DEPOSITION AND PROPERTIES OF MoO$_3$ FOR HYBRID SOLAR CELLS

MOO$_3$ SADESTUS JA OMADUSED RAKENDAMISEKS HÜBRIIDPÄIKESEELEMENTID

Master Thesis
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Tallinn, 2018
AUTHOR’S DECLARATION

Hereby I declare, that I have written this thesis independently.

No academic degree has been applied for based on this material. All works, major viewpoints and data of the other authors used in this thesis have been referenced.

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THESIS TASK

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Thesis main objectives:

1. To fabricate MoO$_3$ thin films using vacuum thermal deposition methods.

2. To determine the structural and optical properties of vacuum deposition MoO$_3$ thin films which is to be used as an interfacial buffer layer for hybrid solar cells.

3. To ascertain if MoO$_3$ thin films is a suitable interfacial buffer layer for hybrid solar cell.

Thesis tasks and time schedule:

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<td>Deposit MoO$_3$ on glass substrate using vacuum thermal evaporation method</td>
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<td>Thermal annealing of produced MoO$_3$ films at different temperatures</td>
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<td>Characterize the properties of as – deposited films and films annealed at different temperatures by UV – VIS, XRD, SEM and EDX.</td>
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<td>Evaluate the performance of the as deposited MoO$_3$ films as interfacial layer in hybrid solar cells ITO/TiO$_2$/Sb$_2$Se$_3$/P$_3$HT/MoO$_3$/Au against a reference solar cell ITO/TiO$_2$/Sb$_2$Se$_3$/P$_3$HT/Au</td>
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Before you lies the thesis titled “Deposition and properties of MoO$_3$ for hybrid solar cells”. The project involves the production of MoO$_3$ thin films via vacuum thermal evaporation and the characterization of the thin films to determine its suitability as interfacial buffer layer for an inverted hybrid solar cell. This thesis has been meticulously written to fulfil the graduation requirements of the Masters of Engineering Degree in Materials and Sustainable Energetics Programme at Tallinn University of Technology, Estonia.

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Jude Awele Okolie
List of abbreviations, terminologies and acronyms

a, b, c and h, k, l     Lattice parameters
CO2                  Carbon dioxide
d_khl                Plane spacing values related to the Miller indices
EDX                  Energy dispersive X-ray spectroscopy
Eg                   Optical energy band gap
ETL                  Electron transport layers
FF                   Fill factor
HTL                  Hole transport layers
J_sc                 Short circuit current
M1–M6                As-deposited films and films heated at 150, 200, 300, 400 and 500 °C respectively
MoO3                  Molybdenum oxide
N2                   Nitrogen
OPV                  Organic photovoltaics
PCE                  Power conversion efficiency
PEDOT:PSS            Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
PV                   Photovoltaics
P3HT                 Poly(3-hexylthiophene 2,5-diyl)
SC                   Solar cells
SEM                  Scanning electron microscopy
V_oc                 Open circuit voltage
XRD                  X-Ray Diffraction
INTRODUCTION

Over the last decade, the emission of carbon dioxide (CO$_2$) and other obnoxious gases that promote global warming has increased tremendously as a result of the continual usage of coal, natural gas, and petroleum resources [1]. In the event of the accelerating impact of greenhouse gases coupled with the depleting nature of fossils fuels, there is an urgent need to explore renewable and sustainable sources of energy for societal and industrial benefits. Wind, biomass, hydro power, solar power and geothermal are renewable energies that has been widely explored to compliment the usage of fossils. However, of all the renewable energy sources only solar, geothermal and biomass can be used to produce adequate heat energy needed for power generation [2]. Most interestingly, solar power exhibits the highest worldwide potential of all the three since biomass is not present everywhere in nature and geothermal sources are restricted to only few locations [3].

Solar energy is the energy from the sun produced for the earth. Hypothetically solar energy has the potential to satisfy the energy demand of the whole world with almost four million exajoules (1 EJ = 10$^{18}$J) of sunlight energy reaching the earth surface yearly [4]. Photovoltaic (PV) Solar cells convert sunlight into a clean and reliable renewable energy sources. In the early years silicon (Si) solar cells has been dominant in the PV market. This is largely due to the abundance of Si, environmental benign nature and high stable cell efficiencies together with the tons of readily available skills related to silicon devices [5]. However, despite the benefits of Si solar cells, high cost due to purification and manufacturing techniques is still a major challenge that slows down the progress of monocrystalline Si. In an attempt to reduce the manufacturing cost of solar cells by eliminating the use of Si materials thin films are used [6]. Nevertheless, thin films solar cells are characterized by limited stability, technological challenges and a relatively small market share [7]. This limitation brought about an interest in the third generation solar cells.

The third generation solar cells comprises of the dye-sensitized solar cells (DSSCs), organic and inorganic solar cells, polymer cells and quantum dot cells [8]. Conventional solar cells produced from inorganic material offers high efficiency [9], they can also be produced as nanoparticles, these gives them distinct features such as high absorption coefficient and size tunability. However, their usage is limited due to the high cost of inorganic materials coupled with the energy intensive processing methods [10]. Recently there has been renewed interest in the use of organic materials for photovoltaic applications. Solar cells made from organic materials are inexpensive and their properties can be adjusted by chemical synthesis.
and molecular design [10]. Organic solar cells can also be produced using phase technologies such as inkjet printing or various roll to roll techniques, which makes them relatively cheap [11,12]. This offers significant benefits compared to the expensive inorganic solar cells. In order to solve the challenges of inorganic solar cells, new methods of producing cost effective and high efficiency solar cells that combines the unique features of inorganic materials with the thin film forming properties of organic materials is invaluable. Hybrid solar cells are produced by combining organic and inorganic materials, they are cheap alternatives to conventional solar cells. Hybrid solar cells are manufactured with the possibility of utilising the inexpensive and cost effective production of organic solar cell materials together with other benefits such as tuneable absorption spectra from the inorganic component. Despite the immense benefits observed in hybrid solar cells their efficiencies are quite low, also they have a limited lifetime and stability [13]. To prolong the lifetime of Hybrid solar cells, increase their efficiency and obtain the desired stability needed for commercial applications interfacial buffer layers are used. Buffer layers prevents the diffusion of the cathode materials into the active layers thereby enhancing the stability of the solar cells and it also helps to smoothen the anode and surface [14]. PEDOT: PSS is the most commonly used anode buffer layer in hybrid solar cells, however its hygroscopic and acidic nature (leading to organic solar cell degradation in ambient conditions) also its inhomogeneous electric properties is still a major challenge [15,16]. So far it has been unsuccessful Substituting the PEDOT: PSS layer and other interfacial layers in maintaining the required conversion efficiencies due to the high resistance possessed by the interfacial layers. Also, the use of high vacuum deposition technique to deposit the low work function electrodes in conventional hybrid solar cells tends to increase fabrication cost. A good alternative to alleviate the problem is to use a PEDOT: PSS free inverted device structure in which the polarity of the electrode collecting the charge is reversed [17]. In that way, electrons can be extracted from the transparent cathode and holes at the anode thereby enhancing the device stability and lifetime [18]. Also, the inverted architecture saves cost by using non-vacuum deposited metal electrode at the top interface [19]. Nevertheless, the performance of an inverted solar cell is still dependent on the interfacial buffer layer, which should be electrically conductive and transparent [17]. Choosing a suitable interfacial buffer layer for an inverted solar cell in order to optimize its performance is an issue that needs further attention.

A number of studies has reported the use of metal oxides as interfacial buffer layers for solar cells [17,18,20,21]. Recently Molybdenum oxide (MoO₃) thin films has drawn more attention as an interfacial buffer layer for hybrid solar cells due to its interesting optical, chemical and electronic properties [22–
MoO$_3$ has a wide band gap, layered structure and it also exhibits multiple valence states and characterized by high transmittance and high work function [26]. The use of thermally evaporated MoO$_3$ in hybrid solar cells shows increased lifetime and comparable performance to that of PEDOT:PSS [27]. MoO$_3$ serves as a protective layer against atmospheric oxygen and humidity. In addition, decreases hole recombination at the electrodes due to its unique electronic properties [27].

Conversely it is important to optimize the growth conditions of MoO$_3$ and produce pure thin films with precise morphology, structure and optical properties for hybrid solar cells [28]. An understanding of the composition, structure and properties of MoO$_3$ thin films is of immense importance in the optimization of the growth conditions. The aim of this research is to investigate for the first time the composition, structural and optical properties of vacuum deposited MoO$_3$ as a protective layer for hybrid solar cells and investigate the effect of thermal annealing on the structural and optical properties of the produced MoO$_3$ thin films. Furthermore, we compared the performance of MoO$_3$ as a protective layer for an inverted solar cell with device configuration of ITO/TiO$_2$/Sb$_2$S$_3$/P$_3$HT/MoO$_3$/Au against a reference solar cell ITO/TiO$_2$/Sb$_2$S$_3$/P3HT/Au. The novelty of this work lies in the fact that no study has reported the use of MoO$_3$ as an interfacial buffer layer for an inverted hybrid solar cell with configuration ITO/TiO$_2$/Sb$_2$S$_3$/P$_3$HT/MoO$_3$/Au.

The thesis is organized as follows:

Chapter I provides an up-to-date literature review with a focus on the characteristics of solar cells and the evolution of solar cells from first to third generations of solar cells with lucid examples. Furthermore, the evolution of hybrid solar cell is introduced together with the structure and working principles, an overview of the advantages and limitations of organic and inorganic materials is also discussed. Additionally, the structure of MoO$_3$ as interfacial layer in hybrid solar cell is also described and different thin film deposition methods are discussed. Finally, the aim and scope of this thesis is elucidated.

Chapter II Describes the experimental methodology used in the deposition of MoO$_3$ on glass substrate as well as the method of characterization. The vacuum thermal evaporation method was used with a detail description provided. Also, a general description of each characterization method used is described.

Chapter III Critical analysis of the experimental results and discussion.

Chapter IV Presents the conclusions and recommendations for future work.
CHAPTER I: LITERATURE REVIEW

1.1 Photovoltaic solar cells

Solar cells convert sunlight energy into electrical power. The electrical power is defined as the product of electric current (I) and electrical voltage or electrical potential (V). The two main functions of a solar cells are: generation of a photovoltage and photocurrent generation [29]. Solar cells operate on the principle of photovoltaic effect. A semiconductor is used as a light absorber to convert photons from sunlight into an electron-hole pair (Photocurrent generation). The holes and electrons are then separated by the device structure. Electrons migrate to the negative terminals while the holes move to the positive terminals thus producing electric power [30]. Charge separation inside the solar cells leads to the generation of a photovoltage. The working principle of a modern solar cell is illustrated in Figure 1.1: Photon absorption occurs throughout the silicon crystal wafer and extends outside the depletion region while the charge separation involves diffusion of photo-excited charge carriers towards the depletion region.

![Diagram of Photovoltaic Solar Cells](image)

*Figure 1.1: Working principles of Si solar cells [Adapted from ref [31]].*
A schematic representation of a solar cell under illumination is presented in Figure 1.2 [31]. Light releases photons from the covalent bonds holding the semiconductor together by entering the gaps between the top contact metal. Mobile charge carriers of the same polarity within the cells are aligned and they move in the same direction with the aid of a p-n junction within the cell. Flow of electrons will complete the circuit and electrical current would be produced if an electric load, such as a lamp is connected between the top and rear contacts of the cell [31].

Figure 1.2: Energy from sunlight is absorbed and converted into electrical current flow in a load such as a lamp connected between the cell contacts [adapted from ref. [31]].

1.1.1 Characteristics of solar cells

The basic characteristics of the solar cells are the short circuit current ($J_{sc}$), open circuit voltage ($V_{oc}$), the fill factor (FF) and the power conversion efficiency (PCE). These parameters are used to ascertain the performance of solar cells. Short circuit current refers to the current produced under illumination without the influence of any external potential. When there is no current flowing through the terminals of the solar cells under illumination, a potential difference exists. This potential difference is known as the open circuit voltage. Fill factor is defined as the ratio of maximum power generated by the solar cell to the product of short circuit current and open circuit voltage. The solar energy conversion efficiency is the ratio of maximum power generated by the solar cell to the energy of incident radiation. Figure 1.3, shows the current voltage characteristics of a solar cell with and without illumination. The short circuit current ($J_{sc}$), open circuit voltage ($V_{oc}$) and fill factor (FF) are identified in the figure 3 [32].
1.1.2 Photovoltaic solar cell evolution.

The first generation solar cells are based on silicon wafer, they are mainly single crystals and bulk polycrystalline silicon wafers. They provide solar conversion efficiencies 16-21% (Figure 1.4) depending on the quality of the wafer and the manufacturing techniques.
Polycrystalline silicon materials are used to replace single crystal silicon materials due to their high cost and sophisticated technological steps involved in the use of single silicon wafer. The second generation solar cells are made from thin films [34]. Thin film technology involves the deposition of thin layers of semiconductor materials on a supporting substrate such as a large glass sheet [31] (Figure 4). Thin film technology requires semiconductor materials with thickness of about 100-10000 times less than that of a silicon wafer. The technology also offers potential cost reduction in manufacturing process compared to the first generation solar cells. In addition, thin layer solar cells require flexible substrates, low temperature processes integrated cell insulation and high automation level in series production. This attributes lowers their production cost and enhances the probability of this solar cells to participate effectively in the energy conversion sector [34]. In thin film solar cells virtually any semiconductor material can be used due to the reduced material requirements. There is also a wide range of semiconductor materials to select from since semiconductors can be formed from single elemental atoms, alloys involving multiple elements and compounds [35]. Cadmium sulphide device dominated the early years of thin film technologies until its stability were perceived insolvable [33]. Some other examples of thin film materials includes copper–indium–gallium–selenide (CIGS) and related compounds, cadmium telluride (CdTe) [33].

Figure 1. 5: Thin film technology approach [adapted from ref. [33]].
Majority of the third generation solar cells comprises of the dye-sensitized solar cells (DSSCs), organic and inorganic solar cells, polymer cells and quantum dot cells [8]. Their sole aim is to increase device efficiency which is one of the demerits of second generation solar cells and also to reduce cost which is one of the disadvantages of the first generation solar cells [8]. Figure 1.6 elucidates different generations of solar cells.

**Figure 1.6**: Different generations of solar cells [adapted from ref. [8]].

### 1.2 Hybrid solar cells.

In the 20th century, the advancement in material developments in the nanometer scale led to the generation of new photovoltaic materials and devices, one of which is the electrochemical dye-sensitized solar cell (DSSC). Grätzel and co-workers were credited for the revolutionary development of the DSSC in 1991 [36]. In this type of solar cell, nanostructured TiO₂ is sensitized by a monolayer of an organic dye as shown in figure 1.7. The DSSC consists of an electrochemical system sandwiched between a counter electrode and a photo anode. However, due to the short lifetime, the electrochemical hole
The conductor was replaced with a solid hole conductor in DSSC. Later, the organic dye was also replaced with an inorganic absorber material which gives rise to hybrid solar cell.

![Figure 1. 7: Structure of a typical dye sensitized solar cell [Adapted from ref [37].](image)](image)

Organic-inorganic hybrid solar cells combine the unique features of both organic and inorganic materials. The advantages of organic solar cells include their low manufacturing cost, easy fabrication method, high processing speed and excellent mechanical properties [38, 39]. Despite the immense benefits of organic solar cells, some challenges still exist. For instance, during the preparation of the conjugated polymers in organic solar cells, the solvents used are usually hazardous and not environmentally friendly [39]. Also, the issues of low power conversion efficiency and poor operational stability are still unsolved [38]. On the contrary, inorganic materials are environmental friendly, improved light absorption spectra, quantum confinement advantages and ultrafast induced charge carriers [40]. In hybrid organic-inorganic solar cells, organic materials (usually the conjugated polymer) is combined with inorganic nanoparticles with the aim of utilizing the benefits associated with both material groups [40, 41]. In that way, the low cost of materials of the organic section can be maintained while the inorganic part provides further advantages to the solar cells [40]. Incorporating organic and inorganic materials in solar cells provides lots of benefits. Firstly, inorganic materials are more environmentally benign compared to the organic counterparts, therefore the additional of the material to organic materials would help prevent the photo induced degradation of conjugated organic semiconductors.
Secondly, light absorption in organic material is greater than that of the organic materials [42]. Lastly it is generally perceived that the inorganic quantum dots produce ultra-fast induced charge carriers to organic materials. The next section introduces the structure and working principle of a typical organic-inorganic hybrid solar cell.

1.2.1 Device structure and Working principle of Organic-Inorganic Hybrid solar cells

A typical hybrid solar cells consists of thin film devices with photoactive layers sandwiched between two electrodes having different work functions. The anode typically consists of transparent and highly conductive indium tin oxide deposited on a flexible glass substrate. The function of the anode is to allow the passage of light through the material and collect holes from the device. The photoactive layers consist of both organic and inorganic part. A metal cathode electrode made of either Al, LiF/Al, Ca/Al is vacuum deposited on the top of the photoactive layer. The cathode collects electrons from the device and the layer is usually deposited via thermal evaporation. Schematic representation of a typical organic – inorganic hybrid solar cell is shown in figure 1.8 [43].

![Schematic representation of a typical Organic - Inorganic Hybrid solar cells](image)

Figure 1. 8: Schematic representation of a typical Organic - Inorganic Hybrid solar cells [43].
The photoactive layers usually exist in two different structures; the bilayer structure and the bulk heterojunction structure as shown in Figure 1.8. The bulk heterojunction structure is obtained by just bending the acceptor and donor materials and depositing the bend on the substrate. On the contrary bulk inorganic photon absorption in organic semiconductor materials do not produce free charge carriers rather they generate strongly exciton which are known as tightly bound electron-hole pair [44]. However for optimum performance the distance between the exciton and the electron donor/acceptor interface should be within the same length range this explains why the bulk- heterojunction structure was introduced to enable the blending together of the donor electrons and acceptor materials [45].

It should be noted that another conducting layer is usually added between the anode and the photoactive layer as shown in figure 1.9. This layer could serve as hole transporting layer (HTL) and exciton blocker. It also smoothenes the indium tin oxide surface helps to seal the active layer from oxygen and also helps to prevent the diffusion of cathode materials into the active layers thereby enhancing the device stability [46]. If the diffusion was to occur it could lead to unwanted trap sites [40].

![Figure 1.8: Structure of an organic- inorganic hybrid solar cell.](image)

PEDOT:PSS is the commonly used HTL because of its high work function, good electrical conductivity and the ability to reduce the surface of the surface roughness of indium tin oxide [47]. However, PEDOT: PSS is known to exhibit several problems which includes; inhomogeneous electrical properties which
often leads to weak long-term stability, highly hydrophilic with bad morphology. On the contrary transition metal oxides such as, V$_2$O$_5$, NiO, MoO$_3$ has been employed as HTL for hybrid solar cells by a plethora of researchers [48–50]. The metal oxides have been used as alternatives to PEDOT:PSS due to their high stability as visible in organic solar cell and flexibility in deposition method as they can be deposited using various methods such as electrodeposition, sputtering or vacuum evaporation [51,52]. Compared to other metal oxides MoO$_3$ has emerged as the promising alternatives to PEDOT: PSS as HTL because of its non-toxicity and non-corrosive nature together with its deep-lying electronic states [53]

1.3 Structure of MoO$_3$ thin films

Molybdenum oxide has been a subject of immense interest due to their unique electrical and optical properties, it is widely perceived that the transition metal oxide can be switched between two different optical states due to its thermochromic, photochromic or electrochromic effect [54]. Thermochromic effect of films refers to the change in the optical properties of a substance with temperature. A film with thermochromic effect changes their optical properties reversibly when heated and reverts back to its original properties when the temperature is cooled to its initial temperature [55]. Photochromic as the name suggests refers to the reversible absorption changes the films undergoes when exposed to different types of irradiation and then retains its original properties without the irradiation while electrochromic effect is the ability of thin films to change their color due to an applied potential and returns back to its original form when the electric potential is reversed [55]. For Molybdenum oxide the MoO$_{3-x}$ with oxygen deficient usually contains excess metal atoms. These metal atoms behave like doping centers that controls the electrical and optical properties of the films. α-MoO$_3$ exists with a layered structure with dual layers of MoO$_6$ octahedral that are joined together in the (1 0 0) and (0 0 1) directions by covalent bonds and (0 1 0) direction by weak Vander waals forces of attractions [54]. Due to the uniqueness of the Molybdenum oxides it finds useful applications in rechargeable micro batteries, optical switching, electrochromic materials and humidity sensors [56].

XRD patterns of MoO$_3$ films has been used to identify and study the phases present by a plethora of researchers [28,54,56]. XRD study of MoO$_3$ thin films by Mahajan et al., [28] showed that the deposited thin films are polycrystalline with well-defined diffraction peaks along (0 2k 0) reflections with k= 1, 2 and 3 (Figure 1. 10). Their results also show that the films contain MoO$_3$ with α-orthorhombic structure. One important observation is the increase in crystallinity with solution concentration, however the authors attributed this to the increment in crystal size as the concentration increases [28]. A similar study by Boudauord et al., [56] also confirm the polycrystalline structure of MoO$_3$ films.
1.3.1 The role of MoO$_3$ in the interface of the hole conductor/cathode electrode

The use of MoO$_3$ as interfacial material in hybrid solar cell is very critical to the performance and stability of the solar cell. MoO$_3$ helps in the optimization of the electric contacts between the electrodes and the active layers leading to improved charge transfer and collection [27]. In bulk heterojunction solar cells (BHJ) a bicontinuous pathway is created for charge carriers to migrate to their corresponding electrode. However, it should be noted that in the active layer of the BHJ, both the donor and acceptor semiconductor are randomly distributed. The donor is usually a polymer most often poly (3-hexylthiophene-2,5-diyl) (P3HT) while the acceptor is a fullerene derivative usually phenyl-fullerene-butyric acid methyl ester (PCBM). There is a possibility that both the donor semiconductor and acceptor semiconductor could be in intimate contact with the cathode and anode in the solar cell. Recombination of charge carriers at the electrode would greatly reduce the PCE and stability of the solar cell. For this reason, interfacial materials such as MoO$_3$ is introduced to ensure that charge carrier recombination is greatly reduced by allowing the movement of the preferred charge carriers and blocking the movement of unwanted charge carriers. With the use of interfacial materials, the PCE of solar cells is greatly improved [27,57–59].

![XRD patterns of MoO$_3$ thin films deposited by spray pyrolysis at different solution concentrations 5 mM (Mo1), 10 mM (Mo2) and 15 mM (Mo3) at 350°C substrate temperature [ adapted from ref. [28]].](image_url)
As shown in figure 1.11 interfacial materials could be HTL or ETL. The diagram illustrates the schematics representation of conventional hybrid solar cell and inverted solar cells with HTL and ETL. Figure 1.12 illustrates the energy level of a solar cell with MoO$_3$ as HTL.

Figure 1. 10: Schematic representation of (a) conventional solar cell and (b) inverted solar cell. [Adapted from Ref. [57]].

In an inverted solar cell, the polarity of the electrode material collecting the charge is reversed. When compared to the conventional solar cell configuration, the inverted structure is suitable for large scale roll to roll processing. Furthermore, the use of high work function metal electrodes provides superior device stability.

Figure 1. 11: Energy diagram of a solar cell with configuration of ITO/Ag$_2$S/P3HT: PCBM/MoO$_3$/Au.
1.4 Method of MoO₃ Deposition

A number of different methods could be used to prepare Molybdenum oxide thin films. Examples of such methods includes, chemical bath deposition, spray pyrolysis, electrodeposition, sputtering and thermal evaporation. The next section would discuss each of the methods.

1.4.1 Chemical bath deposition

Chemical bath deposition methods also known as controlled deposition, solution growth or simply chemical deposition method is relatively inexpensive, flexible and easy for large surface area deposition and does not require the use of sophisticated instruments such as a vacuum system [60]. Instead it uses cheap and readily available materials such as hotplate with magnetic stirrers. Also, the required starting chemicals are inexpensive and available. It is similar in the liquid phase to the common chemical vapor deposition which occurs in the gaseous phase. Figure 1. 13 shows a schematic of the experimental set up for chemical bath deposition.

![Diagram of chemical bath deposition experimental set up system](adapted from ref. [60]).
As shown in the figure 1.13, the substrate and the films are placed stationary in the solution. With the aid of a magnetic stirrer the solution is stirred, and the chemical bath is heated to the desired temperature using paraffin bath or water. It should be noted that the stirring could be continuous from room temperature or it could be started only after attaining the required temperature.

### 1.4.2 Chemical Spray Pyrolysis

Chemical spray pyrolysis has been used over the last decade for the deposition of a variety of materials as thin films. This technique provides one of the most attractive ways for the deposition of thin films of metal oxides, superconducting compounds, noble metals and chalcogenides [61]. Spray pyrolysis method offers the following advantages compared to other deposition methods: (i) its simplicity because it provides an easy way to dope films of any element and in any proportion by simply adding it in the form of a spray solution (ii) Unlike the Vapor deposition methods, spray pyrolysis techniques do not require a vacuum. This is an immense advantage especially when the process is required to be scaled up for industrial applications, also spray pyrolysis does not require substrates and/or high quality targets [61] (iii) The ability to control the thickness and deposition rate of the thin films by simply changing the spray parameters in this way some limitations of chemical methods such as films of limited thickness can be avoided (iv) This method does not produce any additional overheating that could destroy the materials unlike high powered methods like magnetic sputtering (v) Layered films with composition gradients can be obtained by simply changing the composition of the spray solution during the spray process. Figure 1.14 illustrates a typical spray pyrolysis set up. The apparatus consists of a spray nozzle, substrate heater, temperature controller, precursor solution and gas propellant. Liquid and gas flow meters are often used to measure the flow of precursor’s solution and the air. The spray pyrolysis set up is usually mounted on a moving table. It should be noted that properties of the produced films are largely dependent on the carrier gas, ambient temperature, droplet size, and the cooling rate after deposition. On the other hand, the film formation is dependent on the reaction, solvent evaporation and the process of droplet landing. Patil, [45] presents an excellent review of chemical spray pyrolysis technique.
1.4.3 Electrodeposition

Electrodeposition is widely regarded as an environmental friendly deposition technique that does not need vacuum environment or high temperature treatment to produce a solar cell [62]. The technique is good and highly efficient when film thickness and surface profile of the deposited film is to be varied [63]. During electrodeposition, materials wastage can be greatly minimized by controlling the deposition parameters. Analogous to vacuum thermal evaporation, electrodeposition allows the production of different layers of solar cells.

The schematics of a typical electrodeposition process is shown in figure 1.12.
As shown in figure 1.15, electrodeposition the electrochemical reaction starts with PbO which then diffuses into the surface of the electrode (the substrate coated with TiO₂) to form a perovskite thin layer. The uniqueness of this process lies in the ability to produce a uniform thin film by easily controlling the thermodynamic deposition parameters which are directly related to the specific film thickness and smooth surface profile enhancements [62]. It should be noted that uniformly deposited thin films enables the increase in power conversion efficiencies in devices by controlling the deposition time, concentration of the electrolytic solution and the deposits [64].

1.4.4 Vacuum thermal evaporation

In vacuum thermal deposition the substance from the thermal vaporization sources reaches the substrate without collisions or limited collision with the gas molecules in the space between the substrate and the source. The vaporized material is always placed in a manner that it aligns with the sight of the source. The vacuum environment is designed in such a way that it provides the capacity to minimize gaseous contaminants in the deposition system to the lowest level [65]. A gas pressure range of 10⁻⁵ Torr to 10⁻⁹ Torr is usually required for vacuum evaporation depending on the nature and quantity of gaseous material in the system. Compared to other deposition methods vacuum thermal evaporation produces a uniform microstructure and requires low process temperature on the substrate. In this work vacuum thermal deposition was used as the deposition technique.
1.5 The Scope of the present work

Based on literature review it is evident that hybrid solar cells with inverted configuration have immense advantages and would be beneficial in the photovoltaic industry to replace the expensive solar cells made from silicon materials. However, their low efficiency and life span is still a critical issue that needs further attention. This necessitated the use of interfacial buffer layers. Molybdenum oxide is identified as a very important protective for hybrid solar cells due to their wide range of band gap, ability to exist in different valence states and layered structure. In order to use MoO$_3$ as a buffer layer for hybrid solar cells it is important to optimize the growth conditions and produce pure thin films with precise morphology, structure and optical properties. A profound understanding of the composition, structure and properties of MoO$_3$ thin films is invaluable for the optimization of the growth conditions.

The present research focus on using Vacuum evaporation method to prepare MoO$_3$ thin films on glass substrate and investigation of the structural and optical properties of the films. Furthermore, the effect of post deposition temperature on structural and optical properties of MoO$_3$ thin film is studied. The novelty of the work lies in the fact that no study has attempted to investigate the structural and optical properties of MoO$_3$ as an interfacial buffer layer for an inverted hybrid solar cell using vacuum evaporation method. Finally, the prepared MoO$_3$ film was tested as a buffer layer in hybrid solar cell ITO/TiO$_2$/Sb$_2$S$_3$/P3HT/MoO$_3$/Au and the J-V measurement is compared with that of a reference ITO/TiO$_2$/Sb$_2$S$_3$/P3HT/ Au solar cell.

1.6 The Aim of study

The overall aim of the present thesis is to understand the structural and optical properties of vacuum deposition MoO$_3$ thin films which is to be used as an interfacial buffer layer for hybrid solar cells. This is achieved sequentially as thus;

- To deposit MoO$_3$ on glass substrate using vacuum thermal evaporation method.
- To analyze the structural properties of the produced thin films (XRD, SEM, EDX), and the optical properties (transmittance, reflectance and band gap).
- To heat MoO$_3$ thin films at different temperatures and investigate the effect of temperatures on structural and optical properties.
- To deposit MoO$_3$ on an inverted solar cell with configuration ITO/TiO$_2$/Sb$_2$S$_3$/P3HT/MoO$_3$/Au.
- Determine the performance of the hybrid solar cells ITO/TiO$_2$/Sb$_2$S$_3$/P3HT/MoO$_3$/Au against a reference solar cell ITO/TiO$_2$/Sb$_2$S$_3$/P3HT/ Au.
CHAPTER II: EXPERIMENTAL METHODOLOGY

2.1 Preparation of MoO$_3$ thin films

MoO$_3$ thin films were deposited on a glass surface by vacuum thermal evaporation method as shown in Figure 2.1. MoO$_3$ powder was used as the evaporation material which was deposited on a glass substrate. MoO$_3$ powder was purchased from Alfa Aesar with 99.5 % purity. The samples of MoO$_3$ were heated in a vacuum evaporator and then evaporated using Molybdenum (Mo) boat at 19 Amperes from 2 seconds to 10 minutes depending on the thickness of the glass. The quartz crystal control monitor was used to control the thickness of the film produced and the rate of deposition. After the deposition process all films produced were thermal annealed in air for 30 minutes at temperatures of 150, 200, 300, 400 and 500 °C. This procedure is important in order to study the effecting of temperature on the structure and properties of the films produced.

![Vacuum thermal evaporation of method to produce MoO$_3$ thin films.](image)

Figure 2.1: Vacuum thermal evaporation of method to produce MoO$_3$ thin films.
2.2 Characterization of MoO$_3$ thin films produced

MoO$_3$ thin films produced were characterized by Optical transmittance (UV-VIS), scanning electron microscopy (SEM), X-ray diffraction (XRD) methods and energy dispersive X-ray spectroscopy (EDX).

2.2.2 Ultraviolet–visible spectrophotometry

To determine the optical absorption coefficient and energy band gap the optical measurement of MoO$_3$ thin films was carried out using a Jasco V-670 UV-VIS-NIR spectrophotometer (Jasco Corporation, Ishikawa-cho, Hachioji-shi, Tokyo, Japan) in the range of 250-1200 nm. UV-Vis spectrophotometry refers to the absorbance or transmittance spectrophotometry in the visible light region and it works on the principle that the absorption of energy from the incident light allows electrons to be excited from lower energy state to a higher energy state.

2.2.3 Scanning electron microscopy (SEM)

SEM images of MoO$_3$ thin films were observed using EVO MA 15 Zeiss apparatus (Carl Zeiss, Inc., Oberkochen, Germany). SEM images helps to evaluate the thickness as well as the morphology of MoO$_3$ thin films. SEM images of the thin films are taking by focusing the samples on the election beam where the electrons are made to relate with the atoms in the sample. In that way signals that contains information relating to the surface morphology and composition of the samples will be produced. Figure 2.2 represent schematic diagram of SEM.

Figure 2.2: Schematics diagram of SEM.
SEM is a kind of electron microscopy that takes images of a samples by scanning it with high energy beam of electrons. The electrons are made to interact with the atoms present in the samples thereby producing signals that contains the surface topography and morphology of the materials. The apparatus consists of the electron gun unit, scanning unit, demagnification unit, focus unit and detector unit. The electron gun produces a beam of scattered electrons which is narrowed down by the condenser lens in the demagnification unit. The produced electron is focused on the sample with the aid of an electromagnetic lens in the focusing unit which then scans the sample.

2.2.4 X-ray diffraction (XRD) and Energy dispersive X-ray analysis (EDX) Analysis

XRD patterns of MoO₃ thin films were recorded using a Rigaku Ultima IV diffractometer (Rigaku, Shibuya-ku, Tokyo, Japan) with Cu Kα radiation, λ = 1.5406 Å, 40 kV at 40 mA in the 2θ range of 20° - 80°. XRD technique is used to determine the presence of atomic and molecular structure of crystals. The atoms cause a beam of x-rays to diffract into different directions. XRD works on the principles of X-ray diffraction in which an incoming beam of light which is directed towards a crystal is scattered as they pass through atoms of the crystals. The scattered rays relate with each other and generates spots with different intensities that can be recorded on the film.

EDX analysis of MoO₃ thin films was carried out using a Zeiss HR FESEM Ultra 55 with Bruker EDS system. The EDX set up consists of an X-ray detector, pulse processor, the exciton source which is usually the X-ray beam and the analyzer. EDX is often used for the chemical characterization and elemental analysis of a sample. It works by depending on the collaborations between the sample and the source of X-ray. IN this study we use EDX to determine the elemental composition of the produced MoO₃ thin films.

2.3 Determination of the output parameters of the Hybrid solar cells.

To ascertain the performance of the prepared MoO₃ thin film on hybrid solar cells J-V curve measurements of the hybrid solar cells was carried out. The MoO₃ film was vacuum deposited on the cleaned ITO/TiO₂/Sb₂S₃/P3HT structure. It should be noted that the already stacked structure of ITO/TiO₂/Sb₂S₃/P3HT was prepared by another researcher in our laboratory. The preparation of this structure is not within the scope of the current study. This study only aims to ascertain the performance of MoO₃ as interfacial layer in the structure. Then gold (Au) which serves as the cathode material was deposited on the active layer through thermal evaporation method. The J-V characteristics of solar cell ITO/TiO₂/Sb₂S₃/P3HT/MoO₃/Au was measured and compared against a reference solar cell without MoO₃.
Figure 2.3 shows a schematics arrangement of the inverted solar cell and the reference solar cell.

Reference

ITO/TiO$_2$/Sb$_2$S$_3$/P3HT/Au

(Indium tin oxide/ Titanium dioxide/ Antimony trisulfide/ poly (3-hexylthiophene-2,5-diyl) /gold)

Inverted solar cell

ITO/TiO$_2$/Sb$_2$S$_3$/P3HT/MoO$_3$/Au

(Indium tin oxide/ Titanium dioxide/ Antimony trisulfide/ poly (3-hexylthiophene-2,5-diyl) /Molybdenum trioxide/gold)

Figure 2.3: Schematics of the hybrid solar cell used in this study and the reference solar cell. (a) ITO/TiO$_2$/Sb$_2$S$_3$/P3HT/Au and (b) ITO/TiO$_2$/Sb$_2$S$_3$/P3HT/MoO$_3$/Au.
CHAPTER III: ANALYSIS OF RESULTS AND DISCUSSION

3.1 Physical appearance of MoO$_3$ thin films after post deposition thermal annealing

The deposited thin films were heated in air at temperatures of 150, 200, 300, 400 and 500 °C. The resulting MoO$_3$ thin film after thermal treatment are represented by M1, M2, M3, M4, M5 and M6. The as-deposited thin film is denoted by M1, while M2 to M6 represents films annealed at temperatures of 150, 200, 300, 400 and 500 °C respectively. Figure 3.1 shows the appearance of specimens after thermal treatment in air. At different temperatures of the samples there is a variation in transparency. The as-deposited MoO$_3$ samples is identified with a blue color. The blue coloration might be because the film is not prepared in the dark rather through Vacuum thermal evaporation. Due to the Vacuum, Mo atom could possibly change its valence state from 6+ to 5+ [as well as to 4+ (MoO$_2$) if the amorphous film is continuously heated in the Vacuum [66]. Electrons are transferred from valence 2p oxygen orbitals to empty Mo$^{6+}$ (4d) level which gives rise to an incorporation of lower valence Mo$^{5+}$ within the lattice. The color darkens to deep blue after thermal annealing up to 200 °C. This shows that the post deposition heating of MoO$_3$ samples produces free electrons which form color centers when trapped by ion vacancies [67]. Above thermal annealing temperature 200 °C there is an increase in the transparency of MoO$_3$ thin films, which clearly highlights the non-linear dependency of the transparency of MoO$_3$ thin films with temperature when heated in air. On the contrary, a similar study by Lin et al., [68] where the authors prepared MoO$_3$ thin films by electron beam evaporation and carried out their post annealing in Nitrogen they noticed a linear dependency of the transparency of the of MoO$_3$ thin films with temperature. The appearance of their specimen after annealed at different temperatures in N$_2$ is shown in figure 3.2. We envisage that the differences between our findings and theirs might be because of the disparity in deposition and heating methods. Those two parameters could have effect on the transparency of the thin films produced. To validate the hypothesis the physical appearance of the films obtained from our study is compared to that of Sian and Reddy [69] who used a similar vacuum thermal deposition method and thermal annealing in air. It is no surprise that the two results were identical. They also obtain a light blue as deposited thin films, the color becomes darker after thermal annealing in air for an hour. As they increased the annealing temperature above 350 °C the produced films becomes lighter which indicates a non-linear dependency of transparency with annealing temperature.
3.2 Optical Properties of MoO$_3$ films and band gap measurements

Figure 3.3 depicts the optical transmittance spectra of MoO$_3$ films annealed at various temperatures with wavelength ranging from 250-1200 nm. The MoO$_3$ thin film samples show a wide variation in transmittance at different thermal annealing temperatures. Starting with the as-deposited samples, as the temperature increases to 150 °C and to 200 °C, the total transmittance declines in the same order. However, a surge in the total transmittance was observed when the MoO$_3$ thin film samples are annealed at temperatures above 200 °C. A rise in temperature from 300 – 500 °C brings about a subsequent increase in the total transmittance. The change in the transmittance of MoO$_3$ thin films at different annealing temperature could be because of its thermochromic effect. As explained in the previous section, thermochromic properties refers to the reversible change in the optical properties of a substance with temperatures. In terms of increasing total transmittance the thin films could be arranged in the order of M3< M2< M1< M4< M5< M6 with M6 exhibiting the highest total transmittance of about 85% and M3 having the lowest total transmittance of about 20%. One interesting observation is the correlation between the intensity of the blue coloration and the transmittance of MoO$_3$ samples. MoO$_3$ samples annealed at 200 °C (M3) has the lowest transmittance and the deepest blue coloration. We presumed that the variation in transmittance and the color change of molybdenum oxide annealed at various temperature is due to the photochromic and thermochromic effects of the material [70]. The unique feature distinguishes MoO$_3$ as a very interesting metal oxide with great potentials for diverse engineering applications. Analogous to this study, Lin et al., [68] also observed this interesting observation. In their findings there is a correlation between the total transmittance of the MoO$_3$ thin film samples annealed at various temperatures and the transparency of the films. The results from our study shows that both the transparency of the MoO$_3$ thin films and their total transmittance exhibits a non-linear relationship when thermal annealed in air. In another study by Boukhachem et al.[71] the authors prepared MoO$_3$ thin films by spray pyrolysis, they obtained a maximum total transmittance of about 45% for the as-deposited MoO$_3$. As stated earlier, the disparity in total transmittance could be attributed to different deposition methods used.

The absorption coefficient and the optical band gap values were determined from the total transmittance data. The absorption coefficient ($\alpha$) was calculated using the expression:

$$I = I_0 e^{-\alpha d},$$

[1]

Where $I_0$ and $I$ are the intensities of the incident and transmitted radiation, respectively, and $d$ is the thickness of the film. The band gap of MoO$_3$ films were calculated by using the expression [72]:
\[ \alpha h \nu = A (h \nu - E_g)^{\frac{1}{n}}, \]  

[2]

Where \( \alpha \) is the absorption coefficient, \( A \) is a constant related to the effective masses of charge carriers, \( h \) is the Planck constant, \( E_g \) is the band gap energy, \( h \nu \) is the incident photon energy, and \( \frac{1}{n} \) is the exponent that depends on the nature of the optical transition (\( n = 0.5 \) and 2 for direct and indirect transition, respectively). For the direct band gap estimation, a plot of \((\alpha h \nu)^2\) against the photon energy is used to estimate the band gap.

Figure 3.1: Appearance of different specimen after thermal annealing in air at different temperatures (M1 as deposited, M2 – M6 represents annealing temperatures of 150, 200, 300, 400 and 500 °C respectively. The thin film was produced by vacuum thermal evaporation.)
Figure 3.2: Appearance of different specimen after thermal annealing in Nitrogen at different temperatures. (a) as-deposited; (b) 200 °C; (c) 300 °C; (d) 400 °C; (e) 500 °C. The thin film was produced by electron beam evaporation [adapted from ref [68]].

Figure 3.3: Total Transmittance spectra of MoO₃ films annealed at various temperatures in air. Thin films produced by vacuum thermal evaporation.
Band gap of MoO$_3$ films were estimated by fitting the linear region of the plot to the zero axis. Figure 3.4 represents the plot of $(\alpha h\nu)^2$ versus energy of photon for as-deposited films. The band gap estimated from the plot is 3.3 eV. Our optical band gap value for the as-deposited MoO$_3$ thin films is consistent with literature values. Boukhachem et al.[71] obtained an optical band gap of 3.46 eV for MoO$_3$ thin films produced by spray pyrolysis. Lin et al., [68] produced MoO$_3$ thin films with electron beam evaporation and obtained an optical band gap of 3.96 eV. Since the band gap calculated is more than 2.4 eV, MoO$_3$ is considered a wide band gap semiconductor.

To investigate the relationship between the optical band gap ($E_g$) and thermal annealing temperature, we calculated $E_g$ values for all the MoO$_3$ thin film samples annealed at various temperatures. Results of the calculations is presented in Table 3.1. The plots used to estimate $E_g$ values are displayed in Appendix A1. The band gap is within the range of 3.1 – 3.86 eV for thermal annealing temperatures of 150 – 500°C. The variation in optical band gap further elucidates the hypothesis that MoO$_3$ is a wide band gap semiconductor.

![Figure 3.4: Plot of $(\alpha h\nu)^2$ versus energy of photon for as-deposited films.](image-url)
The Eg value of MoO$_3$ films heated at 150 °C is 3.1 eV, the value decreases to 2.8 eV when the sample is heated up to 200 °C. Subsequently as the temperature increases from 300, 400 and 500 °C, Eg values rose to 3.49, 3.78 and 3.86 eV respectively. The drop in Eg as the temperature rises to 200 °C could be as a result of the formation of additional oxygen vacancies in the films. Lin et al., [73] suggested that the vacancies are generated during the deposition and thermal treatment of MoO$_3$ films. These oxygen vacancies produces extra energy level in the energy gap which are relatively close enough to the valence band to act as donor centers and reduce the energy gap [69]. Therefore, as thermal treatment temperature increases up to 200 °C there is a proliferation in the concentration of oxygen vacancies leading to a reduction in the Eg of the films. In contrast, the increase in Eg of the films with annealing temperature from 200 °C to 500 °C is due to the partial filling of oxygen vacancies. Ramana and Julien [74] proposes that the oxygen might be prevented from entering the growing lattice of the substrate if re-evaporation from the film surface occurs. The sudden rise in Eg as the thermal annealing temperature is increased to from 200 to 300 °C could be explained by considering the fact that longer annealing temperature would require extended heating time in air. This means that the films would be exposed to more oxygen than required thereby decreasing the concentration of oxygen vacancies. This also explains the increase in transparency of the films at temperatures above 300 °C.

Table 3.1: The optical band gap (Eg) of as-deposited and after annealed at 150, 200, 300, 400 and 500 °C samples respectively.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Temperature (°C)</th>
<th>Direct band gap Eg, (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>As deposited</td>
<td>3.3</td>
</tr>
<tr>
<td>M2</td>
<td>150</td>
<td>3.1</td>
</tr>
<tr>
<td>M3</td>
<td>200</td>
<td>2.8</td>
</tr>
<tr>
<td>M4</td>
<td>300</td>
<td>3.49</td>
</tr>
<tr>
<td>M5</td>
<td>400</td>
<td>3.78</td>
</tr>
<tr>
<td>M6</td>
<td>500</td>
<td>3.86</td>
</tr>
</tbody>
</table>
3.3 X-Ray Diffraction (XRD) Result Analysis

XRD patterns for the as-deposited MoO$_3$ films and MoO$_3$ films heated at various temperatures in air are presented in figure 3.5a and 3.5b. The as-deposited MoO$_3$ films and films heated up to 200 °C are amorphous because no visible crystalline phase was observed in their XRD pattern. However, the crystallinity of the films increases with temperature above 200 °C. Consequently, the crystalline temperature of MoO$_3$ would probably be above 200 °C. At 500 °C, XRD shows well defined peaks of (020), (010), (040), (101), (060), (211), (171) and (261). At 300 °C the predominant peak is (040), (021) and the main crystalline phase is the α-MoO$_3$ phase. This is confirmed by the presence of peaks like (040) and (060). At about 400 °C XRD patterns detects the existence of two phases (α-MoO$_3$ and Mo$_5$O$_{14}$), as the temperature increases to 500 °C only one phase is present which is (α-MoO$_3$). Hence it can be deduced that α-MoO$_3$ is thermally stable. Similar results was obtained by Lin et al., [73]. Their findings confirm that the as-deposited MoO$_3$ thin films were amorphous, and no crystalline phase was observed as the films are annealed in both air and N$_2$ at temperatures below 200 °C. Another study by Sian and Reddy [69] also displayed similar results. Their XRD results indicate that the as-deposited thin films and films annealed for temperatures up to 150 °C are amorphous. However, they suggested a temperature of 240°C as the offset crystallization temperature of the films.

![XRD Patterns of MoO$_3$ films produced at various annealing temperatures in air.](image_url)
Some structural calculations are carried out to obtain more information about the structural quality of the deposited MoO$_3$ samples.

Lattice parameters were calculated according to the following equations:

\[
\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}
\]  

[3]

Where \(d_{hkl}\) is the plane spacing values related to the Miller indices \(h,k\) and \(l\) and \(a,b\) and \(c\) are the lattice parameters [75,76]. The values of lattice parameters obtained in Table 3.2 ranges from 3.6 to 13.9 Å. The value is similar to the results of Boukhachem et al.,[71]. The values of the lattice parameters are close to that of \(\alpha\)-MoO$_3$.

Dislocation density (\(\delta\)) of a crystal measures the number of defects present in the crystal [77]. It is defined as the length of dislocation lines per unit volume. It can be estimated from the expression [75]:

\[
(\delta) = \frac{1}{D^2}
\]  

[4]

The value of dislocation density of different samples is expressed in the Table 3.2. The dislocation density decreases significantly from $277.8 \cdot 10^{-14}$ lines/m$^2$ to $0.77 \cdot 10^{-14}$ lines/m$^2$ as the annealing
temperature of the samples increases from 300 °C to 500 °C respectively. This could possibly mean an increase in the amount of defects present in each crystal as the temperature increases.

The Debye–Scherer formula was used to estimate the crystallite size. The expression is shown below [75,78]:

\[
D = \frac{k\lambda}{B_1 \cos(\theta)}
\]

[5]

Where \( k = 0.90 \) is the Scherrer constant and \( \lambda = 1.54 \, \text{Å} \) is the wavelength of CuK\( \alpha \) radiation [75]. From the table above it shows that the crystallite size increases with temperature.

Table 2.2: Calculated values of the lattice parameters, crystallite size and dislocation density for MoO\(_3\) thin films at various annealing temperatures.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Lattice parameters</th>
<th>Phase</th>
<th>Crystallite size (nm)</th>
<th>Dislocation density (( \delta )) (10(^{14}) lines/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a (Å)</td>
<td>b (Å)</td>
<td>c (Å)</td>
<td></td>
</tr>
<tr>
<td>M6</td>
<td>3.96</td>
<td>13.8</td>
<td>3.6</td>
<td>135.40</td>
</tr>
<tr>
<td>M5</td>
<td>3.95</td>
<td>13.9</td>
<td>3.7</td>
<td>32.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \alpha)-MoO(_3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \alpha)-MoO(_3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \alpha)-MoO(_3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \alpha)-MoO(_3)</td>
<td></td>
</tr>
<tr>
<td>M4</td>
<td>3.96</td>
<td>13.9</td>
<td>3.7</td>
<td>6.0</td>
</tr>
<tr>
<td>M3</td>
<td>Amorphous</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M2</td>
<td>Amorphous</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M1</td>
<td>Amorphous</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.4 Energy dispersive X-ray spectroscopy (EDX) Analysis

Table 3.3 illustrates the EDX results of MoO$_3$ films and MoO$_3$ films annealed at various temperatures. According to the EDX results the films composed of molybdenum (Mo), oxygen (O), Silicon (Si) and Sodium (Na) with different compositions based on the annealing temperatures. We could deduce from the EDX results that thermal annealing changes the crystalline structure, but the chemical composition remains similar. Since the O/Mo ratio approximately 3 at all temperatures. It should be noted that the presence of Na and Si is due to the glass substrate used for MoO$_3$ deposition.

Table 3.3: EDX results for MoO$_3$ films annealed at various temperatures in air.

<table>
<thead>
<tr>
<th>Na-glass / MoO$_3$</th>
<th>Vacuum evaporation</th>
<th>30 minutes thermal treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>heat treatment, in air, °C</td>
<td>Mo, at%</td>
<td>O, at%</td>
</tr>
<tr>
<td>–</td>
<td>24.2</td>
<td>74.7</td>
</tr>
<tr>
<td>150</td>
<td>26.6</td>
<td>71.7</td>
</tr>
<tr>
<td>200</td>
<td>25.0</td>
<td>72.9</td>
</tr>
<tr>
<td>300</td>
<td>25.8</td>
<td>72.4</td>
</tr>
<tr>
<td>400</td>
<td>20.7</td>
<td>67.5</td>
</tr>
<tr>
<td>500</td>
<td>24.4</td>
<td>75.3</td>
</tr>
<tr>
<td>1. cryst.</td>
<td>35.5</td>
<td>47.2</td>
</tr>
<tr>
<td>2. rest.</td>
<td>19.0</td>
<td>62.0</td>
</tr>
</tbody>
</table>

* In order to calculate the O/Mo atomic ratio we exclude the SiO$_2$ and Na$_2$O from the equation.
3.5 Scanning electron microscopy (SEM) Results

SEM microscopy of MoO₃ films and MoO₃ films annealed at various temperatures was performed to reveal the surface and the thickness of the films. The as-deposited films have smaller and fine grains compared to the films annealed at various temperatures. As the temperature increases to 150 °C the films exhibits a much finer grains having smaller thickness. The visual appearance of as-deposited films and films annealed at 150 °C confirms their amorphous nature. At thermal annealing temperature of 200 °C large particle grains begins to form. MoO₃ films annealed at 200 °C exhibits granular crystalline structures with lattice sites observed in the structure. On the contrary, blisters are observed on the surface of MoO₃ films formed at 300 °C. This could be as a result of the complete dehydration of the films. The grain size also increases with temperature while porous surface are visible [79]. Defects were observed in the SEM images at 300 °C. Formation of defects on the SEM images of MoO₃ films annealed at 300 °C is in agreement with the XRD results. Moreover, grains similar to Nanorods and paralleled to the substrate was formed when MoO₃ films was heated to 500 °C.

One important observation is the relationship between the film thickness and annealing temperature. With increasing annealing temperature, the films thickness decreases progressively as shown in Table 3.4. As MoO₃ films were heated from a temperature of 150 °C to 200 °C, there is a reduction in film thickness from 1348 nm to 1254 nm. Also, 62% decrease in film thickness was observed when MoO₃ films were heated up to 500 °C. Decrease in film thickness with temperature could be attributed to the coalescence of particles in the film structure, which led to the formation of large particle aggregates and scattered the light [80] thereby increasing its transparency.
Figure 3.7: SEM images of M1-M3 samples.
Figure 3.8: SEM images of M4 - M6 samples.
Na-glass / MoO$_3$

Thermal vacuum evaporation, 3·10$^{-7}$ Bar, 10 min, 19 A

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Temperature, °C</th>
<th>film thickness, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>as-dep</td>
<td>1459</td>
</tr>
<tr>
<td>M2</td>
<td>150</td>
<td>1348</td>
</tr>
<tr>
<td>M3</td>
<td>200</td>
<td>1254</td>
</tr>
<tr>
<td>M4</td>
<td>300</td>
<td>1165</td>
</tr>
<tr>
<td>M5</td>
<td>400</td>
<td>645</td>
</tr>
<tr>
<td>M6</td>
<td>500</td>
<td>469</td>
</tr>
</tbody>
</table>

Table 3.4. Film thickness of MoO$_3$ thin films at different annealing temperatures.

3.6 J-V characteristics of solar cells

To ascertain the performance of vacuum thermal deposited MoO$_3$ thin films as interfacial buffer layer for hybrid solar cells, the J-V curve measurements was carried out. The reference solar cell and the solar cell containing MoO$_3$ films are denoted as ITO/TiO$_2$/Sb$_2$S$_3$/P3HT/Au and ITO/TiO$_2$/ Sb$_2$S$_3$/P3HT/MoO$_3$/Au respectively. For both solar cells the anode material is ITO while Au is the cathode material. Figure 3.9 illustrates the diagram of both solar cells placed in one substrate (picture taken from the laboratory). The region with deposited MoO$_3$ is marked with a red square. It should be noted that the MoO$_3$ film used here is the as deposited film (M1). Also, it is noteworthy to revise that the purpose of this study is to prepare the MoO$_3$ thin films and evaluate the performance when placed in a real hybrid solar as an interfacial buffer layer. The performance is evaluated by taken J-V measurements and compared with that of the reference without MoO$_3$ films. The J-V curve measurements is presented in figure 3.9.
Figure 3.8: Pictures of both ITO/TiO$_2$/Sb$_2$S$_3$/P3HT/Au and ITO/TiO$_2$/Sb$_2$S$_3$/P3HT/MoO$_3$/Au hybrid solar cells (Picture taken from the laboratory).

Figure 3.9: J-V measurements for both ITO/TiO$_2$/Sb$_2$S$_3$/P3HT/Au and ITO/TiO$_2$/Sb$_2$S$_3$/P3HT/MoO$_3$/Au hybrid solar cells.
J-V curve measurements for the reference ITO/TiO$_2$/Sb$_2$S$_3$/P3HT/Au solar cells shows that the open circuit voltage (Voc), short circuit current density (Jsc), Fill factor (FF) and power conversion efficiency (PCE) values are 614 mV, 7.2 mA/cm$^2$, 42 % and 1.87 % respectively. On the contrary, hybrid solar cell with the as-deposited MoO$_3$ films shows improved performance. Improved PCE value of 2.1% is achieved compared to the reference solar cell. The Voc, Jsc, FF values of also shows an improvement when compared to the reference ITO/TiO$_2$/Sb$_2$S$_3$/P$_3$HT/Au solar cell. Consequently, we propose that the as-deposited MoO$_3$ film is a good interfacial material for an inverted hybrid solar cell.
Chapter IV: Conclusions and Recommendations for future work

4.1 Conclusions

The main objective of this research is to study the structural and optical properties of MoO$_3$ thin films as interfacial buffer layer for hybrid solar cells. MoO$_3$ does not only acts as a protective layer against environmental oxygen and humidity but also prevents charge recombination at the electrodes thereby prolonging the lifetime and improving the output parameters of the solar cell. A good understanding of the structural and optical properties could help improve the performance and lifetime of the solar cells. MoO$_3$ films were deposited on glass substrates using vacuum thermal evaporation and the films are characterized by optical measurements, XRD, EDX and SEM. The as-deposited MoO$_3$ thin film is then used as an interfacial layer for a hybrid solar cell (ITO/TiO$_2$/Sb$_2$S$_3$/P3HT/MoO$_3$/Au) and the J-V characteristics is compared with that of a reference solar cell (ITO/TiO$_2$/Sb$_2$S$_3$/P3HT/ Au).

The key findings obtained from this study are highlighted below:

- The as-deposited films were amorphous although at temperatures above 200°C the degree of crystallinity of the films starts increasing.
- MoO$_3$ is a wide band gap semiconductor, below the crystalline temperature the band gap decreases with increasing temperature. However, the energy band gap would start to increase after heating beyond the crystalline offset temperature.
- The offset crystalline temperature of MoO$_3$ films is above 200°C.
- The as deposited MoO$_3$ samples is identified with a blue color and the blue color darkens with temperature. However, above the offset crystalline temperature the transparency of the films increases with temperature.
- Optical band gap of amorphous MoO$_3$ film is 3.1 eV which increases to 3.49 eV upon crystallization.
- Physical appearance also illustrates the unique ability of MoO$_3$ to exist in multiple valence states.
- The optical properties (reflectance), $E_g$ and transparency of the MoO$_3$ thin film is largely dependent on the deposition techniques used and the thermal annealing medium.
- Crystallinity of the MoO$_3$ thin films does not depend on the deposition method and heating medium. But it is dependent on the thermal annealing temperature.
• There is a possible increase in the number of defects present in each crystal as the annealing temperature increases.
• Thermal treatment changes the crystalline structure of the material, but its chemical composition still remains unchanged.
• SEM results show that with increasing annealing temperature the films thickness decreases progressively.
• The hybrid solar cells fabricated with as-deposited MoO$_3$ films as an interfacial buffer layer shows improved performance when compared to the standard hybrid solar cell without the MoO$_3$ films. PCE value increases from 1.87% to 2.1%. Voc, Jsc and FF values also show significant increase. Therefore, the amorphous as-deposited MoO$_3$ films are suitable as an interfacial buffer layer for the solar cell.

4.2 Recommendations for future work

The current research has established that the use of vacuum thermal evaporated MoO$_3$ films as interfacial buffer layer for hybrid solar cells could improve the performance of the solar cell. However, it is only the as-deposited MoO$_3$ film that was tested as interfacial material (ETL) for hybrid solar cell. The following recommendations are useful for future research in this field:

1. It is recommended that other thermal annealed MoO$_3$ films should be tested to ascertain the effect of thermal annealing of MoO$_3$ films on the performance of hybrid solar cell.
2. It is also recommended to produce MoO$_3$ films with different thickness and test their performance in a typical hybrid solar cell.
3. Compare the effect of the method of fabrication on the performance of MoO$_3$ as interfacial material in hybrid solar cells.
SUMMARY

Increasing world energy demand, the finite nature of fossil fuels and the issues of climate change has intensified the search for renewable, environmentally benign and sustainable energy sources of which photovoltaics (PV) solar cell is an attractive example. The early years of PV solar cell devices was dominated by silicon solar cells due to their availability, excellent power conversion efficiencies and environmental stability. However, they are expensive in terms of purifying and manufacturing techniques. In order to compete with fossil fuels the cost of renewable energies needs to be reduced.

Hybrid solar cells provides a cheap alternative to conventional solar cells by combining organic and inorganic materials, in that way, the benefits of both materials can be utilized. However, hybrid solar cells are faced with the challenges of low efficiency and life time. Interfacial buffer layers are used to increase the efficiency and lifetime of hybrid solar cells. They smoothen the anode surface, acts as protective layers against atmospheric oxygen and humidity and minimizes charge recombination and the resistance at the interface between the anode and the photoactive layers of hybrid solar cells.

Molybdenum oxide (MoO$_3$) is a promising material as interfacial layers for hybrid solar cells due to its unique optical, structural and electronic properties. However, to use this material effectively it is important to understand the structural and optical properties of MoO$_3$ thin films which is the main aim of this study. This research also attempts to investigate the effect of thermal annealing on the structure and properties of MoO$_3$ thin film as interfacial buffer layers for hybrid solar cells.

Thin films MoO$_3$ were prepared by Vacuum thermal evaporation method on glass substrates using powdered MoO$_3$. The samples of MoO$_3$ were heated in a vacuum evaporator and then evaporated using Molybdenum (Mo) boat at 19 Amperes from 2 seconds to 10 minutes depending on the thickness of the glass. Prepared thin films were made to undergo thermal annealing temperatures of 150, 200, 300, 400 and 500 °C after which they are characterized by Optical transmittance, XRD, SEM, EDX. Furthermore, the performance of the as-deposited MoO$_3$ film as a buffer layer is evaluated in a real inverted hybrid solar cell with configuration ITO/TiO$_2$/Sb$_2$S$_3$/P3HT/MoO$_3$/Au against a reference ITO/TiO$_2$/Sb$_2$S$_3$/P3HT/Au solar cell.

Result of MoO$_3$ thin films on glass substrate shows that the as-deposited thin films are amorphous and at temperatures above 200°C crystallinity starts increasing. The optical properties (reflectance), band gap and transparency of the MoO$_3$ thin film is largely dependent on the deposition techniques used and the thermal annealing medium used. On the contrary, Crystallinity of the MoO$_3$ thin films is only
dependent on the thermal annealing temperatures. One important observation is the fact that thermal treatment changes the crystalline structure of the material, but its chemical composition still remains unchanged. The performance of the as-deposited MoO₃ film on hybrid solar cell shows an improvement in the power conversion efficiency (PCE) (1.87% to 2.1%), Open circuit voltage (Voc) (614 mV to 620 mV), and fill factor (FF) (42% to 44%) and short circuit current (JSC) (7.2 mA/cm² to 7.6 mA/cm²). The results obtained from this study shows that the amorphous as-deposited MoO₃ thin films prepared by vacuum thermal evaporation can be effectively used to improve the efficiency and performance of a hybrid solar cell. For further studies it is recommended to investigate the effect of thermal annealing of MoO₃ thin films on the performance of hybrid solar.
List of References


Appendices

A1: Optical Properties

Optical Properties of MoO$_3$

- **M1**: Direct band gap and Indirect band gap graphs.
- **M2**: Direct band gap graph.
- **M3**: Indirect band gap graph.
Optical Properties of MoO$_3$

M4

M5

M6
A2: XRD patterns

MA4, 300 °C, 30 min.

MA5, 400 °C, 30 min.
MA6, 500 °C, 30 min.
MoO$_3$