Investigation of interfacial engineering and charge dynamics in (Sb₂S₃)-based solar cells

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**Investigation of interfacial engineering and
charge dynamics in (Sb₂S₃)-Based Solar Cells**

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the Degree of Philosophy

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Abstract

Solid-state dye-sensitized solar cell (ssDSCs) is an emerging technology with the potential to surpass first and second generation solar cells. To date, ssDSC has demonstrated efficiency up to 12.3 %. Challenges due to organic dye stability, degradation and leakage of liquid electrolyte posed difficulties in commercialization. Henceforth, efforts were invested to replace dye and liquid electrolyte materials. A promising semiconductor material antimony sulphide (Sb_2S_3) owing to its high absorption coefficient ($\alpha = 1.8 \times 10^5 \text{ cm}^{-1}$) and relatively low band gap (1.7 - 1.9 eV) is used to fabricate ssDSCs. For these types of solar cells, the sensitizer is sandwiched in between the mesoporous TiO_2 layer and hole-transporting material (HTM). The absorber layer thickness ranges from several nm to tens of nanometers, also known as extremely thin absorber (ETA) solar cells.

Antimony sulphide is synthesized by a facile low cost chemical bath deposition (CBD) method. For device fabrication, different strategies were pursued to evaluate antimony sulphide layer in the device. The photo-anode, control of recombination through interfacial layers such as $\text{In}(\text{OH})_x\text{S}_y$, surface modification and different hole-transporting materials were studied to investigate and enhance photovoltaic performance in devices. Studies on different sized TiO_2 nanoparticles allowed a better understanding of the growth mechanism of chemical bath deposition. Although smaller nanoparticle size provides a much larger effective surface area for sensitizer attachment, the smaller pore size leads to an over-aggregation of Sb_2S_3 particles on the surface pores. An optimum nanoparticle size of $>100 \text{ nm}$ was established and reported to exhibit light scattering effect, achieving an efficiency of 2.3 % after post treatment.

The photo-physical behavior of the annealed prepared by atomic layer deposition (ALD) Sb_2S_3 was studied by transient absorption spectroscopy (TAS). Crystallized Sb_2S_3 domains give

rise to strong non-degenerate two-photon absorption and slower hot charge carrier cooling (~ 17 ps). The crystallized domains also slow down the charge carrier recombination from 7.5 ns to 16.7 ns. The increased light absorption, slower hot charge carrier cooling and charge carrier recombination suggest that the annealed Sb_2S_3 is more suitable for light harvesting application than the as-deposited. The findings suggest that the significance of tuning the morphology of this material system to enhance its photovoltaic performance.

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List of Abbreviations

DSC	Dye-sensitized solar cells
k_B	Boltzmann's constant, $k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$
q	Electronic charge, $q = 1.60 \times 10^{-19} \text{ Coulomb}$
FTO	Fluorine-doped Tin Oxide
HOMO	Highest occupied molecular orbital
HTM/HTL	Hole-transporting material/Hole-transporting layer
IPCE	Incident photon-to-current conversion efficiency
$J-V$	Current density – voltage
LiTFSI	$\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$
LUMO	Lowest unoccupied molecular orbital
P3HT	Poly(3-hexylthiophene)
PCE	Power conversion efficiency
IPCE	Incident-to-photon conversion efficiency
EQE	External quantum efficiency
CBD	Chemical bath deposition
PEDOT	Poly(3,4-ethylenedioxythiophene)
Spiro-OMeTAD	2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine) 9,9'-spirobifluorene
SSSCs	Semiconductor-sensitized solar cells
<i>t</i> -BP	4- <i>tert</i> -butylpyridine
TCO	Transparent conducting oxide
UV-Vis	Ultraviolet-visible
FF	Fill factor
J_{sc}	Short-circuit current density
V_{oc}	Open-circuit voltage
η	Power conversion efficiency

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Chapter 1

Introduction

1.1 Background and Motivation

The first solar cell was introduced and built by Charles Fritts in 1883 [1] with a power conversion efficiency (PCE) of ~1 %. Since then, solar cells have evolved into three generations. The first generation solar cells are the single crystal silicon based cells with high power conversion efficiency (PCE) and they remained as the dominant technology in the commercial production of solar cells, amorphous-Si (a-Si), constituting over 86 % of solar cell market. The motivation for development of the second and third generation solar cells is to manufacture solar cells with lower fabrication and labour costs. The most successful second generation thin film solar cells are the copper indium gallium selenide (CIGS) and cadmium telluride (CdTe) cells[2]. Third generation solar cells such as the solid-state dye-sensitized solar cells (ssDSCs) and the organic photovoltaic are driven by the low cost and properties such as environmental friendliness and recyclability.

To date, liquid-based dye sensitized solar cells (l-DSCs) have attained efficiencies exceeding 12.3 % [3] while its counterparts, the solid electrolyte based-ssDSCs achieved 5.1 % using a Ruthenium-based dye.[4] Studies in the performance, reliability and other intrinsic factors like outdoor testing, temperature cycling and humidity are in progress. In a recent

review, it was reported that ssDSCs modules have shown promising results with output efficiency of 8 % has been passed for outdoor testing. Furthermore, based on European climate environmental condition, the life-cycle depicts that energy payback time for ssDSCs is estimated to be approximately less than one year whereas the silicon solar cells counterparts shows a higher energy payback time of longer than 3 years [5].

Figure 1.1 A schematic figure of the progress of the different categories of solar cells. [5]

Figure 1.1 shows the progress of the different category of solar cells and the efficiency progress which has increased with the ssDSCs. In contrast to ssDSCs, solution processed inorganic solar cells such as the copper indium gallium solar cells (CIGS) [6], copper zinc tin sulphide [7] (CZTS) and colloidal quantum dot solar cells have also been introduced and reviewed in the last decade. The youngest technology, colloidal quantum dot solar cells, demonstrates a potential development in cell device performance as well as the possibility in studies towards multi-exciton generation[5].

Dye-sensitized solar cells, also known as Graetzel cells, work on the principle of sensitization, which involves the decoupling of the light absorption and charge transport within the solar cell. These cells are attractive due to its low cost, good manufacturability and impressive efficiencies up to 12.3 %. There exist some potential problems such as (i) dye degradation and (ii) electrolyte leakage issues. Thus, much extensive work has been done on the solid-state equivalents of the sensitized cell. This involved the replacement of the iodine/iodide redox with inorganic and organic hole-transporting materials like copper (I) thiocyanate (CuSCN)[8], poly(3-hexylthiophene) (P3HT)[9], poly(3,4-ethylenedioxythiophene) PEDOT [10], Spiro-OMeTAD [11] and other novel p-type semiconducting materials [12]. It is highlighted that the interfacial recombination [13, 14] and the reduced thickness attributed from the difficulty in filling the pores of TiO₂ network [15-17] are some examples to the limitations of solar cell, which keeps the efficiency low.

This study aimed at exploring Sb₂S₃-sensitized solar cells where abundant semiconductor material (e.g sulphides) functions as absorbers due to their high absorption coefficient, high light harvesting capability and chemical stability in place of dye. Other semiconductor materials such as sulphides, selenides and tellurides have been reviewed. This includes lead sulphides (PbS) [18], cadmium sulphide (CdS) [19], cadmium selenide (CdSe) [20-23], cadmium telluride (CdTe) [24], indium selenide (In₂S₃) [25], copper sulphide (Cu_{2-x}S) [26] and CuInS₂ [27]. In the last two decades, antimony sulphide with a band gap of 1.7 eV - 1.9 eV [28] and high absorption coefficient of $1.8 \times 10^5 \text{ cm}^{-1}$ at 450 nm has attracted much attention by Moon et al. [29] and Chang et al. [30] as sensitizers in ssDSCs where antimony sulphide is prepared via conceptually simple chemical bath deposition. [31] These reports have shown promising potential capability

of employing Sb_2S_3 as a replacement for dye as a light harvesting material. Interestingly, the solar cell performance of semiconductor sensitized solar cells is particularly sensitive to the particle size of underlying TiO_2 platform [29]. There is also a lack of understanding on the interfacial engineering and charge dynamics in the single and hetero-junctions. Figure 1.2 shows the schematic of semiconductor-sensitized solar cells and the various main components of the solid-state device.

Figure 1.2 Schematic diagram illustrating (a) the individual key aspects of an organic sensitized nanoporous solar cell. (b) Molecular structure of P3HT, poly (3-hexylthiophene-2, 5-diyl).

1.2 Objectives

The project focused on semiconductor-sensitized nanoporous solar cells (SSSC) where the solar absorbing materials is antimony sulphide (Sb_2S_3) instead of dye. One of the objectives of the project is to understand the interfacial engineering and charge dynamics for semiconductor sensitized solar cells, with the aim to realize solar cells which are robust, low cost and highly

efficient for future solar panel market. In a typical solar cell, the solar cell architecture consists of many different layers, as shown in Figure 1.2.

Based on the above mentioned motivations, the project has been designed to

1. Investigate the physical properties of Sb_2S_3 as an absorber material for ETA cell
  - Develop the experimental set up, processing and deposition parameters for deposition of absorber thin films.
  - Study the effect of annealing of absorber material.
  - Evaluate the physical properties (morphological, structural, compositional, optical) of inorganic thin films through various material characterization techniques.
2. Investigate the influence of morphology in a solar cell configuration.
  - Develop the methodologies (deposition times, crystallite size) for successful incorporation of absorber material into a solar cell device configuration and study the devices PCE and IPCE.
  - Control charge recombination through interfacial buffer layers.
  - Develop the methodologies for surface modification of antimony sulphide layer to improve power conversion efficiency (PCE) and solar cell incident to photon conversion efficiency (IPCE).
  - Evaluate the effect of underlying photo-anode platform towards device performance.

3. Conduct fundamental studies on the charge dynamics of absorber material by laser spectroscopic methods
  - Evaluate the photo-physical and the charge dynamics of Sb_2S_3 films.

1.3 Thesis Outline

The content of the thesis is arranged and summarized in the following chapters:

Chapter one provides a brief introduction on the background, motivation as well as the objectives and lastly scope of the project. **Chapter two** provides the literature review on third generation solar cells. The various components and the mechanism of the conventional ssDSC are highlighted. **Chapter three** outlines the experimental techniques, procedures and materials used in chemical bath deposition of antimony sulphide and solar cell device fabrication. Results and discussions will be presented in **Chapter four** starts with the growth and characterization of Sb_2S_3 films and the successful incorporation of Sb_2S_3 as an absorber in solar cells. This section also presents work on the study of nanoparticle particle size effect of photo-anode and controlling recombination through interfacial barriers such as $\text{In}(\text{OH})\text{S}$ and antimony oxide. **Chapter five** presents the photo-physical behavior of Sb_2S_3 films. The conclusions are summarized in chapter six. **Chapter seven** summarizes the suggested recommendations and future work for the thesis.

1.4 Scope

The scope of the project focused on the study of semiconductor-sensitized solar cells (SSSC) where the sensitizer material is antimony sulphide (Sb_2S_3). Growth technique is limited to

chemical bath deposition and atomic layer deposition. For device fabrication, the counter electrode of the device is confined to gold contact. For transient absorption spectroscopy studies, the focus was on sample preparation, planning of the experiments and data analysis. In addition, special thanks to Dr Stevin S Pramana for the TEM image and Dr Xing Guichuan for the TAS measurements.

1.5 Contribution of Thesis

The original contributions arising from my PhD work are listed as follows:

- (i) Successfully integrated Sb_2S_3 as the absorber material in a solar cell, obtained an efficiency of 2.3 % after post-treatment.
- (ii) Investigated the photo-anode structure effect in the solar cell, and understand the effect of chemical bath deposition and its mechanism in Sb_2S_3 solar cells.
- (iii) Controlled recombination through interfacial barrier layer such as $\text{In}(\text{OH})_x\text{S}_y$, which showed improvement in photovoltaic performance (in both J_{sc} and V_{oc} parameters)
- (iv) Introduced a surface modification on antimony sulphide which improved photovoltaic performance.
- (v) Analyzed the photo-physical behavior in antimony sulphide behavior of atomic layer deposition (ALD) Sb_2S_3 thin films.
- (vi) Findings showed that crystallized Sb_2S_3 (prepared by ALD method) domains give rise to a stronger non-degenerate two-photon absorption, slower hot charge carrier cooling (~ 17 ps). The crystallized domains also slow down the charge carrier recombination from 7.5 ns to 16.7 ns. The increased light absorption, slower hot charge carrier

cooling and charge carrier recombination suggest that the annealed Sb_2S_3 is more suitable for light-harvesting application than the as-deposited.

Chapter 2

Literature Review

2.0 Third generation Solar Cells

The third generation solar cells consists of polymer solar cells, dye sensitized solar cells, quantum dot cells and tandem/multi-junction cells.[32-35] Dye sensitized solar cells provide low cost, cheap and simple devices useful for commercial applications. The introduction to the concept, mechanism and the methodology of ssDSCs are described below. Table 1 provides the performance of photovoltaic and photo-electrochemical solar cells as listed.

Table 2.1 Performance of the photovoltaic and photo-electrochemical solar cells. [32]

Performance of photovoltaic and photoelectrochemical solar cells			
Type of cell	Efficiency Cell	(%) * Module	Research and technology needs
Crystalline silicon	24	10-15	Higher production yields, lowering of cost and energy content
Multi-crystalline silicon	18	9-12	Lower manufacturing cost and complexity
Amorphous silicon	13	7	Lower production costs, increase production volume and stability
CuInSe ₂	19	12	Replace indium (too expensive and limited supply), replace CdS window layer, scale up production
Dye-Sensitized nanostructured materials	10-11	7	Improve efficiency and high-temperature stability, scale up production
Bipolar AlGaAs/Si photoelectrochemical cells	19-20	--	Reduce materials cost, scale up
Organic solar cells	2-3	--	Improve stability and efficiency

*Efficiency defined as conversion efficiency from solar to electric power

Chapter 2: Literature Review

2.1 Operating mechanism of a solid-state DSC (ssDSC)

Dye sensitized solar cells (DSCs) were first introduced by O'Regan and Graetzel in 1991, [36]. The major breakthrough was when a nanoporous electrode was used instead of a flat electrode. This allowed for a higher absorption of dye loading and light harvesting efficiency over flat electrodes. The promising device performance from these electrochemical solar cells (dye sensitized solar cells) utilized a sponge-like mesoporous titanium dioxide film fabricated from sintered nanoparticles. The size of nanoparticles is about 18 to 20 nm with a film thickness of 2 to 3 μm . TiO_2 coated films are immersed into the dye solution for a period of time and covered with a monolayer of dye material. The photo-anode is then infiltrated with an electrolyte (e.g. organic solvent mixed with iodine/iodide redox couple) sandwiched with a counter electrode consisting of a platinum coated transparent conducting oxide (TCO).

Figure 2.1 Schematic figure of the operating mechanism of a liquid-based dye-sensitized solar cell. [37]

Chapter 2: Literature Review

Figure 2.1 shows the schematic of the operation mechanism of a liquid-state DSC. The liquid-state DSC is composed of a nanoporous TiO_2 electrode on FTO, an electrolyte containing an iodine/iodide redox couple to completely fill the pores of the nanopores structure and sandwiched with another platinum counter electrode (cathode). Under light illumination, the dyes are excited and generate an electron, which is then rapidly injected into the conduction band of the n-type titanium dioxide. Meanwhile, the electrons are transferred to the platinum electrode. Afterwards, the dye cation is reduced back to their ground state after receiving the electrons from the electrode. Through this cycle, the device is able to generate current without any chemical transformation as long as the light device is illuminated. Thus, light is converted to electrical energy. The V_{oc} generated corresponds to the difference between the Fermi level of the electron and the redox potential of electrolyte [37]. Figure 2.2 shows the structure of an ssDSCs and its electron transfer processes.

Figure 2.2 Electron transfer of solid-state dye-sensitized solar cell. (ssDSC) [38]

Chapter 2: Literature Review

The primary processes in photocurrent generation remains largely the same as compared to liquid state dye-sensitized solar cell. In an ssDSCs, the iodine/iodide electrolyte is replaced by hole-transporting materials. The mechanism can be summarized in the following processes:

Step 1: Electron-hole pair generation of sensitizer (e.g Sb_2S_3 or dye)

Step 2: Electron injection into n-type titanium dioxide

Step 3: Dye regeneration. For the regeneration processes, the hole transfer takes place directly from the sensitizer to the hole-transporting material (HTM) and hole is transported to the counter electrode by hopping mechanism within the polymeric HTM. [39, 40]

2.2 Key components in a cell

The key components in an ssDSCs will be discussed in the following sections. The key aspects of the solar cell consists of (i) photo-anode consisting of a porous TiO_2 layer coated on conductor substrate FTO (ii) Sensitizer layer (iii) an electrolyte and (iv) a counter electrode.

a.Photo-anode

An ideal photo-anode is fabricated from a nanoporous semiconducting metal oxide layer which should possess high specific surface area for absorption of dye and a good interconnection between the nanoparticles after sintering process. The study of photo-anode structure is crucial as light harvesting, electron injection and electron collection are processes related to the photo-anode, which also includes undesirable recombination processes which would be discussed at the later section.

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b.Blocking layer

A thin blocking layer is coated at the interface between the HTM and FTO glass. The preparation of thin blocking layer are done by spray-pyrolysis[41], sol gel[42], dip coating[43] and spin-coating[44]. This is to prevent the HTM from penetrating beyond the nanoporous electrode, forming an ohmic contact with the FTO glass. The direct contact between the two materials could lead to short circuiting of cell and/or loss of current due to recombination on the FTO glass. The optimum blocking layer thickness of solar cells is about 80-100 nm. Reports have shown that too thick TiO_2 blocking layer can increase the series resistance and thus lower the efficiency of solar cells.[45]

2.3 Mesoporous TiO_2 film

The mesoporous TiO_2 film may be prepared by different fabrication techniques such as screen-printing[46], spin-coating or doctor-blading[47]. Higher degree of absorber materials can be loaded onto the TiO_2 due to the sponge like structure in contrast to flat electrodes. Generally, for I-DSC, a thick mesoporous TiO_2 layer consisting of ~10 to 20 μm thickness is employed whereas in ssDSCs, the thickness of mesoporous TiO_2 can only be about 2 to 3 μm . The TiO_2 nanoparticles are sintered at 500 $^{\circ}\text{C}$ which undergo necking during the process of sintering without growth of the crystalline size and the necking between the TiO_2 and FTO is not perfect. Upon illumination, excited electrons in the adsorbed dye are then injected into the TiO_2 conduction band. The reduced TiO_2 thickness in ssDSC is limited by the difficulty in infiltrating HTM into porous structure, resulting in lower device photovoltaic performance due to lesser amount of sensitizer loaded and less pores infiltrated.[12, 17]

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2.4 Sensitizer in General

The role of sensitizer is to absorb light and convert it into photocurrent. This determines the light harvesting efficiency and overall power conversion efficiency of the cell. An ideal sensitizer should absorb over a wide range of the solar spectrum and exhibit high molar extinction coefficient so as to absorb more light with a thinner TiO_2 film. Inorganic sensitizers display excellent optical properties and light harvesting property[48], high extinction coefficient[49] and large intrinsic dipole moment [50]. Furthermore, there is evidence of quantum confinement in the absorbers, leading to a multi exciton phenomenon[21].

2.5 Sb_2S_3 as absorber material

Figure 2.3 Molecular structure of antimony sulphide (Sb_2S_3) and its unit cell structure. [51, 52]

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Antimony sulphide (also known as antimonite) is of orthorhombic space group with a Pbnm space group. The unit cell parameters are as described as $a = 11.229 \text{ \AA}$, $b = 11.31 \text{ \AA}$, $c = 3.8389 \text{ \AA}$ with a coordination number of 4. The Sb (III) centers are packed such that they are pyramidal and three-coordinate, and they are link by the sulphide ions as shown in figure above. The molecular weight is 339.70 g/mol and it has attracted much attention due to its high absorption coefficient of $7.5 \times 10^4 \text{ cm}^{-1}$. Crystalline antimony sulphide (Sb_2S_3 , stibnite phase) is one of the p-type semiconductor with a narrow band gap of $1.7 - 1.9 \text{ eV}$. It has been reported as a sensitizer in solar cells [29] with compatible energy levels to the other components.

Chemical bath deposition, otherwise known as solution deposition began as early as 140 years old, has been used to deposit films of metal sulfides, selenides and oxides, together with some miscellaneous compounds [31]. Sulphide layers were first obtained from chemical bath deposition with thiosulfate solution of copper, lead and antimony salt [53] dated back to 1869. The formations of the crystals are often very small and films deposited are nano-crystalline. Due to the small nano-crystalline particles formed, it is a useful technique to fill the nanoporous structure of the TiO_2 electrode in ssDSCs. Figure 2.4 shows the schematic of the direct and indirect band gap representations where antimony sulphide is an indirect band gap material. In semiconductors, the band gap can be determined from the equation $(h\nu\alpha)$ proportional to $(h\nu - E_g)^{1/n}$ where $n = 2, 2/3, 1/2$ for respectively direct allowed, allowed indirect and forbidden direct transitions.

Figure 2.4 Schematic of direct band gap and indirect band gap transition.[54]

2.6 Mechanism of chemical bath deposition

Chemical bath deposition (CBD) can either be deposited via a cluster mechanism or ion-by-ion mechanism, with cluster mechanism forming smaller crystal size[55]. Nucleation is generally slower in ion-by-ion reactions and growth often occurs only at a solid surface and not in the bulk of solution. The size quantization could be exhibited should the crystal size be small enough. In chemical bath deposition, it generally refers to depositions from solution where the required deposits are both chemically generated and deposited in the same bath[31]. The film growth in CBD is highly dependent on parameters such as the temperature, concentration and pH of the chemical bath. These parameters will determine the growth kinetics as well as thermodynamic stability of the small crystals. The formation of antimony sulphide in chemical bath deposition containing SbCl_3 and sodium thiosulphate was described.

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In addition, it is also pointed out from Froment and Lincot[55] that the lateral homogeneity of CBD film tends to be good, even if surface is irregular since growth is often under kinetic control via surface reactions. In metal sulphide growth, the precursors used are dependent on the medium of CBD. While thiourea is probably the most commonly used sulfur precursor, thioacetamide and thiosulfate are also used. Thiourea is usually used in alkaline solutions while thioacetamide and thiosulfate are used in more acidic solutions and that thioacetamide is commonly used for ions which hydrolyze readily in acidic solutions, e.g. In^{3+} .

2.7 Hole-Transporting Material (HTM)

There are several criteria for selection of a good hole-transporting material. For instance, one of the requirements is the high hole mobility for efficient charge transport. Inorganic HTM, such as CuI [56-58] and CuSCN [59, 60], generally have good conductivity over 10^{-2} S/cm, facilitating hole conducting ability. Successful reports using CuSCN HTM with semiconductor sensitizers by Hodes [31] has been demonstrated. The other important criteria of HTM refer to the energy level alignment in the solar cell. The energy level alignment of the HTM is also critical in ensuring charge transfer process. The requirements of HTM have been reported by several reviews. It is suggested that the HOMO of the HTM has to be slightly higher than the ground state of the sensitizer to facilitate electron transfer. Promising HTM should fulfill good wetting properties of the sensitizer-coated TiO_2 , allowing better penetration/pore filling into the nanoporous structure. Wetting of HTM, often characterized by dynamic contact angle

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measurements, is also an important criteria. Lastly, the HTM should be transparent in the visible light region where the sensitizer absorbs light. The figure below shows the molecular structure of various HTM, Spiro-OMeTAD, Poly(3,4-ethylenedioxythiophene)PEDOT and poly(3hexylthiophene-2,5-diyl), P3HT, poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT: PSS).

Figure 2.5 Molecular structures of various HTMs. [40]

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2.8 Limitations in ssDSC

Despite the continuous search for better materials and process fabrication techniques, efficiency of ssDSCs remains lower than the l-DSC. As a result, it is crucial to understand charge transfer dynamics in ssDSCs to find the limiting factors. Several key aspects which hindered its performance have been proposed: (i) incomplete pore-filling into the pores of nanocrystalline TiO₂ film [61, 62] (ii) interfacial charge recombination. It was reported by Feng and co-authors [63] that the improvement in efficiency is improved by enlargement of the effective interface between the TiO₂ and the hole conductor.

Research efforts started with Kroeze et al.[60] showed that HTM hole mobility is not a major determining factor for solar cell performance but rather best solar cell performance attributed from solar cell corresponded with best HTM penetration. Incomplete pore filling is a major limitation for device performance, which drives the development of in situ deposition of HTM in comparison with the conventional method (i.e. spin-coating). Several techniques were engaged to compare the pore filling. Schmidt Mende et al.[17] have illustrated the penetration of organic HTM through SEM cross-section analysis and results showed that devices with good pore filling demonstrate better solar cell performance as compared to higher hole mobility organic HTM. X-Ray photon spectroscopy (XPS) [61] was also used to probe the concentration of HTM versus depth.

Organic HTM displayed low crystallinity and ease of application. By far, 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)9,9'-spirobifluorene (Spiro-OMeTAD) is one of the most favorable HTM with mobility of order of 10^{-4} cm²/Vs and glass transition temperature of

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120 °C. Crystallization is undesirable as it may affect the formation of good contact between the HTM and the mesoporous TiO_2 layer. The first reported solid-state ssDSCs with organic HTM was made by Bach et al. in 1998 [11] with the use of ruthenium dye and TiO_2 as photo-anode. Further development in hole-transporting materials involving the addition of additives[59], $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ and 4-*tert*-butylpyridine, increased the J_{sc} and V_{oc} , leading to an increase in efficiency. Due to its low hole mobility and high fabrication cost of Spiro-OMeTAD, other alternative conjugated polymers such as poly(3-hexylthiophene) (P3HT) and poly(3,4-ethylenedioxythiophene) (PEDOT) [60] have been intensively investigated. Figure 2.6 shows the schematic energy band-diagram of a Sb_2S_3 -sensitized solar cell whereby the HOMO level of P3HT is of 5.2 eV, a close match with work function of gold contact (5.1 eV). In addition to the selection of hole-transport materials, controlled recombination also enhanced output efficiency. An $\text{In}(\text{OH})_x\text{S}_y$, formed from a thin CBD coating, with a LUMO level 500 mV higher than TiO_2 is expected to lead to improved current density, J_{sc} . The loss mechanism of ssDSC is further highlighted in next section.

Figure 2.6: Energy band-diagram of a Sb_2S_3 -sensitized solar cells.

2.9 Interfacial charge recombination

The study of interfacial charge recombination [64] is an important loss mechanism in ssDSC, affecting parameters such as V_{oc} and J_{sc} . The interfacial charge recombination could affect photovoltaic parameters both V_{oc} by decreasing the concentration of electrons in the conduction band of semiconductor and J_{sc} by decreasing the forward injection current. Figure 2.7 shows the redox processes involved in the conversion of light to electric power by dye sensitized solar cells. There are two possible recombination pathways which could be categorized as direct recombination or indirect recombination. Direct recombination involved the reduction of the oxidized absorber by an electron from TiO_2 before the absorber compound is regenerated by hole conductor whereas indirect recombination is due to recombination of an electron from TiO_2 with a hole in the hole conductor. The insertion of interfacial buffer layer in between TiO_2 /sensitizer interface is of interest by (i) exploiting the kinetic redundancy of charge injection relative to the decay of excited state to the ground (ii) focusing on the kinetic redundancy of the hole regeneration system in competition with indirect recombination.

Figure 2.7 Redox processes involving the conversion of light to electric power by dye-sensitized solar cells. [65]

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a. Core shell structures

One of the approaches in reducing recombination is the pioneering work done by Zaban et al. [66] on the formation of core-shell structures. The surface modification is done on the nanoporous TiO_2 electrodes by dip-coating of electrodes with selected materials. For instance, the formation of $\text{TiO}_2/\text{Nb}_2\text{O}_5$ electrode has led to the improvement in both J_{sc} and V_{oc} where Nb_2O_5 shell is 100 mV higher than TiO_2 . The formation of core-shell structures as shown in Figure 2.8 (a) and Figure 2.8 (b) illustrates the schematic band energy diagrams. Different materials such as Nb_2O_5 [67], Al_2O_3 , SrTiO_3 [68] and SiO_2 have been demonstrated. Shell materials such as the coating of Nb_2O_5 have led to improvement in cell performance for both J_{sc} and V_{oc} .

Figure 2.8 (a) Schematic diagram of a buffer layer (shell) coated onto the TiO_2 nanoparticle.

(core) (b) Schematic diagram of band for core-shell structures. [69]

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b. TiCl_4 treatment

The TiO_2 electrode is usually coated with a surface treatment (i.e. TiCl_4 treatment) employed during ssDSC fabrication. This treatment helps to enhance roughness and improve the necking of the nano- TiO_2 particles during the sintering process. Figure 2.9 shows a typical cross-sectional view of the electrode and the interface in ssDSC. It has been demonstrated that TiCl_4 treatment helps to improve the electron injection and hence improved the J_{sc} . [70] With the treatment, it can also lead to improved dye loading and eventually with more dye adsorption, hence accounting for increased J_{sc} in comparison to without the treatment (corresponding to cell efficiencies). [65, 71]

Figure 2.9 Cross-sectional view of a TiO_2 electrode and the interface of ssDSC. [64]

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c. Indium hydroxyl sulphide In(OH)S

$\text{In(OH)}_x\text{S}_y$ has been used as a cadmium free buffer layer in copper indium selenide (CIS) solar cells and it is obtaining good J - V characteristics.[72, 73] Buffer layer functions like insulating spacers, is used to increase the spatial distance between charges and henceforth, reducing or retarding recombination. This thin film is formed from acidic bath (pH 2.2 to 2.5) using indium (III) chloride, thioacetamide and acetic acid where the band gap of material is reported in the range of 2 eV to 3.7 eV. A well-defined buffer layer should provide coverage of the TiO_2 mesoporous layer homogenously while not blocking the pores of TiO_2 layer.[74] Furthermore, the buffer layer should be thin enough for electrons to tunnel through. (~1 to 2 nm)

By incorporating a buffer material which has a higher conduction band edge and a higher band gap than the TiO_2 , the buffer layer can help to suppress the recombination of electrons with the oxidized molecules or with the oxidized hole-transporting material. With the retardation of recombination, the electron concentration will increase, causing quasi-Fermi level of TiO_2 nanoparticles to increase. As a result, V_{oc} will increase due to the increased offset between the quasi-Fermi level of TiO_2 and HTM hole-transporting material. Figure 2.10 shows a detailed schematic flow of the coating process of buffer material, In(OH)S . The chemical reaction is formed from a bath reaction with the reactants indium chloride (InCl_3) and thioacetamide (CH_3CSNH_2) where the band gap of byproducts produced such as In(OH)_3 and In_2S_3 are pH dependent.

Figure 2.10 Schematic flow of the coating process of indium hydroxyl sulphide by bath deposition where band gap is pH independent. [75]

Figure 2.11 shows the schematic diagram of band-structure including interfacial charge-transfer processes occurring at the TiO_2 /sensitizer/hole-transporting layer. Here, Al_2O_3 is used as a large band gap barrier material to retard recombination. The element mapping in Figure 2.11 (b) shows conformal coating of Al_2O_3 on TiO_2 nanoparticles. The elemental mapping of Al (green) and Ti (in red) is shown and dispersed uniformly.

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Figure 2.11 (a) Schematic diagram of band structure including interfacial charge-transfer processes occurring at TiO₂/sensitizer/hole-transporting layer interface in dye-sensitized solar cells. (b) Elemental mapping of Al₂O₃ coating on TiO₂ nanoparticles. [76]

The advantages of atomic layer deposited films include high deposition conformity on nanoporous surface and high resolution film thickness (up to ~0.1 nm for 1 cycle of Al₂O₃). [77, 78] The ALD of Al₂O₃ is well established. For number of cycles less than 10, non-continuous

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film with an isolated island structure is expected to be formed on TiO_2 surface. For more than 10 cycles, continuous films are likely to be formed to give a core-shell structure. [76]

Several metal oxide materials have been studied as potential barrier materials such as Al_2O_3 . An approximately 10 % to 35 % increase in PCE for solar cells using insulating Al_2O_3 [66, 79, 80] over-coating in ssDSCs was introduced by Zaban et al. for ssDSC. Furthermore, band gap and electron affinity of the monolayer are highly tunable by varying the number of cycles[81]. Through ALD, the thickness and recombination barrier height could be finely tuned to reduce series resistance and obtain optimum work function difference. Both V_{oc} and J_{sc} are expected to increase.

2.10 Charge Dynamics

Transient absorption spectroscopy [82, 83] is the measurement of the photo-physical and photochemical reactions upon light absorption. The time scale of measurement of energy transfer process is usually in the scale of picoseconds (usually less than 100 ps) or femtoseconds. In this technique, a fraction of the molecules is excited, promoted by means of a pump or other excitation pulse, and a weak pulse is sent with a delay time with respect to the pump. (refer to Figure 3.5). It is noted that the difference in transmittance is measured (i.e ΔT) or otherwise $(T' - T_0)/T_0$). By changing the time delay, the profiles can be measured as a function of ΔT (λ , Γ). As such, from the ΔT (λ , Γ), the various dynamic fast processes (i.e. auger recombination, charge carrier cooling, etc) that could have occurred during the photo excitation could be determined. Transient absorption spectroscopy (TAS) is reported to be widely used to investigate charge

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carrier recombination, separation and recombination in a single or hetero-junctions. [84, 85] For instance, in the transient absorption profiles (ΔA) on CdS quantum dots done by Prashant V. Kamat et al. [86], carrier cooling was monitored and calculated through the rise time of the transient bleach, where the maximum bleach corresponds with the maximum population of electrons at the conduction band edge. The linear best fit plot for the rise gives a slot which is estimated and defined as carrier cooling rates (in picoseconds/eV). [87, 88] Figure 2.12 shows the delay between the pump and probe pulses and the intensity of the transmitted pulse is measured as a function of the delay. This is an example of data acquired via transient absorption technique, showing photo-induced transmission bleach with ultrafast rise and partial signal decay, ΔT (Γ).

(a)

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(b)

(c)

Figure 2.12 (a) Schematic of a typical pump-probe experiment. [89](b) Energy band diagram of the various types of recombination. (c) Auger effect in an atom. [90]

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Recombination can also be categorized as (i) unavoidable recombination process which are due to the essential physical process in the intrinsic material itself and (ii) avoidable processes which are due to the impurities or imperfection of the material crystal.[83] Figure 2.12 (b) shows the various recombination which can be in the form of (i) band-to band transition (ii) trap-assisted recombination [87] (iii) Auger recombination[91, 92]. The most important would be the spontaneous band to band recombination, otherwise known as the radiative recombination. For trap-assisted recombination, this is attributed to relaxation by trap states due to impurities or defects which are present in the crystal structure of semiconductor. In bulk semiconductor, Auger recombination occurs when electron hole pair recombines and release its energy to a third particle which can either be a hole or electron. This phenomenon is a reverse of a rare generation process, and often, the significant heating of the e-h system during Auger recombination can dramatically change energy relaxation dynamics. [93] Usually, Auger recombination is important where carrier concentration is very high and whereby carrier-carrier interactions are strong. As the Auger process involves three particles, the rate of Auger recombination can be expressed in the following:

$$R_{\text{Aug}} = Bn^2p \text{ or } Bnp^2$$

Where B refers to the proportionality constant which has strong temperature dependence, n refers to the number of electrons available in conduction band and p refers to the number of electrons in valence band. For an Auger effect, it requires 2 electrons and a hole. Alternatively, it may occur when there are 2 holes and an electron. The first part is electron collision and the second part refers to holes collision. Auger effect occurs in low band gap material, highly doped or at high temperature.

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Similarly, in an atom, the Auger effect is described as a physical process where an inner shell electron is filled and that this process is accompanied by the emission of an electron. In the atom, during the electron collision process, the incident electron (or photon) creates a core hole in the 1s shell. The higher energy electron can fall back to occupy the hole, releasing the energy. The energy which is released can be either in the form of an emitted photon or the energy can be absorbed by another electron (E Auger) in Figure 2.12(c). The kinetic energy of the E Auger is attributed to the difference between the energy of the electron transition with the ionization energy from which the electron shell is ejected. Figure 2.13 depicts a bulk semiconductor which has continuous conduction and valence bands, separated with energy band gap (E_g) and a nanocrystalline semiconductor with its characteristic discrete atomic states and nanocrystalline size dependent band gap. With an increasing quantum dot size, the band gap decreases.

Figure 2.13 Band gap of bulk semiconductor and a nanocrystalline semiconductor.[83, 94]

Chapter 3

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3.1 General device assembly

Figure 3.1 Device schematic of a ssDSC.

3.2 Device Fabrication

Figure 3.1 shows the device schematic of a ssDSC. The device schematic consists of the several layers stacked one after another and the layers are made from different fabrication processes. The first layer: A compact and dense TiO_2 layer with an approximate thickness of 80-100 nm was coated on the surface of FTO glass. (Pilkington, $15 \Omega \text{ sq}^{-1}$). The function of the blocking layer is to prevent short circuiting due to contact between P3HT and FTO. Methodology for preparation of blocking layer: These blocking layers used in the study were prepared by e-beam deposition of titanium and then oxidation in air flow at ambient. Subsequently, a porous TiO_2 layer ($\sim 2 \mu\text{m}$) was screen-printed onto the dense TiO_2 layer from either a home-made titania paste made from MK Nano, 50 nm Anatase TiO_2 or a commercial available TiO_2 paste (Solaronix R/SP) as described. The commercial TiO_2 paste consists of particle size $\sim 100 \text{ nm}$.

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Titanium films prepared by screen-printing were sintered and treated with 20 mM TiCl_4 solution for a period of 12 h in dark conditions at 25 °C. Then the TiO_2 electrodes are rinsed copiously with de-ionized water before sintering under air flow at 500 °C for 30 min. A barrier layer of $\text{In}_x(\text{OH})_y\text{S}_z$ (In-OH-S) was deposited using the procedures[29] reported. 10 ml of 25 mM of InCl_3 , 10 ml of 0.1 M TA and 10 ml of 0.1 M of AcOH were prepared in separate beakers. Substrates were positioned into a staining jar and submerged into a water bath pre-heated at 65 °C together with the 3 precursors prepared above. Precursors and substrates were submerged for about 5 min to reach 65 °C. Precursors were mixed and poured into staining jar and sealed with para-film to prevent moisture change due to water bath. Substrates were soaked in bath for 60 min, rinsed with de-ionized water and subsequently blown dry with nitrogen gas. Sb_2S_3 film was coated onto the $\text{TiO}_2/\text{In}(\text{OH})\text{S}$ substrates using procedures as described by Messina et al. [28] Figure 3.2 shows the structures of molecules used for post-treatment.

Figure 3.2 Schematic structure of (a) decyl-phosphonic acid (DPA) and (b) hexyl-phosphonic acid (HPA). [95]

Synthesis of antimony sulphide films

650 mg of antimony chloride (SbCl_3) initially in 2.5 ml acetone and adding 25 ml of 1M sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) solution and sufficient water to make the volume to 100 ml. Deposition timings of the antimony sulphide chemical bath deposition were varied. Annealing process is done at 330 °C under argon atmosphere for a period of 30 min. In all cases, the

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precursors were allowed to cool till 10 °C before mixing and immersing the substrates. Deposited substrates were rinsed with deionized water and blown dry with nitrogen gas.

Post surface treatment or surface modification of absorber layer

The post-surface treatment or surface modification of absorber layer was introduced in a two-step process. The Sb_2S_3 coated TiO_2 substrates were firstly heated at 200 °C for 30 min and then surface etched with diluted HCl for 30 min. Subsequently, substrates were then surface treated with decyl-phosphonic acid (DPA) for a period of 30 min and rinsed briefly with de-ionized water. Referring to Figure 3.2 (a), the structure of the decyl-phosphonic acid (DPA) consists of a phosphonic acid group for TiO_2 attachment and an alkyl group to provide for the spatial distance. The alkyl group functions as insulating spacers. A shorter alkyl group molecule, otherwise known as hexyl-phosphonic acid is shown in Figure 3.2 (b).

Application of P3HT solution

The P3HT solution (15 mg ml^{-1} in 1, 2-dichlorobenzene) was spin-coated onto the substrates with 2500 rpm for 30 sec. To improve the contact between P3HT and Au, a poly (3-4-ethylenedioxythiophene) doped with poly (4-stylenesulfonate) (PEDOT:PSS; Clevios P VP Al 4083) diluted with two volumes of methanol was introduced onto the $\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{P3HT}$ layer by spin-coating at 2000 rpm for 30 s. In order to form a hybrid hetero-junction, the $\text{TiO}_2/\text{Sb}_2\text{S}_3/\text{P3HT}/\text{PEDOT:PSS}$ layer was then annealed at 90 °C for 30 min in a vacuum oven. The devices are then completed with a gold contact at high vacuum (10^{-6} Pa) with a device area of 0.2 cm^2 .

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3.3 Photovoltaic Device Characterization

The photovoltaic devices are examined by current-voltage (I - V) measurement under both dark (in black) and light illumination (in red) conditions. The current-voltage characteristics (J - V) will provide the following parameters such as V_{oc} , FF and J_{sc} . Figure 3.3 shows the typical curve of solar cell under both dark and light illumination.

Figure 3.3 Representative current-voltage characteristics curve of a typical solar cell. [96]

Basic parameters of the current-voltage characteristics (J_{sc} , V_{oc} and FF)

The four parameters J_{sc} , V_{oc} , FF and η are the key performance to the photovoltaic performance of solar cells shown in Figure 3.3. All measurements were conducted at standard conditions of AM 1.5 spectrum illumination with an incident power density 100 mW/cm^2 at 298 K.

Open circuit voltage (V_{oc}) refers to the cell potential under illumination with no external load. At V_{oc} , there is no external electric current between the terminals.

Short circuit current (I_{sc}) refers to the cell current measured at zero potential under illumination.

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Fill factor (FF) describes the maximum power rectangle fit under the current-voltage characteristics and this is governed by the series resistance (R_s) and shunt resistance (R_p) due to the leakage of current. In order to obtain high FF , series resistance (R_s) should be low while the shunt resistance (R_p) needs to be as high as possible. The operating regime of a solar cell is in the range of bias, from 0V to V_{oc} (open circuit voltage), whereby the cell delivers power. The cell power density is:

$$P = J \cdot V \text{ ----- Equation 3.1}$$

Where J refers to current density, V refers to voltage.

From the J - V curve in Figure 3.3, fill factor refers to the “square-ness” of the curve. Fill factor (FF) is represented by equation 3.2.

$$FF = \frac{V_{max} \cdot I_{max}}{V_{oc} \cdot I_{sc}} \text{ ----- Equation 3.2}$$

V_{max} refers to maximum voltage and I_{max} refers to maximum current density. V_{oc} refers to the open circuit voltage and I_{sc} refers to the short circuit current.

a. Power Conversion Efficiency

The light to power conversion efficiency (η) (PCE) is defined by the ratio of maximum power output (P_{max}) over the incident radiation power (P_{in}) as described in equation 3.3

$$\eta = \frac{P_{max}}{P_{in}} = \frac{V_{oc} \cdot I_{sc} \cdot FF}{P_{in}} \text{ ----- Equation 3.3}$$

This parameter is the direct measure of the performance of a solar cell. Standard test conditions were used for measurements of all devices.

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Figure 3.4 Equivalent circuit of a solar cell.

The net current density in the cell is represented by the following: [96]

$$J(V) = J_{sc} - J_{dark} \quad \text{-----} \quad \text{Equation 3.4}$$

This becomes for an ideal diode,

$$J = J_{sc} - J_o (e^{qV/K_B T} - 1) \quad \text{-----} \quad \text{Equation 3.5}$$

q refers to the electronic charge, V refers to the voltage across the terminals and T refers to the absolute temperature and a constant J_o .

When parasite resistances (series resistance (R_s) and the shunt resistances (R_{sh})) are included, the diode equation becomes:

$$J = J_{sc} - J_o (e^{q(V+J A R_s)/kT} - 1) - (V + J A R_s)/R_{sh} \quad \text{-----} \quad \text{Equation 3.6}$$

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b. Incident photon-to-current conversion efficiency (IPCE)

The incident photon-to-current conversion efficiency is defined as the ratio of the electrons generated in the device to the incident photons at a certain wavelength. It can also be considered as the effective quantum yield of the device and mathematically, it is defined as the product of light harvesting efficiency (η_{LHE}), charge injection yield (η_{inj}) from the photo-excited electron dye into TiO_2 and charge collection efficiency (η_{ncc}) at the electrodes.

$$\text{IPCE}(\lambda) = \eta_{\text{LHE}} \cdot \eta_{\text{ncc}} \cdot \eta_{\text{inj}} \quad \text{————— Equation 3.7}$$

Device Characterization: Solar cells are illuminated with a xenon light source (XEC-301S) from San-Ei Electronics, with power regulated to 1 sun at 100 mW/cm^2 calibrated using a Silicon reference cell. The light to power conversion efficiencies (PCE) were recorded using a PC-controlled voltage-current source meter (Agilent 4155C Semiconductor Parameter Analyzer) under a solar simulator illumination (San-Ei Electronics, XEC-301S) of air mass 1.5 (100 mWcm^{-2}). The incident photon-to-current conversion efficiency (IPCE) was measured using 150 W Newport-Oriel Xenon light source, Cornerstone 260 1/4M monochromator, optical chopper set at 60 Hz and Merlin radiometry system. It is noted that the fabrication processes and performance measurements were carried out in inert glove box atmosphere.

3.4 Surface Profilometry

The thickness measurements of the various thin films on bare substrates were conducted using surface profiler (Alpha step IQ) using a step height analysis. The scanning details used are 2000 μm , scan speed of 50 $\mu\text{m/sec}$, sampling rate of 50 Hz and a sensor range of 550 $\mu\text{m}/32.8 \text{ pm}$.

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3.5 Field emission scanning electron microscopy

The composition of antimony sulphide thin films (Sb_2S_3) were systemically evaluated with a field emission scanning electron microscope (JEOL HSM-7600F) equipped with an Energy Dispersive X-Ray Detector. The composition of the material is measured at 15 kV.

3.6 X-Ray diffraction

The crystalline properties of the films were investigated by thin film X-Ray diffraction (XRD) using Bruker D8 Advance. The X-Ray diffraction patterns in the 2θ range of (10° - 80°) were recorded using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418\text{\AA}$) at room temperature.

3.7 Uv vis spectroscopy

The UV-visible absorption spectra were measured and collected using a Shimadzu UV-3600 UV-VIS NIR spectrophotometer.

3.8 Atomic Force Spectroscopy

The surface topography is measured using the atomic force microscopy, ($1\mu\text{m} \times 1\mu\text{m}$) under tapping mode. The root mean square (RMS) analysis on the roughness of the films was obtained. From the software, it is also noted that the AFM images of the thin films were also scanned over the area to see the step height features.

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3.9 BET surface area measurement

The surface areas of the nanoporous thin films are measured using Brunauer-Emmett-Teller (BET). It aims to explain the physical adsorption of gas molecules to provide measurement for the specific surface area of the material and units is given in m^2/g .

3.10 Transmission Electron Microscopy (TEM)

The as-prepared films on substrate were treated in an ultrasonic bath for a period of 10 - 15 min in ethanol and the high resolution transmission images were captured by a TEM (JEOL JEM-2000) operating at 200 kV. For Sb_2S_3 coated samples, as reflective films are well adhered, the films are scraped off and images are obtained.

3.11 Transient absorption spectroscopy (TAS)

Figure 3.5 Schematic diagram of transient absorption spectroscopy setup.[82]

Figure 3.5 shows the schematic diagram of transient absorption spectroscopy setup. The experimental procedure for transient absorption spectroscopy measurements is as follows: For

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femtosecond TAS, the laser source was a Coherent Legend^{TM} regenerative amplifier (150 fs, 1 KHz, 800 nm) that was seeded by a Coherent Mira^{TM} oscillator (100 fs, 80 MHz). 800 nm wavelength laser pulses were from the regenerative amplifier's output while 400 nm wavelength laser pulses were obtained with a barium borate (BBO) doubling crystal. Broadband probe pulses (400-800 nm) were generated by focusing a small portion ($\sim 5 \mu\text{J}$) of the fundamental 800 nm laser pulses into a 2 mm-thick sapphire plate.

Referring to Figure 3.5, in the setup, a pump excitation pulse is used to excite a fraction of the molecules of sample cell. A weak probe pulse is then sent with a delay time with respect to the pump to the sample. It is noted that the pump and probe pulses were cross-polarized to eliminate any contribution from coherent artifacts at early times. Pump-induced changes in transmission ($\Delta T/T$) of the probe beam were monitored using a standard monochromator/PMT configuration with lock-in detection. The pump beam was chopped at 83 Hz and this was used as the reference frequency for the lock-in amplifier.

Chapter 4

Results and Discussions

4.1 Introduction

Sb_2S_3 is a promising absorber material and has attracted much attention owing to its relatively low band gap material and high absorption coefficient. This chapter is organized into several sections. The initial development describes the synthesis and characterization of Sb_2S_3 thin films as a sensitizer and the different strategies to incorporate it in a solar cell. The film growth by chemical bath deposition technique and measurement of the optical, structural and morphological properties of the film were investigated by the various characterization techniques.

4.2 Chemical Bath Deposited Sb_2S_3 films

a. Effect of annealing

Films of Sb_2S_3 were deposited on glass substrates and with varying time and deposition conditions to study the phase and the stoichiometry of the Sb_2S_3 formed. Figure 4.1 (a) shows the X-Ray diffraction pattern (XRD) for the annealed Sb_2S_3 film where sharp peaks at 2θ of 15.8° , 17.6° and 25.2° are observed and they correspond to the crystalline Sb_2S_3 (stibnite) phase with orientation (020), (120) and (130) respectively (marked by the blue squares). The annealed films were also examined against the oxide phase, Sb_2O_3 where traces of oxide ($\sim 10.15\%$) was

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found and examined with peaks of (111) and (222) at 2θ of 13.8° and 27.8° (marked by the red circles). It is postulated that antimony oxide identified as the Senarmontite phase could have formed during the annealing process. Referring to figure 4.1(b), it shows the XRD pattern of annealed and as-deposited Sb_2S_3 thin films. Prior to annealing, the as-deposited film is suggested to be amorphous, with no characteristic peaks detected. A broad peak for as-deposited films is in agreement with the previous report. [29] In contrast, post-annealed films are crystalline. It is noted that the as-deposited Sb_2S_3 turned dark brown after the annealing process.

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Figure 4.1 (a) X-Ray diffraction pattern of a 3 h annealed Sb_2S_3 thin film. (b) X-Ray diffraction pattern of as-deposited and post-annealed Sb_2S_3 thin films. (c) UV-visible spectrum of an annealed Sb_2S_3 film (Inset shows the band gap of absorber material). (d) UV-visible spectrum of as-deposited Sb_2S_3 film (Inset shows the band gap of absorber material). (e) Graph of semi-quantitative EDX of Sb:S ratio (2:x) against deposition time. (f) Pictures of as-deposited (orange-coloured) and annealed (brown coloured) Sb_2S_3 films.

The optical absorption spectrum of the Sb_2S_3 thin films are shown in Figure 4.1(c). The onset of the absorption spectra is about 750 nm. The band gap is estimated and extracted from the uv vis spectrum of Sb_2S_3 . For allowed direct transitions, $\alpha h\nu$ is given by equation: [28]

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$$(\alpha h\nu)^2 = A(h\nu - E_g) \text{ -----Equation 4.1}$$

where A is constant and E_g is optical band gap. The values of the optical band gap due to band-to-band transition which can be obtained from the best straight line fits in $(\alpha h\nu)^n$ versus $h\nu$ plots where $n = 2$. It is estimated that the as-deposited Sb_2S_3 film has a band gap of ~ 2.7 eV (Figure 4.1 (d)).

The E_g value of the thermally annealed Sb_2S_3 is estimated to be ~ 1.8 eV (inset) which is in agreement with report from 1.7-1.9 eV [28]. The composition of the Sb_2S_3 films were characterized with the field emission scanning electron microscope equipped with an energy dispersive X-ray (EDX) detector. The elemental composition of the films was obtained using a 15 kV accelerating voltage. The semi-quantitative analysis EDX was done for the annealed Sb_2S_3 films. From the compositional analysis, the sulphur to antimony (S/Sb) ratio of the 3 h film is defined as 1.23 (i.e. $2.46/2 = 1.23$) which is consistent with Sb_2S_3 (Figure 4.1 (e)). The pictures of the as-deposited (orange-coloured) and annealed brown coloured antimony sulphide is shown in Figure 4.1 (e).

b. Deposition Temperature

Temperature is one of the main parameters determining the kinetics of reaction and is an important factor in CBD. The use of higher temperature will result in faster deposition rate while lower temperature might allow reactants to sufficiently infiltrate the pores of the TiO_2 electrodes.

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The devices were fabricated on the TiO₂ substrates under different temperature (0 °C, 4 °C and 8 °C) which is controlled digitally on the circulating chiller. All other parameters such as the concentration of reactants for CBD were kept constant. [28]

Figure 4.2 J-V plot of devices fabricated with different temperatures.

Table 4.1 Photovoltaic parameters of devices with different temperature.

Temp (°C)	Time (h)	PCE (%)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)
0	3	0.0003	-0.01	0.21	0.24
4	3	0.6446	-3.97	0.53	0.31
8	3	0.1176	-1.01	0.42	0.28

Table 4.1 presents the current-voltage characteristics measured at 1 sun intensity (100 m W/cm²). 3 different temperatures were investigated. 4 °C was found to be the optimum temperature to maximize the photovoltaic performance of the solar cells. The low temperature (0 °C) was not

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able to provide sufficient coverage of Sb_2S_3 thickness while higher temperatures achieved a higher thickness, but could create complications such as complete reaction in the solution before the substances are coated or even covering of surface pores is made possible. This prevents the inner pores from being coated. This characteristic is reflected in the change in V_{oc} and J_{sc} .

At 0 °C, the low V_{oc} suggests that the TiO_2 might not be sufficiently coated to prevent contact with the HTM and low J_{sc} can be attributed to insufficient absorbing materials being deposited. Higher V_{oc} and J_{sc} were observed for the 8 °C device but performance is still lower than the 4 °C, the slight drop in V_{oc} could be due to over-aggregation of Sb_2S_3 particles, clogging the surface pores. This could lead to voids within the mesoporous structure which acts as recombination center and limits the current extraction. It is noted that the thickness of the TiO_2 films are about 2 to 2.5 μm .

c. Morphology of Sb_2S_3 films

The morphology differences between the as-deposited and annealed films are shown using transmission electron microscopy (TEM). Clear, but random diffraction spots are depicted in SAED in Figure 4.3 (c) and these diffraction spots are not observable as compared to the as-deposited films in Figure 4.3 (a)). The diffuse rings in the pattern of figure 4.3 (a) suggest that the nano-crystalline grains in films are too small to be detected. The average thickness for these films for imaging is about ~102.3 nm (measured with ref. to planar substrates). The transmission electron images of Sb_2S_3 film (both as-deposited and annealed) are reflected in 4.3 (b) and 4.3 (d). Clear crystallographic planes are observed which shows the crystalline regions of the films (indicated by arrows).

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Figure 4.3 (a) Selected area electron diffraction (SAED) image of as-deposited Sb_2S_3 film and (b) its corresponding transmission electron micrograph. (c) SAED of an annealed Sb_2S_3 thin film and (d) its corresponding transmission electron micrograph.

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Figure 4.4 shows the energy dispersive spectra of the as-deposited and annealed Sb_2S_3 thin films.

The energy dispersive spectra are obtained for the samples imaged in figure 4.3.

(a) As-deposited Sb_2S_3 film

(b) Annealed Sb_2S_3 film

Figure 4.4 Energy dispersive X-Ray spectrum of (a) as-deposited Sb_2S_3 thin film (b) annealed Sb_2S_3 thin films. Cu lines at ~ 0.8 k eV are labelled.

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From the energy dispersive spectrum, sulphur (S), antimony (Sb) elements were imaged and confirms the Sb_2S_3 films. Some trace amounts or traces of aluminum (Al) were also detected which is from the TEM column.

d. Thickness deposition and Crystallite Size

In this study, two important parameters such as the (i) deposition thickness of Sb_2S_3 layer and (ii) the grain size effect of the antimony sulphide were studied. The grain size is evaluated using Scherrer's equation, evaluated from the broadening of the peak according to the formula as reflected in equation 4.2. The crystallite size is extracted for 1 h, 2 h and 3 h deposition time since these films are able to cover the substrate uniformly. The Scherrer formula can be written as:

$$\text{Crystallite size (D)} = K\lambda/\beta \cos \theta \text{ -----Equation 4.2}$$

Where crystallite size (D) is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size, K refers to the dimensionless shape factor (typically close to unity, about 0.9), λ is the X-ray of $\lambda = 1.5418 \text{ \AA}$, β is the line broadening at half the maximum intensity (FWHM) in radians (rad). This quantity is also sometimes denoted as $\Delta(2\theta)$; θ is the Bragg angle. Figure 4.5 (a) shows the XRD pattern for the various 30 min, 45 min, 1 h, 2 h and 3 h deposited films. From the calculation, the grain size is estimated to be about 19 - 20 nm for all 1 h, 2 h and 3 h deposition times, hence indicating that there is no large, significant changes in grain size with the different various deposition times.

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(c)

(d)

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(e)

Figure 4.5(a) XRD pattern of 30 min, 45 min, 1 h, 2 h and 3 h Sb_2S_3 thin films on planar substrate. (b) Growth curve of antimony sulphide with various time depositions on planar substrate. (c) Plot of uv-visible spectrum of Sb_2S_3 thin films from 30 min to 3 h. (d) Plot of $(\alpha h\nu)^n$ against $h\nu$ plots of Sb_2S_3 films. (e) Plot of band gap against deposition time of Sb_2S_3 films.

The thickness of Sb_2S_3 film coating is plotted as a function of time against the chemical bath deposition times (ranging 0.5 h – 3 h) measured with respect to planar glass using the surface profiler. As observed, the film thickness increased with increasing deposition time where the change in Sb_2S_3 thickness (Δt) doubled within a time deposition of between 2 h to 3 h interval. In general, the film thickness increases from 50 nm up to 250 nm film to a 3 h deposition. The film thickness required for the absorption of 90 % of the photons is $(2.3)/\alpha$ where α is the optical absorption coefficient of a material. A Sb_2S_3 thickness of ~300 nm will ensure 90 % absorption of 550 nm wavelength, indicating that the deposited film is of sufficient thickness for optical

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absorption. [97] Figure 4.5 shows the absorbance of films deposited for 30 min, 45 min, 1 h, 2 h and 3 h, plotted against the wavelength region of 400 nm to 800 nm. It is observed that the absorbance of the films increases with increasing deposition times. It is noted that 30 min and 45 min films do not provide sufficient coverage on the substrates henceforth only 1 h, 2 h and 3 h deposition time (hence thickness) were used for device fabrication. Figure 4.5 (d) shows the corresponding plot of $(\alpha h\nu)^n$ against $h\nu$ plots of Sb_2S_3 films and Figure 4.5 (e) shows the plot of band gap against deposition time of Sb_2S_3 films.

Figure 4.6 TEM images of Sb_2S_3 coating on TiO_2 nanoparticles (100 nm scale) and the various elemental mapping of Ti, Sb and S of Sb_2S_3 coating on TiO_2 nanoparticles.

Lastly, we have observed Sb_2S_3 films coated onto the TiO_2 nanoparticles by using (TEM) element analysis imaging and technique. The elemental mapping of Sb_2S_3 coating on TiO_2 nanoparticles is shown in Figure 4.6. Each image shows the respective elemental mapping of Ti, Sb and S. The figure on the bottom right hand corner shows the image of the TiO_2 nanoparticles

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coated with Sb_2S_3 . Here, the denser titanium (Ti) is imaged at the center core, which correlates to the TiO_2 nanoparticles. When coated with a thin layer of antimony sulphide, a less dense coating from elements of sulphur (S) and antimony (Sb) are imaged at the outer shell.

4.3 Antimony Sulphide as absorber in Solar Cells

The fabrication of antimony sulphide based solar cells and the study of some of the factors which modulate the efficiency of these devices are reported. The incorporation of buffer layer in solar cell architecture on the device performance of solar cells is briefly investigated. The effect of surface area and porosity of the TiO_2 mesoporous films was also evaluated. In addition, a surface treatment was also employed to explain the relationship between the TiO_2 morphology and solar cell performance. The effect of deposition time (and hence thickness) of Sb_2S_3 on the performance of solar cells is studied briefly as shown. For these studies, a TiO_2 photo-anode fabrication by screen printing a home-made paste consisting of MK Nano 50nm anatase particles and a commercial paste of Solaronix R/SP. The thickness of antimony sulphide is varied by varying the chemical bath deposition times from 1 h to 3 h.

To determine the effect of antimony sulphide as an absorber on photocurrent generation in the ssDSCs, current density-voltage (J - V) measurements and incident-photon-to current measurements (IPCE) were measured and tabulated. Table 4.2 summarized the solar cell performance for devices fabricated with varying absorber deposition times of 1 h, 2 h and 3 h. Photovoltaic results of Sb_2S_3 films coated with 30 min and 45 min are not reflected in graph as they did not show any response during the J - V measurements.

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Table 4.2 Photovoltaic parameters of electrodes with different Sb₂S₃ deposition time.

CBD Time (h)	Average thickness (nm)	PCE (%)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)
1	104.3	0.11± 0.0150	-0.94±0.1	0.31±0.02	0.39±0
2	201.6	0.36±0.09	-2.15±0.44	0.42±0.025	0.40±0.005
3	261.0	0.74±0.005	-4.78±0.06	0.43±0.005	0.36±0

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(b)

Figure 4.7 (a) Current density-voltage (J - V) curves for devices fabricated with varying Sb_2S_3 deposition timings. (1 h, 2 h and 3 h) (b) IPCE of a 3 h- Sb_2S_3 chemical bath deposited device.

Figure 4.7 (a) shows the J - V characteristics of the Sb_2S_3 -sensitized cells with varying deposition time (from 1 h to 3 h), measured under simulated AM 1.5, 100 mW/cm^2 illumination. Upon increasing the deposition times, (from 1 h to 3 h) it is observed that there is an increase in the current density J_{sc} starts from 0.94 mA/cm^2 to 4.78 mA/cm^2 , which contributes to a large increase in power conversion efficiency (PCE). In contrast, the V_{oc} and FF largely remains the same for devices fabricated with 2 h and 3 h deposition time (deposition thickness). The significant increase in J_{sc} with increasing deposition times is attributed to the enhanced absorption (light harvesting) and injection with a thicker Sb_2S_3 absorber layer in semiconductor-sensitized nanoporous solar cells. In such inorganic-based semiconductor (Sb_2S_3) sensitized solar cell, the control of the absorber thickness is of paramount importance. Hodes and co-workers[31]

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mentioned that a too thick semiconductor layer can result in internal recombination in Sb_2S_3 film, hence resulting in poor device efficiency. The corresponding IPCE spectrum for best cell at 3 h- Sb_2S_3 device is shown. (Figure 4.7 (b)) The IPCE of a $\text{TiO}_2/\text{Sb}_2\text{S}_3$ -3 h sensitized solar cells typically exhibit peak values of ~45 % between excitation wavelength of 400 nm-650 nm and onset of the observed IPCE is ~750 nm. It is noted that for the entire device fabricated above, the TiO_2 electrodes are passivated with an indium hydroxyl sulphide ($\text{In}(\text{OH})_x\text{S}_y$) interfacial layer to reduce recombination. The effect of the interfacial buffer layer on photovoltaic parameters (J_{sc} , V_{oc}) will be described in the following section.

4.4 Controlling Recombination

a. Interfacial buffer layer, $\text{In}(\text{OH})_x\text{S}_y$

The approach introduces indium hydroxyl buffer layer as a passivation layer coated onto the electrodes prepared by chemical bath deposition. The motivation for incorporation of an interfacial buffer layer, $\text{In}(\text{OH})_x\text{S}_y$ in between $\text{TiO}_2/\text{Sb}_2\text{S}_3$ interface is to suppress recombination of injected charge carriers that limits the power conversion efficiency of solar cells. The photovoltaic performance of solar cells fabricated with and without $\text{In}(\text{OH})_x\text{S}_y$ were compared.

Figure 4.8 (a) shows the proposed scheme of band diagrams for the passivated TiO_2 electrodes by interfacial buffer layer. $\text{In}(\text{OH})_x\text{S}_y$ has been successfully demonstrated as a interfacial layer in this work as well as for PbS semiconductor absorber in an extreme thin absorber (ETA) configuration. The $\text{In}(\text{OH})\text{S}$ is reported to possess a band gap of 2.5 eV[74]. For $\text{In}(\text{OH})_3$ and In_2S_3 , band gaps are estimated in between 2 eV and 3.7 eV. In this work, there is an addition of a chemical bath deposited $\text{In}(\text{OH})_x\text{S}_y$ onto the TiO_2 electrodes prior to Sb_2S_3 deposition, it is observed that there is an improvement in photovoltaic parameters for both J_{sc} and V_{oc} to a great extent. It is postulated that $\text{In}(\text{OH})_x\text{S}_y$ acts as an interfacial layer (sufficiently thin) to suppress recombination and henceforth accounting for the increase in efficiency of semiconductor-sensitized solar cells. Figure 4.8 (b) shows the J - V characteristics for a 3 h deposited Sb_2S_3 -sensitized solar cell with and without $\text{In}(\text{OH})_x\text{S}_y$.

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(a)

(b)

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Figure 4.8 (a) Energy band diagram of In(OH)_xS_y coating on TiO₂ nanoparticles. (b) *J-V* characteristics of devices with and without In(OH)_xS_y. (c, d) TEM images of TiO₂ coated with In(OH)_xS_y and (e) its corresponding EDX.

Table 4.3 Photovoltaic parameters of devices with and without $\text{In}(\text{OH})_x\text{S}_y$

Device	PCE (%)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)
Without $\text{In}(\text{OH})_x\text{S}_y$	0.16	-1.59	0.27	0.37
with $\text{In}(\text{OH})_x\text{S}_y$	0.70	-5.92	0.37	0.32

For electrodes without the $\text{In}(\text{OH})_x\text{S}_y$ interfacial layer, the devices are of very much lower cell efficiency of 0.16%, current density (J_{sc}) of 1.59mA/cm², open circuit voltage (V_{oc}) of 0.27 and fill factor (FjF) of 0.37 (Table 4.3). Both J_{sc} and V_{oc} improved when an interfacial $\text{In}(\text{OH})_x\text{S}_y$ buffer layer was incorporated in between TiO_2 and Sb_2S_3 interface. This could be because of the highly insulating nature of $\text{In}(\text{OH})_x\text{S}_y$, leading to the “tunnel barrier” effect. The electrons from Sb_2S_3 could tunnel through the thin layer of $\text{In}(\text{OH})_x\text{S}_y$ [98] to reach the TiO_2 layer. However, the photo-injected electrons will be energetically forbidden to fall back to the absorber. [99] As a result, the rate of recombination in the absorber decreases, leading to an increase in the electron concentration at constant illumination, resulting in higher J_{sc} . The drop in V_{oc} due to recombination was also decreased. In addition, this is based on the assumptions that the chemical bath deposited $\text{In}(\text{OH})_x\text{S}_y$ is sufficiently thin for electrons to tunnel through, and that there is a sufficient coverage of $\text{In}(\text{OH})_x\text{S}_y$ coated onto the TiO_2 nanoparticles without blocking the pores of mesoporous thin films. The EDX spectrum confirms the presence of the In, S, Ti, O element corresponding to $\text{In}(\text{OH})_x\text{S}_y$ coating. Some traces of Cu is also detected from the Cu grid.

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Figure 4.9 shows the cross-sectional view of a $\text{TiO}_2\text{-Sb}_2\text{S}_3$ electrode with a film thickness of about $2\ \mu\text{m}$ at $10\,000\times$ magnification. The image shows good adherence of mesoporous films onto the substrate which is essential for good photovoltaic cells performance.

Figure 4.9 Cross sectional analysis of a $\text{TiO}_2\text{-Sb}_2\text{S}_3$ electrode prior to coating of hole-transport material, P3HT.

Figure 4.10 illustrates the AFM image ($1\ \mu\text{m} \times 1\ \mu\text{m}$) of as-deposited $\text{In}(\text{OH})_x\text{S}_y$ on planar substrate with similar deposition conditions in the device fabrication. The physical appearance of the surface coating is rough and clusters were shown. The root mean square (r.m.s) value for $\text{In}(\text{OH})_x\text{S}_y$ film on planar substrate is about $\sim 13.7\ \text{nm}$.

Figure 4.10(a) AFM image ($1.0\ \mu\text{m} \times 1.0\ \mu\text{m}$) of $\text{In}(\text{OH})_x\text{S}_y$ coating on planar substrate.

(b) Surface topography in 3D of $\text{In}(\text{OH})_x\text{S}_y$ coating on plain glass.

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b. Passivation Oxide layer (Sb_2O_3)

Antimony oxide (Sb_2O_3) is an insulator with a large band gap of ~ 4 eV. The presence of Sb_2O_3 in large amount could reduce the device performance due to a significant difficulty in the pore-filling of hole-transporting material into the $\text{TiO}_2/\text{Sb}_2\text{S}_3$ electrodes. The FESEM images of the $\text{TiO}_2/\text{Sb}_2\text{S}_3$ electrodes with some amount of impurities of antimony oxide crystals are shown. (Figure 4.11) The large crystals are of Senarmontite phase of octahedral shape. Interestingly, it is has been reported by Y. Itzhaik that the presence of some amount of oxide could act as a passivation oxide for better device performance in photovoltaic solar cell for Sb_2S_3 absorber.[50][29] Thus in the following section, a two-step surface treatment is introduced to the $\text{TiO}_2/\text{Sb}_2\text{S}_3$ electrodes. A similar treatment has also been reported on CdS absorber for interface control.[100] It is estimated that there is about 10.1 % Senarmontite (Sb_2O_3) present in a $\text{TiO}_2/\text{Sb}_2\text{S}_3$ electrode from the XRD pattern. (Appendix A)

Figure 4.11 FESEM image of antimony oxide (Sb_2O_3) crystals before surface modification/post treatment.

4.5 Surface modification/ post-treatment

A surface treatment consisting of a thermal oxidation and subsequent HCl etching of antimony sulphide layer was introduced subsequent to the chemical bath deposition. The surface treatment was adopted on a different system[101] as used here to treat the Sb_2S_3 films. The post-treatment is carried out on Sb_2S_3 in between Sb_2S_3 interface. Post-treated Sb_2S_3 showed marked improvement in solar cell performance. A schematic process of the post-treatment is illustrated. (Figure 4.12)

Two-step post-treatment

- 1) 1st step of post treatment: Thermal oxidation at 200 °C for 10 min.
- 2) 2nd step of post-treatment: HCl treatment.

Figure 4.12 Schematic of a two-step post-treatment /surface modification of Sb_2S_3 .

The photovoltaic performance of solar cells with and without post-treatment are measured and illustrated in Table 4.4.

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Table 4.4 Photovoltaic parameters of devices after Sb₂S₃ post-treatment

Process	Device	PCE (%)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)
No post-treatment	Control	0.74	-4.78	0.43	0.36
(Thermal oxidation)	Oxide	0.31	-1.89	0.42	0.40
(Thermal oxidation & HCl treatment)	HCl-treated	1.15	-6.52	0.46	0.38

Figure 4.13 (a) J - V characteristics of TiO₂/Sb₂S₃ electrode after thermal oxidation whereby an oxide layer is formed.

Sb₂O₃ was first discussed by Yatik et al.[50] and it was reported that small amounts of surface oxide could possibly reduce electron-hole recombination in Sb₂S₃ or in another case to reduce the recombination of electrons in Sb₂S₃ with the hole-transporting material. With the formation of the oxide layer, it was observed that there is a drastic reduction of $J_{sc} = 4.78$ mA/cm² to 1.7 mA/cm² (Figure 4.13). The V_{oc} remained constant at 0.42 V -0.43 V.

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With the hydrochloric acid (HCl) treatment, good cells can be obtained again. The current density and V_{oc} improved to a large extent, even as compared to the control device without any post-treatment. A current density of $6.5\text{mA}/\text{cm}^2$ and an efficiency of 1.15 % are obtained. From the IPCE, an enhancement to 50 % after surface modification step is observed. (Figure 4.14)

(a)

(b)

Figure 4.14 (a) J - V characteristics of control devices with and without Sb_2S_3 surface modification. (b) IPCE spectrum of devices with and without Sb_2S_3 surface modification.

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the series resistances as well as act as recombination centers. Optimum porosity has to be achieved to maximize the amount of materials deposited while achieving minimal unfilled pores. The degree of pore size after Sb_2S_3 coating is illustrated (Figure 4.16) for a larger sized TiO_2 nanoparticle film and smaller sized TiO_2 nanoparticle film. It is observed that fewer pores were observed for the 18-20 nm particle paste (refer to Figure 4.16 (b), the circle red region) as compared to the number of pores observed for the larger sized nanoparticle paste. (refer to Figure 4.16 (a), the circled red region).

Figure 4.16 Degree of pore size after Sb_2S_3 coating for (a) larger-sized nanoparticle (~ 100 nm TiO_2 nanoparticle) (b) smaller TiO_2 nanoparticles (18-20 nm TiO_2 nanoparticle).

The photo-anode structure is briefly studied by varying the nanoparticle size of the TiO_2 layer. Devices were fabricated with a home-made paste of ~ 50 nm TiO_2 nanoparticles and from a Solaronix ~ 100 nm TiO_2 paste. The J - V characteristics are shown in Figure 4.17.

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Figure 4.15 FESEM image of ~50 nm particle TiO₂ films (a) before etching (b) after etching and FESEM images of ~ 100 nm particle TiO₂ films (c) before etching (d) after etching.

4.6 Effect of Photo-anode Structure

a. Nanoparticle Size

The nano-scale size of the TiO₂ nano-particles allows a mesoporous structure of TiO₂ particles. The TiO₂ electrodes are formed by screen-printing and a sintering process to form the interconnected mesoporous TiO₂ layer. Smaller nanoparticle size provides higher effective surface area for the sensitizers to be adsorbed; however, it also hinders the penetration of materials which may produce unfilled pores in the structure. The unfilled pores can contribute to

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the series resistances as well as act as recombination centers. Optimum porosity has to be achieved to maximize the amount of materials deposited while achieving minimal unfilled pores. The degree of pore size after Sb_2S_3 coating is illustrated (Figure 4.16) for a larger sized TiO_2 nanoparticle film and smaller sized TiO_2 nanoparticle film. It is observed that fewer pores were observed for the 18-20 nm particle paste (refer to Figure 4.16 (b), the circle red region) as compared to the number of pores observed for the larger sized nanoparticle paste. (refer to Figure 4.16 (a), the circled red region).

Figure 4.16 Degree of pore size after Sb_2S_3 coating for (a) larger-sized nanoparticle (~ 100 nm TiO_2 nanoparticle) (b) smaller TiO_2 nanoparticles (18-20 nm TiO_2 nanoparticle).

The photo-anode structure is briefly studied by varying the nanoparticle size of the TiO_2 layer. Devices were fabricated with a home-made paste of ~ 50 nm TiO_2 nanoparticles and from a Solaronix ~ 100 nm TiO_2 paste. The J - V characteristics are shown in Figure 4.17.

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Table 4.5 Photovoltaic parameters of devices with different TiO₂ particle size.

TiO ₂ size (nm)	J_{sc} ($mAcm^{-2}$)	V_{oc} [V]	FF [%]	η [%]
~50	6.52	0.46	38	1.15
~100	10.84	0.49	44	2.32

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Figure 4.17 (a) J - V curves of devices fabricated from different sized TiO_2 nanoparticles film. (b) IPCE spectrum of different sized TiO_2 nanoparticles film.

Best performance comes from solar cells with $>100\text{nm}$ nanoparticles size TiO_2 nanoparticles with 2.3 % efficiency with a high J_{sc} of 10.84 mA/cm^2 . This illustrates that chemical bath deposition of Sb_2S_3 is sensitive to the underlying TiO_2 nanoparticle. For devices with smaller nanoparticles size, it produces poorer photovoltaic results. This could be due to the coupling of small pore sizes and mechanism of chemical bath deposition.

Chemical bath deposition is a simplistic approach where it is sensitive to pH of solutions, concentrations, temperature. Reactants need to diffuse into the mesoporous sites of TiO_2 in order to deposit the materials, but is hindered by the narrow path of diffusion. This is further

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aggravated when the particles aggregate and clog the surface pores, preventing reactants from entering the matrix. Larger-sized nanoparticle film, having a larger porosity than smaller sized nanoparticles, could probably facilitate the access of precursor into TiO_2 pores which resulted in better solar cell performance. Previous works illustrated by Grant et al. is carried out on a slightly different area focused on the use of much larger bulky polymers for pore filling and concluded that pore size is important for access of long-chain conjugated polymer sensitizer. [102]. The external quantum efficiency (EQE) of $>100\text{nm}$ nanoparticles sized device showed peak values of about 65 % for excitation wavelengths of 400 nm-650 nm (Figure 4.17).

4.7 Modulating Thickness of TiO_2 electrode

The thickness of the home made paste is modulated by dilution with solvent alpha-terpineol and an ultrasonic bath. It is postulated that a reduction in mesoporous TiO_2 layer was proposed to decrease the series resistance of the solar cells. This could also improve the infiltration of the Sb_2S_3 into the mesoporous structure. However, a reduction in the layer thickness could also decrease the surface area for Sb_2S_3 particles deposition, resulting in less photocurrent being generated. Henceforth, a compromise between the layer thickness and photocurrent generation has to be achieved. Figure 4.18 and Table 4.6 show the photovoltaic performance and $J-V$ characteristics respectively.

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Figure 4.18 J - V characteristics of devices fabricated from different TiO_2 layer thicknesses.

Table 4.6 Photovoltaic parameters of devices in Figure 4.18

mp- TiO_2	CBD Time (h)	PCE (%)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF
1.8 μm	3	1.91	-9.56	0.49	0.41
1.2 μm	3	0.64	-3.97	0.53	0.31
550 nm	3	0.42	-2.59	0.52	0.31

The chemical deposition time is 3 h for all samples. In comparing the photovoltaic performance, the trend of device performances was not within expectation. It is shown that PCE decreases with decreasing mp- TiO_2 thickness. The mp- TiO_2 thickness led to a decrease in the amount of light absorbing Sb_2S_3 materials being deposited resulting in the decrease in J_{sc} . The control device with 1.8 μm thickness (measured with surface profiler) was screen-printed as-prepared with no dilution. Thinner layers were printed with paste with dilution. The 1.8 μm thick mp- TiO_2 device exhibited the best performance, η of 1.91 %, with a reported current density (J_{sc}) of 9.56

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mA/cm², open circuit voltage (V_{oc}) of 490 mV and a fill factor (FF) of 41 %. However, it is noted that the photovoltaic performance was difficult to replicate. One of the reasons could be because of the dilution of the home-paste. The increase in paste viscosity means that more solvent need to be evaporated during thermal annealing of substrates to produce the porous structure. One of the reasons for the decline in PCE of device is that the technique of thinning the layer may not be the best method to form the mp-TiO₂ structure. The porosity may be increased but the mesoporous structure may have collapsed during the annealing process due to the degradation in the structural integrity. The collapse could prevent the CBD reactants from reaching the pores for complete absorber coverage during the bath deposition.

The external quantum efficiency of the devices was measured and an EQE of 50 % was achieved for the device with an overall efficiency of 1.91 %. It was interesting to note that the 1.2 μ m and 550 nm device demonstrated the same IPCE spectra, both achieving about 25 % EQE. This highly suggests that the diluted paste is not so suitable for forming the porous structure as the mp-TiO₂ could have collapsed during thermal annealing. Hence, the EQE was similar for both despite the difference in J_{sc} , suggesting more voids or unfilled pores for the 550 nm printed device.

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Figure 4.19 IPCE measurements of devices with 3 h of Sb_2S_3 CBD with different TiO_2 layer thicknesses.

4.8 Modulating Hole-transporting Materials

Two different hole-transporting materials were used to modulate the fermi level of the HTM to the Sb_2S_3 absorber. Spiro-OMeTAD is one of the best hole-transporting materials. However, from the findings, devices fabricated with P3HT hole-transporting material exhibit better photovoltaic response than the spiro-OMeTAD.

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Table 4.7 Photovoltaic parameters of devices with different hole-transporting materials (HTM)

Device	PCE (%)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)
18NR-T/In(OH)S/Sb ₂ S ₃ -2 h /HPA/Spiro-OMeTAD/Au	0.30	-1.82	0.61	0.27
P50/In(OH)S/ Sb ₂ S ₃ -3 h /DPA/Spiro-OMeTAD/Au	0.19	-1.24	0.38	0.40
P50/In(OH)S/Sb ₂ S ₃ -3 h /P3HT/PEDOT:PSS/Au	1.91	-9.56	0.49	0.41

Figure 4.20 J - V curves of devices with the different hole-transporting materials.

Figure 4.21 Energy band diagram of the Sb₂S₃ sensitized solar cells with Spiro-OMeTAD.

The J - V characteristics depend on the wetting and pore-filling properties of the hole-transporting material. In order to improve the wetting of spiro-OMeTAD, a pre-treatment of soaking in co-adsorption of organic small molecule such as alkyl-phosphonic acids were applied on the devices prior to HTM coating. Some examples of small molecules are decyl-phosphonic acid (DPA) and hexyl-phosphonic acid (HPA), see Figure 3.2 [103]. Presently, it is important to find methods to facilitate pore-filling which is highly suspected to be the main cause of low efficiency of the spiro-OMeTAD devices. A fairly low current density (J_{sc}) of 1.24 mA/cm² for device fabricated with spiro-OMeTAD is attributed to the high series resistances from unfilled pores.[17] The higher efficiencies obtained for the P3HT devices could be because that the metal-sulphide bond led to an improvement in wetting properties of TiO₂ in contrast to Spiro-OMeTAD. [104] Devices fabricated with spiro-OMeTAD has, however, achieved a high V_{oc} of

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0.61 V. Further study is required to optimize the fabrication process of using spiro-OMeTAD as HTM.

4.9 Photo-physical properties

a. Introduction

Despite the extensive studies, reports on the innate dynamical behavior of the photo-excited charge carriers in Sb_2S_3 in the different phases are far and few between. The influence of morphology on the charge carrier dynamics, which in turn plays a deterministic role in driving the high efficiencies (6.3 %) in these solar cells, have yet to be well understood. Herein, through femtosecond transient absorption spectroscopy (TAS), we directly probe the photo-induced charge carrier dynamical processes in as grown and post annealed ALD-grown Sb_2S_3 thin films. The post treatment annealing effect on the crystallinity and ultrafast charge carrier dynamics in these Sb_2S_3 thin films are uncovered. From the findings, it indicates that the crystallinity of the Sb_2S_3 thin film is of crucial importance for enhancing the photovoltaic performance of such solar cells.

Sb_2S_3 is a promising semiconductor which has attracted much attention in the last two decades. A variety of techniques (both physical and chemical methods) have been demonstrated for the synthesis of Sb_2S_3 e.g solution deposition method[28], successive ionic layer adsorption and reaction (SILAR) of antimony sulphide[81], chemical vapour deposition[105, 106] and atomic layer deposition (ALD).[107, 108] Crystalline Sb_2S_3 has been reported as an absorber material in solar cell applications by several groups, attaining an efficiency of up to 6.3 %[109]

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using PCPDTBT(poly(2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7(2,1,3-benzothiadiazole)) which functions both as a absorber and a hole-transporting material. Nanoporous TiO_2 provides the high surface area necessary for loading of Sb_2S_3 in which the control of the absorber layer is of paramount importance, as too thick an absorber layer [31, 110] or aggregation[111] could result in undesirable internal recombination in the semiconductor layer, leading to poor solar cell performance. Many different methods have been evaluated to optimize the thicknesses of absorber layer and one of the most promising approaches is by atomic layer deposition. [112]

In this work, as grown and post-treated films (prepared by ALD) are characterized using the various analytical methods. The advantages of atomic layer deposition include precise thickness control and in addition, it is a gaseous homogenous deposition done in vacuum. The atomic layer deposition Sb_2S_3 was performed using the following precursors: tris(dimethylamido)antimony $\text{Sb}(\text{NMe}_2)_3$ 99.99 % Sb streamline and hydrogen sulphide (H_2S) 99.8% NOX in a home-made equipment. The films were annealed at 330 °C, for 30 min in N_2 ambient. The pulse, exposure and purging durations for $\text{Sb}(\text{NMe}_2)_3$ were 1 s, 3 s and 10 s respectively, while for H_2S they were 0.05 s, 2 s and 15 s. 30 sccm of nitrogen gas was used as a carrier and the base pressure during the deposition was about 0.8 Torr [112]. The ALD films are coated onto planar substrates with an estimated thickness of 57-60 nm (~500 deposition cycles) from ellipsometry. It is noted that as grown films of Sb_2S_3 appear as orange in colour and when annealed turned dark brown in colour. For high resolution transmission electron microscopy, the film is exfoliated from the substrate by ultrasonification and subsequently deposited on a holey carbon coated copper grid. Images were collected digitally using JEOL JEM-2100F microscope

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fitted with a field emission gun, operating at 200 kV. The sample was mounted on a double tilt holder to obtain high resolution images along the [100] direction.

b.Physical Characterization

Figure 4.22 (a) shows the X-Ray diffraction pattern of an annealed Sb_2S_3 thin film. The crystalline thin film showed sharp peaks at (020) and (130) matching the characteristics of stibnite phase (PDF 00-042-1393). The thicknesses of the as-deposited ALD Sb_2S_3 films are approximately 57-60 nm fabricated with deposition cycles ~500 cycles. Before annealing, the physical appearance of Sb_2S_3 is orange in color and after annealing, these films turned dark brown. X-Ray diffraction pattern of an amorphous Sb_2S_3 thin film indicates a broad spectrum with no characteristic peaks. The optical spectrum of Sb_2S_3 film is illustrated in Figure 4.22(b). The annealing process is carried out in an inert environment at a temperature of 330° C for a period of 30 min in N_2 ambient. Using this approach, pure Sb_2S_3 films without Sb_2O_3 (senarmontite) is obtained.

For allowed direct transitions, $\alpha h\nu$ is given by the equation:

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

where A is constant and E_g is the optical band gap.

Thus E_g can be obtained from a plot of $(\alpha h\nu)^2$ versus $h\nu$, and its extrapolation to $(\alpha h\nu)^2 = 0$. It is estimated that the as-deposited atomic layer deposited antimony sulphide film has a band gap of ~2.4 eV (amorphous) and the annealed atomic layer deposited antimony sulphide has a band gap of about 2.0 eV (crystalline) as illustrated in Figure 4.22(b). In general, there is a reduction in photon energy after annealing.

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Figure 4.22 (a) XRD diffraction pattern of ALD Sb_2S_3 thin film for annealed (in black) and as-deposited (in red) (b) Photon energy of ALD Sb_2S_3 films for annealed (in black) and as-deposited (in red).

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However, compared to the XRD of bulk highly crystallized Sb_2S_3 , the present diffraction lines for annealed Sb_2S_3 film are generally broader in Figure 4.22. The finite size of the crystallites, strain, and instrumental effects contribute to the broadening. Assuming that the crystalline domains are spherical in shape, the size of the domains can be estimated according to the Debye-Scherrer formula.

$$D = 4/3 [(K \lambda)/\beta \cos \theta] \text{ -----Equation 4.2}$$

Where D is the crystallite size, K is the dimensionless factor (typically close to unity, usually 0.9), λ is the wavelength of X-rays ($\lambda= 1.5418\text{\AA}$), β refers to FWHM of diffraction peak, θ refers to angle corresponding to the peak. In this equation, the stress-related and instrument-related broadening is neglected. In order to obtain the diameters of the crystalline domains, the XRD 130 peak profile is fitted with Lorentzian function. The calculation shows that the average crystallized domain size is around 30 nm.

Figure 4.23 (a) SAED pattern of Sb_2S_3 film and (b) TEM images of ALD Sb_2S_3 films.

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The crystallographic planes of the ALD films were characterized using the available analytical software and TEM at 200 kV. Figure 4.23 (a) shows the selected area diffraction (SAED) pattern of an annealed ALD film. The crystalline films demonstrate clear, concise diffraction spots with a zone axis of [100] using the JEOL JEM-2100F instrument. $10 \text{ }^{-1} / \text{nm}$ refers to the scale bar in reciprocal space. Figure 4.23 (b) shows the TEM image of the morphology of ALD Sb_2S_3 . Nevertheless, it is noted that the film is not perfectly crystalline as some amorphous regions (as indicated by the arrows) have been observed.

Figure 4.24 shows the femtosecond photo-excited charge carrier dynamics in as-deposited and thermal annealed Sb_2S_3 films. Here, 400 nm (3.1 eV), 150 fs laser pulses were used to excite the excitons from the ground state to the energy states which are much higher than the band gap of Sb_2S_3 . A broad white light spectrum was used to probe the sub-sequential photo-excited charge carrier dynamics (especially the electron dynamics).[94, 113-117] For as-deposited Sb_2S_3 film, as shown in figure 4.24, the transient absorption spectra were dominated by a broad featureless photo-induced-absorption (PIA) band (i.e., $\Delta T/T < 0$ over 420 – 780 nm spectra range). This photo-induced absorption band is attributed to the photo-induced charge carrier transition from excited states to higher energy states. For annealed Sb_2S_3 film, the transient absorption spectra were also dominated by photo-induced absorption (PIA) in the visible light probe range, with a peak at 550 nm. The featured peaks appearing at 550 nm in the transient absorption spectra is postulated due to formation of nano-crystalline domains. As illustrated, the amplitude of the photo-induced absorption is increased by approximately a factor of 2 in the thermal annealed samples as compared to the as-deposited (Figure 4.24). This result closely matches with the large increase of light absorption in the visible range by thermal

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annealing. The greatly enhanced light absorption in the solar spectrum range makes the annealed Sb_2S_3 more suitable for light harvesting application as compared to the as-deposited (optical thick, physical thin).

Figure 4.24 Transient absorption spectra of ALD Sb_2S_3 films on quartz substrate (a) after annealing (b) before annealing. Photo-excitation at 400 nm (pump intensity = $19 \mu\text{J}/\text{cm}^2$)

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c. Charge carrier dynamics

To extract the detailed charge carrier lifetimes, the photo-induced absorption dynamics at the probe wavelength of 570 nm were monitored for both the as-deposited and annealed Sb_2S_3 films.

Figure 4.25 Transient decay kinetics of annealed and as-deposited ALD Sb_2S_3 absorption probed at 570 nm in short time (a) and long time (b) window. Photo-excitation at 400 nm (pump intensity $3.2 \mu\text{J}/\text{cm}^2$)

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Figure 4.25 shows an example of data acquired via transient absorption technique, showing a photo-induced transmission bleach with ultrafast rise and partial signal decay. Here, the pump fluence was kept to a minimal of $3.2 \mu\text{J}/\text{cm}^2$ per pulse. The decay curves and multi-exponential fits are shown in Figure 4.26 and Figure 4.27. The fitted results are listed in Table 4.8. For as-deposited Sb_2S_3 film, the photo-induced absorption decreases monotonically with increasing the probe delay time.

Table 4.8 Summary of the lifetime (τ_i) and corresponding amplitude (A_i) used for the TA fits. Photoexcitation at 400 nm ($3.2 \mu\text{J}/\text{cm}^2$), probe at 570 nm.

	A_1	τ_1	A_2	τ_2	A_3	τ_3	A_4	τ_4
Samples	(%)	(ps)	(%)	(ps)	(%)	(ps)	(%)	(ns)
As-deposited			-	-	25	90	59	7.5
Sb_2S_3	16	0.8						
Annealed Sb_2S_3	47	0.15	13	17	3	520	37	16.7

In amorphous phase, the photo-induced absorption is attributed to the transition between the strongly localized excited electronic states. The initial fast decay (~ 0.8 ps) could be assigned to the hot charge carrier cooling process. The cooling time is similar to that for organic molecules. [116] The slow decay in nanosecond time range (~ 7.5 ns) represents the charge carrier recombination within this localized area. By increasing the pump fluence, an additional fast decay process (several tens of picoseconds) could be observed for the as-deposited Sb_2S_3 film (Figure 4.26). The lifetime of this process decreases with increasing the pump fluence. As

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the corresponding amplitude increases super-linearly with the pump fluence, these results strongly suggest that this process originates from the multi-exciton Auger recombination. [94]

For the annealed Sb_2S_3 film, the photo-induced absorption dynamics at 570 nm are totally different from the non-annealed sample. As shown in figure 4.27 an extremely short-lived (~ 150 fs) PIA process is observed at the initial time. The amplitude of this process increases linearly with the pump fluence. Considering the near continuous valence band (V_B) and conduction band (C_B) in the crystallized domains, this process could be attributed to the non-degenerate two photon absorption (2PA) between the pump beam and probe beam. [116] Following this 2PA process, the PIA slowly builds up with time (~ 10 ps). This process could be assigned to the slow hot charge carrier cooling within the nano-crystallized domains. In most of the semiconductors, the excited state absorption cross-section for the charge carriers located at the band edge is larger than that for the hot charge carriers. In large crystallized Sb_2S_3 domains (~ 30 nm), the multi-exciton Auger recombination lifetime is expected to lengthen. As shown in Figure 4.27, the lifetime of the pump fluence dependent process in annealed Sb_2S_3 is in several hundreds picoseconds, which closely matched with the reported values for large size semiconductor nano-crystals prepared with solution methods. [94] Lastly, the charge carrier recombination time in crystallized Sb_2S_3 is determined to be 16.7 ns.

Figure 4.26 Pump fluence dependence of the transient decay kinetics with 400 nm pump and 570 nm probe for as-deposited ALD Sb_2S_3 film in short-time (a) and long-time (b) window.

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Figure 4.27 Pump fluence dependence of the transient decay kinetics with 400 nm pump and 570 nm probe for annealed ALD Sb_2S_3 film in short-time (a) and long-time (b) window.

Chapter 5

Conclusions

5.1 Device fabrication

Nano-crystalline Sb_2S_3 were prepared by chemical bath deposition method, and characterized by XRD, UV VIS spectroscopy, TEM and EDX. From XRD, the stibnite phase with orthorhombic structure was identified with diffraction peaks of (020), (120) and (130). The band gap of annealed Sb_2S_3 was determined to be about 1.8 eV. Traces of antimony oxide (Sb_2O_3) were also observed. The effect of oxidation has led to a decrease in current density J_{sc} , from 4.52 mA/cm^2 to 1.89 mA/cm^2 , a 3 fold decrease in J_{sc} . A further HCl etching step has lead to an improved current density, J_{sc} to 6.5 mA/cm^2 . With variation in the photo-anode structure, a TiO_2 film with $>100 \text{ nm}$ nanoparticles exhibited efficiencies of 2.3 %, a J_{sc} of 10.84 mA/cm^2 and a peak EQE of $\sim 65 \%$. In contrast, home-made paste devices fabricated from 50 nm particles exhibited about 1.15 %, with J_{sc} of 6.52 mA/cm^2 and a maximum EQE of 45 %. An interfacial buffer $\text{In}(\text{OH})_x\text{S}_y$ and Sb_2O_3 was utilized for controlling surface recombination in the ssDSC. From the results, it is shown that the addition of $\text{In}(\text{OH})\text{S}$ led to improvement both in J_{sc} and V_{oc} . The variation of the thickness study of photo-anode structure prepared by screen-printing provides information that the $1.8 \mu\text{m}$ thick films were more suitable for the deposition of the Sb_2S_3 absorbers. The structure formed from the thinner films ($1.2 \mu\text{m}$ and 550 nm) might not provide a good structure for bath deposition. Antimony sulfide solar cells fabricated with two different hole transport materials, P3HT and Spiro were also investigated, with devices

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fabricated with P3HT yielding better photovoltaic performance. The wetting property of Spiro-OMeTAD requires further study although a high V_{oc} of 0.61V was achieved. P3HT showed better photovoltaic performance attributed to metal-sulphide bonding and supported by computational studies. The crystallite size of the CBD antimony sulfide films with 1 h -3 h deposition times (and hence varying thicknesses) is about 19-20 nm and did not appear to impact solar cell performances. The possibility of using Sb_2S_3 as an extremely thin absorber was finally investigated using ALD deposited absorber layers. As deposited ALD films were amorphous in nature, and compared with the amorphous films, crystallized Sb_2S_3 (prepared by ALD) domains gave rise to a stronger non-degenerate two photon absorption, slower hot charge carrier cooling (~ 17 ps) and slower multi-exciton Auger recombination when probed with transient absorption spectroscopy. From the findings, the crystallized domains slow down the photo-induced charge carrier recombination from 7.5 ns to 16.7 ns. The increased light absorption, slower hot charge carrier cooling and charge carrier recombination strongly suggest that the annealed Sb_2S_3 is more suitable for light harvesting application than the as-deposited (non-annealed). Finally, ALD deposited layers could provide suitable pathways for solar cell fabrication.

Chapter 6

Recommendations for Future Work

6.1 Overview

Interfacial engineering is one of the important aspects in semiconductor sensitized nano-porous solar cells, with the aim to realize solar cells which are robust, low cost and highly efficient for future solar panel market. A summary of the recommendations for future work is described below.

6.2 Effect of TiO₂ nanostructures

One-dimensional (1D) nano-structure such as TiO₂ nanorods have also been used of sensitization for ssDSCs. TiO₂ nanorods offer advantages as compared to TiO₂ nanoparticles in terms of better conductivity, higher light absorption efficiency due to light scattering mechanism and less grain boundaries. The electron, once it is injected from the sensitizer, can reach FTO faster in TiO₂ nanorods due to the lesser distance travelled.

Figure 6.1 Schematic structure of a nanoparticle and a nanorod structure. [118]

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The infiltration of sensitizer and HTM into the tubes could also be facilitated by the 1-D structure. Preliminary study was conducted via a two-step anodization to produce a free standing membrane of titania nanotube array.

Figure 6.2 (a) and (b) FESEM images of TiO₂ nanotubes via anodisation process. [119]

Chapter 6: Recommendations for future work

6.3 To investigate the charge transport with use of polysulphide/electrolyte

Despite the emergence of semiconductors as sensitizers in nanoporous solar cells, the efficiency is still very much lower than the liquid-based dye sensitized solar cells. One of the challenges to achieving higher power conversion efficiency is due to difficulty in pore infiltration of the mesopores in TiO_2 with solid-electrolyte and a uniform coating of the semiconductor on TiO_2 . Hence, with I-DSCs employing a photo-anode of ~ 10 to $12\ \mu\text{m}$ mesoporous TiO_2 layer adsorbed dye, the photo-anode of solid-state based cells is limited to only 2 to $3\ \mu\text{m}$. [120]

In the preliminary work, 2 different hole-transporting materials (Spiro-OMeTAD and P3HT) are studied. One of the recommendations for future work is to evaluate $\text{Sb}_2\text{S}_3/\text{TiO}_2$ charge transport using polysulphide electrolyte/Pt. Polysulphide has been demonstrated as a suitable electrolyte with PbS, CdS [121] quantum dots cells and cell function stability without photo-degradation. It is commonly prepared using aqueous solution. However, as aqueous electrolyte has higher surface tension and hence posed difficulty for penetration into the TiO_2 matrix, alcohol/water co-solvent is used. Furthermore the composition in the electrolyte system can be varied for tuning energy alignment to better match with antimony sulphide sensitizer for efficient hole transport.

6.4 Vapour Phase (VPP-PEDOT) deposition

Figure 6.3 (a) and (b) FESEM images of the coated nanostructures from PEDOT vapour phase deposition. [122] (c) Molecular structure of EDOT monomer and iron(III) tosylate molecular structure for PEDOT deposition. (d) Schematic of PEDOT polymerization setup.

One of the crucial factors for evaluating the low efficiency of solar cells is incomplete pore filling of solar cells, resulting in lower J_{sc} and FF . Vapour phase deposition is one of the techniques which could assist in filling the pores of TiO_2 electrode. The setup is shown in Figure 6.3 (d) where thin films of PEDOT polymer are coated on substrates/fibers. PEDOT films are formed from monomers of EDOT and the oxidizing agent iron (III) tosylate. [122, 123] However, further study on the film formation as a result of the wettability, hydrophobicity and thicknesses could be discussed in future.

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6.5 Electrochemical Impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is a steady-state method which measures the current response to an applied ac voltage as a function of frequency. This technique is advantageous as very tiny ac voltage exerting a small perturbation on the system. Subsequently, the transient response is fitted to an equivalent circuit which consists of circuit elements such as resistors, capacitors, inductors. For ssDSC, several models have been developed. Generally, the data could be represented in the Nyquist diagram (complex plot) as reactance vs. resistance which gives information such as sheet resistance, transport resistance, charge transfer resistance at counter electrode, and charge transfer resistance between TiO_2 film and electrolyte at different frequencies. Parameters such as diffusion length can be extracted.

$$L_n = \sqrt{(D_o \cdot \tau_o)}$$

Where L_n represents the diffusion length

D_o represent the diffusion coefficient,

τ_o represents the lifetime of electrons in the conduction band

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Figure 6.4 Two channel transmission line model used to fit the impedance data of (a) ssDSCs (b) solid-state ssDSC. r_t represents the transport resistance in TiO_2 , r_{ct} the interfacial charge-transfer resistance (or recombination resistance) between electron and hole carrier media, q_μ the chemical capacitance of TiO_2 , and r_{HTM} the resistance of the hole-transporting material[124, 125].

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Appendix

Appendix A

TOPAS analysis

XRD pattern of the FTO glass, FTO/TiO₂ films and FTO/TiO₂/Sb₂S₃ film

TOPAS analysis of a 3 h-deposited TiO₂/Sb₂S₃ electrode.

Appendix B

Sintering conditions of TiO₂ films

Appendix C

Sintering conditions of TiO₂ films

Material	Φ (eV)	X (eV)	E_g (eV)
FTO	4.5[32]	5.0[32]	3.8[32]
TiO ₂	4.5[32]	4.2[32]	3.2[32]
In(OH)S	4.7[18]	3.7[126]	2.4[127]
Sb ₂ S ₃	4.7	4.18[128]	1.72[128]
Au	5.1[129]		
	HOMO	LUMO	
Spiro-OMeTAD	4.8[130]		
P3HT	5.0-5.1[131]	3.0[131]	
PEDOT:PSS	5.2[132]	3.2[133]	

Appendix D

Fig. Morphology of TiO₂ film consisting of ~100 nm sized particles.

Publications

1. Gui, E.L., *et al.*, Effect of TiO₂ Mesoporous Layer and Surface Treatments in Determining Efficiencies in Antimony Sulfide-(Sb₂S₃) Sensitized Solar Cells. Journal of the Electrochemical Society, 2012. **159**(3): p. B247-B250
2. Investigation of the effect of TiO₂ nanoparticle/nanowire in semiconductor (Sb₂S₃) sensitized solar cells , ICMAT 2011 [poster presentation]
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