments on Cu(In,Ga)Se ₂ Thin Films and Solar Cell Performance.Chemistry ofMaterials, 29(22):9695–9704, 2017.	Copyright © 2017, American Chemical Society	07/10/2020	Yes	Permission granted at no charge
94	figure	Figure 2.8:Schematic of interactions between primary electrons and the atom and the signals generated due to this interaction.	Electron-matter interaction volume and various types of signal generated. Producedby Ponor - Own work, CC BY-SA 4.0. https://commons.wikimedia.org/w/index.php?curid=93635964 .	The image owner	07/10/2020	Yes	Creative Commons Attribution-Share Alike 4.0 International
94	figure	Figure 2.9 Chirilǎ et al. Highly efficient Cu(In,Ga)Se ₂ solar cells grown on flexiblepolymer films.Nature Materials, 10, 2011.	Chirilǎ, A., Buecheler, S., Pianezzi, F. et al. Highly efficient Cu(In,Ga)Se ₂ solar cells grown on flexible polymer films. Nature Mater 10, 857–861 (2011). https://doi.org/10.1038/nmat3122	Springer Nature	07/10/2020	Yes	License: 4923751004967

Table D.5: Permissions summary for third party copyright works - 5.