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The purpose of this project was to investigate the potential of two different material systems for the improvement of solar cell efficiency; one based on a titanium oxynitride system and the other molybdenum disulfide. Both phases of the project utilized different fabrication methods and approach in designing the photovoltaic devices.

For the titanium based system (TiNO), thin films were formed using pulsed laser deposition, a phase vapor deposition (PVD) technique. The photovoltaic cells deposited on ITO coated glass with copper electrodes yielded an average power conversion efficiency (PCE) of 4.47%, with a fill factor (FF) of 0.246, open circuit voltage (V_{oc}) of 0.18 V, and a short circuit current density (J_{sc}) of 58.43 mA/cm². XRD and XPS results provide insight into the materials composition and give evidence of multiple bandgap mediated transfer of charge carriers.

For the molybdenum based device, monolayer molybdenum disulfide was incorporated into a current organic-based solar cell (OSC) as an electron transport layer. The active layer consists of a blend of donor Poly(3-hexylthiophene-2,5diyl) and acceptor PCBM. MoS₂ incorporated devices showed improved PCE, at 0.88% compared to that of the control samples which yielded a PCE of 0.22%.

BANDGAP ENGINEERING OF TITANIUM BASED OXYNITRIDE THIN FILMS AND MOLYBDENUM DISULFIDE THIN FILMS FOR PHOTOVOLTAIC APPLICATIONS

by

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CHAPTER I

INTRODUCTION

1.1 Overview

Energy provided by the sun is unlimited, clean, abundant, and sustainable. Solar technologies use the sun to generate energy that is in line with the environment-security nexus. The U.S. Department of Energy (DOE) has established a Grid Modernization Initiative (GMI) in recognition of changes that must be made to establish the "grid of the future" [1]. With continued modernization efforts and rapid population growth, the security of water, food, and energy is a major concern. Much higher demands are placed on energy requirements and supplies. Fossil fuels reduced availability and a worsening environment paired with an energy demand that is expected to reach 778 Etta Joule by 2035, a clean and reliable source of energy is essential to the future health of our planet [2, 3]. Renewable energy technologies such as photovoltaics (PV) enable the opportunities for sustainable and cost-competitive synergy to water, energy and food security [4-8].

Although the power quality and voltage profile of solar cells is less than ideal, efforts continue to push the boundary on solar possibilities. An important concern with large-scale solar energy lies in a need for improved voltage stability, allowing for better reliability and grid support as we push communities towards greener ecofriendly renewable energy generation. However, achieving costeffective, light weight, and efficient solar cells has been a challenge for the scientific community [9-12]. Among solar cell technologies, inorganic solar cell devices, based on Group III – V elements and silicon, have emerged as the standard for solar energy conversion with the power conversion efficiency reaching up to 34% [13-15]. Heavy weight, rigidity, fragileness, and high-cost associated with the inorganic solar cells hinder their effective competition with fossil energy and wide applicability for energy generation. The current limitations of traditional inorganic solar cell have been addressed by thin film technology research efforts focused on organic [16-18], inorganic [19, 20], dye sensitized [21-23], and organic-inorganic hybrid solar cells [24, 25] in the last decade.

This research expands upon the field of photovoltaics, focusing on a novel titanium system comprised of titanium, nitrogen, and oxygen (Ti-N-O). Also explored in this research is the use of molybdenum disulfide monolayer thin films. These thin films are produced using chemical vapor deposition and fabricated into an organic-inorganic hybrid based photovoltaic device design.

1.2 Research Goals

1.2.1 Ti-N-O Material System and Device Design

The primary objective of this project is to explore the potential utilization of TiNO thin films in solar cells and improve the solar cell efficiency. Efficiency of solar cell technology can come down to multiple aspects, including cost efficiency, material access, and energy conversion efficiency. Although PLD is utilized in this research, which can be attributed to a high cost form of fabrication, the purpose of PLD is to overcome deficits in power conversion efficiency. A more efficient material system studied in this manner could lead to further research endeavors devoted to the development of a more cost effective path for device fabrication. These steps would help provide the scientific community with new forms of alternative energy generation.

The overall goal in the findings of this research is the development of a novel TiN_xO_y (TNO) material system in thin film form that has real potential to improve the field of alternative energy generation. The terminal stoichiometric compounds of the TiN_xO_y system (For TiN x = 1 and y = 0 while for TiO₂ x = 0 and y =2) are known for their well-established properties [26-33]. The ability to vary x and y in the range of $0 \le x \le 1$ and $0 \le y \le 2$, respectively brings uniqueness to the current research and TNO material system [32, 34-36]. This allows for resulting compounds to display properties of conductors at one end and insulators

at the other end with intermediate compounds. This provides limited control over variable resistivity, optical transparency and bandgap, providing suitable design for a variety of fundamental studies and novel devices. [13, 37-45]. Thin film designs utilized in this research based on the titanium can be seen in Figure 1.



Figure 1. Thin Film Architecture for Photoactive TiNO Design

1.2.2 Molybdenum Disulfide System and Device Design

The objective of this project is to explore the use of molybdenum disulfide monolayer thin films for the improvement of power quality and voltage stability seen in organic-based solar cells (OSC). This was done through the incorporation of molybdenum disulfide into current OSC designs comprised of P3HT and PCBM. Organic solar cells are competitors of current state of the art inorganic devices due to their affordability, ease of fabrication, and ability to be integrated into designs based on flexible substrate. Currently, one of the major limiting factors in OSC designs lies with poor charge transport and inadequate light absorption. Previous work shows MoS_2 to have a high charge-carrier mobility of 200-500 cm² V⁻¹ s⁻² [46]. Monolayer MoS_2 has been shown to have a bandgap of 1.9ev [47].

The design will build off previous work accomplished by Dr. Rathnayake, establishing a control device comprised of Al/P3HT&PCBM/PEDOT:PSS/ITO. The incorporation of MoS₂ into the OSC design can be seen in Figure 2. The band structure and energy levels diagram are fully explained in section 2.5.3.



Figure 2. Thin Film Design for Incorporating MoS₂

CHAPTER II

BACKGROUND

2.1 Photovoltaics

This research is focused on photovoltaics and it is important to have a good understanding of solar energy, solar cells (devices operating as photovoltaics), and power generation. Understanding electronic characteristics of solar cells will pertain to results obtained using solar simulation and other characterization techniques in both the titanium-based system and molybdenum based photovoltaic devices.

Solar energy has been provided by the sun for billions of years. The sun has been utilized for years and provides renewable and pollutant free green ecofriendly energy. Although solar energy is free, devices used to capture or store this energy are not. Increasing the efficiencies of these devices in cost, performance, size, and lifespan are crucial to optimizing solar energies potential.

Photovoltaic solar cells are electronic devices which convert electromagnetic radiation into electric energy. Other forms of solar cell technologies convert solar heat into electric energy. Simply put, sun light or heat reaching a solar cell results in the production of electricity. In photovoltaics, for this to occur, and for devices to operate correctly, materials must produce proper electron-hole pairings. This requires careful consideration in fabrication design for solar cells. Certain semiconductors display hole forming n-type donor, or electron accepting p-type acceptor materials. The presence of materials such as TiN, TiNO, and TiO₂ with multiple bandgaps enables the fabrication of different photovoltaic solar cells with higher efficiencies with respect to single bandgap solar cell devices. If the incident solar photons have enough (greater than band gap) energy, they will initiate charge excitation within a semiconductor. However, because of the low fraction of short wavelength solar light, wide band gap solar cells generate a high photovoltage but have low photocurrent. Smaller band gap cells can utilize a larger fraction of the incident photons but generate lower photovoltage. In stacked or composite multijunction systems, the wide bandgap materials absorb energetic photons, but are transparent to lower energy photons. Low bandgap materials absorb the lower energy photons.

2.2 Principles Behind PLD Deposition

Pulsed laser deposition (PLD) originated in the 1960's. This method of physical vapor deposition (PVD) was made possible at the creation of the first high-powered ruby laser [48]. As shown in Figure 3, PLD is a technique which makes use of a high-powered laser to ablate a solid target of material. This material, placed inside of a vacuum chamber, is then deposited through a plasma plume onto a surface facing the target. This surface consists of a substrate holder and heater for the purpose of holding a sample and the ability to anneal substrates still under PLD parameters.



Figure 3. Pulsed Laser Deposition Chamber and Features

Many process parameters must be considered, but also may be varied, to produce different deposition characteristics. For example, the presence of different background gases, laser pulse duration, frequency, number of pulses, or pressure can be varied.

Further development of q-switches allowed for shorter pulses and higher peak power density. In the late 1908's PLD was shown to produce nanostructures under conditions of ambient gas [49]. For the purpose of this research, a krypton fluoride laser was used. Further parameters can be found in Chapter 3: Device Fabrication.

2.3 TiN State of the Art

Of many semiconductor metal oxides and their heteroatoms-doped derivatives, titanium dioxide (TiO₂), titanium nitride (TiN), and stoichiometric doped TiN_xO_y nanomaterials appear to be emerging candidates due to high chemical and optical stability, non-toxicity, high abundancy, low-cost, and corrosion resistance. Owing to additional unique optical properties in the visible to mid-infrared region and ability to tailor the band gap through doping, TiN has recently gained enormous interest in solar heat transducers, broadband photodetectors, non-linear optical devices, and thermal emitters at high temperatures [50, 51]. In contrast, from an environmental prospective, TiO_2 is one of the most predominantly used materials for photocatalytic and solar cell applications but it does not have visible absorption due to deep valence band positions (Oxygen 2p Orbitals) and a bandgap that is too large to harvest the solar light [52]. Since the Nitrogen 2p orbitals has a higher potential energy than Oxygen 2p orbital, using a metal nitride or metal oxynitride as a photoelectrode has significant potential. However, the applicability of TiN material as a direct active layer component for harvesting solar energy and to convert this energy into electricity has not been explored so far.

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2.4 Molybdenum Disulfide

Molybdenum can be found on the periodic table in Group VI, Period V, as a transition metal with the atomic number 42. Its appearance is often confused with that of lead, however the metal does not appear in nature as a pure or free metal. Molybdenum disulfide, as molybdenite or molybdena, is the principle ore from which molybdenum can be found and extracted. It has similar utilizations to graphite, due to its atomic structure, containing sheets of sulfur atoms sandwiched in with sheets of molybdenum [53]. This allows for the material to blacken surfaces or act as a solid lubricant. Electronically, MoS₂ can be used in a wide variety of applications, including demodulators, low-voltage transistors, solar cells, and other semiconductor applications requiring high charge carrier mobility.

This research will take advantage of MoS_2 's charge carrier quality. Due to a lack of good charge carriers seen in most cheap, or easily manufactured OPVs [54], we would like to analyze methods of fabricating organic-inorganic solar cells containing MoS_2 to improve the power conversion efficiency. The bandgap of MoS_2 as a monolayer is very attractive, at 1.9 eV [47], and matches up properly, as discussed further in section 2.5.3 on MoS_2 device design approach and reasoning.

2.5 Scientific Significance

2.5.1 Ti-N-O System

The approach taken for architecting the chemical properties of the TNO system via controlled oxidation has an advantage over conventional methods of bandgap manipulation of TiO₂ via nitridation due to the higher activation energy of a nitridation process (672 kJ/mol) than that of an oxidation process (496 kJ/mol). The TNO material system also has a strong potential for integration with technologically important substrates such as silicon and sapphire due to a small mismatch in lattice constants and thermal expansion coefficients [55, 56]. The concept behind transforming metallic TiN into a semiconducting TNO with desired optical and photovoltaic properties is based on the partial substitution of nitrogen by oxygen.



Figure 4. Conduction and Valence Band Changes through Oxidation (Bandgap Creation) and Nitridation (Bandgap Reduction)

When N atoms in TiN are partially substituted by O atoms, the top of the valence band (valence band maximum) moves down without affecting the bottom of the conduction band (conduction band minimum), as shown schematically in Figure 4 (bandgap).

The valence band maximum for oxynitride is located at higher potential energy than that for pure TiO_2 due to the contribution of N 2p orbitals. The bandgap of the resulting compound, shown in the center of the inset, can be tuned to be lower than 3.5 eV enabling it to respond to visible solar light (< 3eV) [57-59]. The activation energy barrier for the proposed method of TNO formation is \sim 35% lower than the traditional path of TiO₂ bandgap manipulation via nitridation.

The approach taken for thin film fabrication, making use of PLD, provided a fast, time efficient, proof of concept that could serve as a starting block for future research invested in a more cost effective, mass producible method of fabrication, perhaps using a wet chemical synthesis.

2.5.2 Molybdenum Disulfide

The approach taken for incorporation of molybdenum disulfide into OPV design stemmed from the use of molybdenum disulfide as a charge transport layer. As mentioned previously, one of the limiting factors in organic solar cell design is often seen in poor charge transport. Shown in Figure 5, the bandgap and energy level of MoS₂ lowest unoccupied molecular orbital (LUMO) is a good pairing for P3HT:PCBM active layer. As electrons excite and reach the LUMO band of P3HT absorber, they fall, reaching the LUMO level of MoS₂, which are then directed towards the aluminum electrode. As this occurs, holes formed during exciton formation are easily transported in the direction of ITO, establishing an electrical circuit and current.



Figure 5. Bandgap Diagram Representing Molybdenum Disulfide as an Electron Transport Layer (ETL)

CHAPTER III

EXPERIMENTS

3.1 Device Fabrication

3.1.1 Preliminary AuPd/TiN/Sapphire Thin Films

The preliminary round of thin film samples was deposited on c-plane sapphire (Al₂O₃) wafer cut into irregular sizes ranging from 4 to 7mm in width and 6 to 8mm in length. The samples were mounted in the PLD system as shown in Figure 3. PLD phase vapor deposition was used to deposit TiN onto the substrate surface. The PLD parameters used can be seen in Table 3. The films appear to be of high quality, with very little to no opacity. SEM images further show conditions for the TiN thin films. The SEM images can be seen in Figure 15. The image taken for the film surface is from an angle to show film thickness.

Gold palladium coating with an approximate thickness of 3nm was deposited onto each of the preliminary samples to provide a cathode terminal. This is done for obtaining conductance and current density-voltage (J-V) curves. J-V measurements throughout this research were done using a 4 prong probe setup. The method of obtaining our current-voltage data is further explained in detail in Chapter 2. Challenges were experienced in measuring accurate and reliable J V characteristic data. These challenges are discussed more in depth in Chapter 4.

3.1.2 Cu/TiNO/ITO Thin Films

Overcoming challenges from the previous round of samples a new choice in substrate was utilized. TNO films were deposited instead on indium tin oxide (ITO) coated glass. The deposition was performed using PLD. Full PLD parameters can be seen in Table 3, Appendix A. The laser used in this deposition was a krypton fluoride (KrF) laser with a wavelength of 248nm. The target used in the deposition was titanium nitride with 99.99% high purity. The surface of each substrate was plasma cleaned, and then put into the chamber which was pumped down to a pressure of 1×10^{-6} Torr. Pumping was done using rotary vane pumps and turbo-molecular pump units. PLD parameters are the substrate temperature held at 500 °C and the laser pulse frequency of 10 Hz.

Deposition of Copper contacts to serve as the device cathode were deposited using ebeam phase vapor deposition. The copper cathodes are approximately 100nm thick.

3.1.3 Cu/MoS₂/P3HT-PCBM/PEDOT:PSS/ITO Thin Films

Molybdenum Disulfide based devices were fabricated using a combination of methods, including chemical vapor deposition, and spin coating techniques that were performed in nitrogen environment. The films were deposited on a substrate of ITO coated glass. Fresh substrates were cleaned prior to fabrication using isopropyl alcohol sonication for ten minutes. These substrates were then handwashed, rinsed under deionized water, and treated in a bath of ammonium hydroxide and hydrogen peroxide for 15 minutes at 50 °C. Substrates were once again rinsed with deionized water and blown dry with nitrogen. The final cleaning step involved UV cleaning for 25 minutes. From here the substrates were moved into a nitrogen environment glove box.

Deposition of PEDOT:PSS solution took place immediately after substrates entry into the glove box. Spin coating PEDOT:PSS films required 350 μ L of solution spun at 1400 rpm for 10 seconds followed by 5000 rpm for 60 seconds back to back. Step one achieves a consistent film, and the faster second step acts to dry the film. Following PEDOT:PSS the film is moved to a heater within the same environment at 150 °C for 2 hours.

The active layer for this device design was deposited next, consisting of a blend of P3HT and PCBM. To prepare the solutions, 12.5mg of P3HT was added to 350 μ L of 1,2-dichlorobenzene and 10mg of PCBM was added to a separate vial of 250 μ L of 1,2-dichlorobenzene. These solutions were stirred for approximately 24 hours. The solutions were then combined, providing a P3HT:PCBM ratio of 1.0:0.8. Next, the combined solution was passed through a 0.22 μ m PVDF filter. The solution of P3HT&PCBM was deposited onto the

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PEDOT:PSS layer using similar spin coating technique, this time in one step of 3000 rpm for 45 seconds. The substrate and films were then dried for 7 minutes, subject to solvent annealing. Devices were further dried in the glove box under nitrogen conditions before being transferred into a vacuum box and transported out of the glove box for deposition of MoS₂. Prior to MoS₂ deposition the films were treated in acetone, and deposition of MoS₂ was performed using chemical vapor deposition.

The films were then transferred into a vacuum phase vapor deposition (PVD) where a cathode of 100nm copper was deposited. Of note, after initial samples of copper, a strategic switch was made to aluminum electrodes for the purpose of closing the energy gap between molybdenum disulfide and electrode, shown in Figure 5, in the previous chapter regarding approach and reasoning. The aluminum electrodes were deposited the exact same way.

3.1.4 Cu/P3HT-PCBM/PEDOT:PSS/ITO Thin Films

The procedure for this device design is identical to the previous design, omitting steps pertaining to acetone bath and MoS₂ deposition. This device design was important for establishing a baseline to see improvements or concerns in adding a layer of MoS₂ to serve as a charge transport layer. Other more simplistic designs were also used as the control device structure.

3.1.5 Control Devices

Along with standard solar cell that is provided with the solar simulator setup for calibrations, a series of standard devices were made. These devices included a blank ITO coated glass substrate, an ITO coated substrate with copper/aluminum electrodes (Cu/ITO or Al/ITO), and a similar design consisting of ITO coated glass, P3HT, and electrodes (Al/P3HT/ITO).

3.2 TiN-Based Device Fabrication

The following images in Figure 6 show fabrication results of pulsed laser deposition. These films have been removed from the PLD chamber, brought into a PVD chamber where ebeam was used to deposited 100nm copper electrodes.



Figure 6. TiNO Thin Film Depositions Using Pulsed Laser Deposition

3.3 Molybdenum Disulfide-Based Device Fabrication

The following images show fabrication results of spin coating single layer P3HT onto ITO coated glass substrate. These films have been removed from the glove box and brought into a PVD chamber where ebeam was used to deposited 100nm copper electrodes. Figure 8 shows the mask used for placement of electrodes.



Figure 7. P3HT Thin Films Deposited on ITO Using Spin Coating



Figure 8. Mask Utilized During Electrode Deposition

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Evaluation of TiN Thin Films Towards Photovoltaic Devices

Characterization of TNO thin films were carried out using current-voltage (I-V), x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). To achieve current voltage characteristics measurements were taken with a Keithley 2400 source meter. The source meter is connected to a 4-prong probe and a PC utilizing solar software. The cells were exposed to a solar simulator (AM 1.5G filter) with the intensity of 100 mW/cm².Using the measured current over a sweep of voltage, a calculation was made for both fill factor (FF) and power conversion efficiency (PCE). The equation used to calculate fill factor and power conversion efficiency are as follows, with Ps representing intensity of the light:

$$FF = \frac{J_m V_m}{J_{sc} V_{oc}} \qquad PCE = \frac{J_{sc} V_{oc} FF}{P_s}$$

4.1.1 I-V Characteristics Ti-N-O Based Test Devices



Figure 9. Current-Voltage Curves of TNO System

To evaluate photovoltaic performance of TNO system, J-V curves were recorded under the previously described setup using a Cu/TNO/ITO configuration (Figure 1). Fabrication for this configuration can be found in Chapter 3. The maximum performance for this solar cell measured for a power conversion efficiency as high as 4.47%. A short circuit current density (Jsc) of 58.43 mA/cm², an open circuit voltage (V_{oc}) of 0.18 V, and fill factor (FF) of 24.6% was observed in this sample. This shows a high potential PCE for thin films based on TNO systems as an active layer in PV solar cells. The full set of devices prepared in similar manner was shown to exhibit an average PCE of 4.41% with the Jsc ranging from 38.66 mA/cm² to 58.43 mA/cm², Voc of 0.18 V, and FF of 24.5%. Shown in Figure 9 are also the photo-power density of these samples as a function of voltage applied. The photovoltaic results of TNO thin films can be seen in Table 1. The higher efficiency realized with TNO system is explained using a double bandgap photovoltaic (MBPV) configuration containing two adjacent bandgap materials. The bandgap material consists of TiO and TiNO. As shown in Figure 10, a dual gap cell generates two smaller photo-potentials, which can be separately applied to the same PV, minimizing electron-hole recombination.



Figure 10. Double Bandgap Photovoltaic Configuration

This figure presents an inverted pn/np regenerative ohmic configuration. The wide band gap material (TiO in the present case) works as a p-type semiconductor while the small band gap material (TNO) serves as an n-type semiconductor. As seen for the inverted pn/np case, a quasi-fermi level is shared by the conduction bands of the wide band gap p-type (TiO or TiO₂) and the small band gap n-type layers (O-doped TiN, i.e. TiNO). Light incident from the figure left side generates charge through a common intermediate node, comprising a two photon per two electron photoelectrochemical process: $2hv\rightarrow 2e$.

The following legend represents Figure 10:

- Ecw Energy in wide bandgap semiconductor (TiO) conduction band
- Evw Energy in wide bandgap valence band
- Ecs Energy in small bandgap (TNO) conduction band
- Evs -Energy in small bandgap valence band
- EFermi (ns) Fermi level in n-type small bandgap semiconductor
- EFermi (pw) Fermi level in p-type wide bandgap semiconductor
- Vw voltage in wide band gap semiconductor
- Vs -voltage in small band gap semiconductor
- Hυ Photon Energy

Table 1

TNO Device Parameters

J _{sc} (mA/cm ²)	$V_{\infty}(V)$	FF	PCE (%)
58.43	0.18	0.246	4.47



Figure 11. XRD Results Identifying Presence of ITO, Cu, and TiN

After obtaining I-V curves for the representative photoactive material, XRD was necessary to show what the composition was for the bulk PLD deposition. Looking at the full device, Figure 11 shows the XRD pattern which identifies ITO, Cu, and TiN like materials. Peaks marked with an * are labeled for TiN like materials. (TiN: 36.6°, 77.2°, TiO: 43.2°, 75.26° and TNO: 62.13°) as per JCPDS00-038-1420, JCPDS01-072-2741, and JCPD04-006-2415, respectively

The chemical composition of TiN_xO_y was determined using XPS. Chemical composition can be seen in Figure 12. Ar+ sputtering was performed to remove the initial layer of Cu contact. Depth profiling across the remaining Ti-N-O layer was performed. The XPS signature peaks of O1s, Ti2p and N1s at 530, 454 and 400 eV are shown in Figure 12.



Figure 12. XPS Data Show Signature Peaks of O1s, Ti2p, and N1s

Figure 12 also shows the element survey of depth profile: (a) surface scan after hydrocarbon cleaning, (b) sub-surface after sputtering for 211 seconds where no copper is present, (c) sub-surface after sputtering for 301 s showing only Ti-N-O layer, and (d) sub-surface after sputtering for 361 s where the presence of ITO layer starts to appear.

After deconvolution of the Ti-2p spectra, six peaks corresponding to three pairs of spin-orbit split doublets were assigned as follows: Ti-N (2p3/2 BE 454 eV), Ti-O (2p3/2 BE 458 eV), Ti-N-O (2p3/2 BE 456 eV)

This Suggests that the TNO film is a mixture of Ti-N-O, Ti-N, and Ti-O chemical binding states [60-64]. The compositional profile was also determined through depth profiling across the Ti-N-O layer (Figure 13) and confirms the presence of mixed chemical binding states in the TNO films.



Figure 13. Compositional Profile Determined through Depth Profiling. This Shows Proper Doping Took Place throughout the Thin Film

A uniform composition is seen throughout the TNO thin film. Beginning at approximately 150 s, Cu is almost entirely nonexistent, and the remaining composition is seen to be 40% titanium, 20% nitrogen, and 40 % oxygen. The empirical formula associated with this composition could be formulated based on this atomic composition. The empirical formula of TiN_xO_y could be written as $Ti_1N_{0.5}O_1$. With this information, it is evident that the bulk material is oxygen doped TiN. During the doping process -3 valence state nitrogen is substituted with bivalent oxygen in TiN, creating a charge imbalance. To maintain neutrality, one cation vacancy (Ti^{+3}) is created for every two oxygens incorporated. $Ti_1N_{0.5}O_1$ transforms to $Ti_{0.5}N_{0.5}O_{0.5}$ and $Ti_1O_{0.5}$, or TiNO and TiO. All three, TiN, TiNO, and TiO have rock salt structures.

4.1.3 Optical Properties of Ti-N-O Thin Films

Figure 14 shows UV-vis spectra taken for the Ti-N-O active layer for the development of a TAUC plot, used to establish an approximated bandgap of the active layer component.



Figure 14. UV-vis Spectra and TAUC Plot Generated to Determine the Bandgap

4.1.4 TiN Thin Film Morphologies

SEM data was used to verify thin film characteristics and show thin film quality for TiN films. Energy dispersive x-ray spectroscopy (EDS) was done in addition to SEM image capture to provide a better picture of film composition. In the case for TiN, film thickness was also measured using SEM in conjunction with image measurement software. Cross-sectional thickness measurements are summarized in Table 4, Appendix A.



Figure 15. SEM Image of TiNO Deposit

4.2 Evaluation of MoS₂ Thin Films Towards Photovoltaic Devices

Characterization of molybdenum disulfide thin films were done using I-V, SEM, and UV-vis spectra for the purpose of identifying optical properties. For characterization of I-V the same setup was utilized as previously used for TNO thin films. In the case of molybdenum samples, extra controls were used to establish I-V characteristics for P3HT, along with a blend of P3HT/PCBM, and PEDOT:PSS to establish the full role and impact of MoS₂ on device performance.

4.2.1 I-V Characteristics of Molybdenum Disulfide Based Test Devices

To evaluate photovoltaic performance of the molybdenum disulfide-based system, J-V curves were recorded under the previously described solar simulator setup using an Al/MoS₂/P3HT-PCBM/PEDOT:PSS/ITO configuration (Figure 2 and 5). Fabrication for this configuration can be found in Chapter 3. The performance for this device can be seen in Figure 16.

With the introduction of MoS₂ into the sample, photoactivity was increased compared to the control device. The MoS₂ device produced a fill factor of 0.77 and a PCE of 0.88%. These performances are summarized in Table 2. The I-V curves show the presence of a semi conducting material, which is what we believe to have. Many conclusions have been made regarding potential reasons for the results in Chapter VI, and also some insight into where the fabrication can be improved or rethought in the following chapter. One leading fact to be aware of in considering the overall performance of the MoS₂ device requires attention on the control device, composed of Al/P3HT&PCBM/PEDOT:PSS/ITO, which did show to be photoactive but with a lesser performance. Measurements were taken the same way for the control device and full results can be seen in Table 2. The two photoactive control devices measured for an average PCE of 0.22, a short circuit current density of 0.01425 mA/cm², an open circuit voltage of 0.2778 V, and an FF of 0.22.



Figure 16. Current-Voltage Curves for Molybdenum Based Device

Table 2

MoS₂ Device and Control Parameters

	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	PCE (%)
Full Device	0.005	0.04545	0.77	0.88
Control Device	0.01425	0.2778	0.22	0.22



Figure 17. Current-Voltage Curves for Control Device

4.2.2 Optical Properties of P3HT and PCBM

Prior to evaluation of UV-vis absorption intensity for P3HT, the sample was subject to solvent annealing. This was done for the purpose of improved absorption. This approach was used previously in research performed by Dr. Rathnayake [65]. Absorption for P3HT and PCBM can be seen in Figure 18,

showing a peak wavelength maximum at approximately 552nm with a peak also observed at 480nm and a shoulder seen as 605nm.



Figure 18. UV-visible Spectrum for P3HT

CHAPTER V

CONCLUSION

5.1 Titanium Oxynitride System

The photovoltaic solar cells fabricated utilizing the TNO material system show promise and a direction for further research directly related to the use of titanium as a material choice in improved energy efficiency, low cost, easy manufactured PV design. The process used for testing the material system (PLD) was high cost, but can be looked at as a form of proof of concept in order to achieve easy and telling results for a future research direction to reduce the cost, and improvement in repeatability, as this was another difficulty expressed in this research.

With difficulty seen in repeated acts of achieving photoactive devices related to our titanium oxynitride, it is still important that once results were achieved, they do show promise as the titanium based solar cells with power conversion efficiencies as high as 4.47%, with titanium serving as the active layer for photoconversion. The device design made use of a bulk heterojunction and the power conversion efficiency was attributed to a multiple bandgap mediated electron hole transfer pathway. Evidence of this multiple bandgap transfer of

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charge is seen through XRD and XPS characterization, showing presence of Ti-N-O, Ti-N, and Ti-O chemical binding states.

5.2 Molybdenum Disulfide System

The devices made based on MoS₂ design, expressed throughout this research, has shown an increase in photoactive performance. The purpose behind an additional layer of MoS₂ was supported by the hypothesis of improved charge transport of electrons to the aluminum electrodes found on the top layer of the devices. A current deficit in OPV based on P3HT/PCBM is poor charge transport. The attempt of this portion of research was to overcome this issue.

Although the overall solar energy conversion made by the device was small with a PCE of 0.88%, relative to control devices, this is a considerable improvement. Thus, it still serves as a point of entry into further molybdenum disulfide research towards photovoltaics, specifically if crossed with currently existing (or not-yet existing) organic PV's. The control devices, measured alongside the MoS₂ design, did show photovoltaic performance at a power conversion of only 0.22%. The overall lower values in both devices can be attributed to a lack of electron transport layer with matching work function for the photoactive layer of the control device and its electrode, or between the MoS₂ layer and its electrode. However, the improvements we have seen from the control device to our experimental device is our greater concern. With this additional layer of electron transport layer, the control device could match up with standards found in literature and the MoS₂ would take on the same benefits. This would be worth diving into in future work to see what degree of improvement is still needed to have pilot devices.

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APPENDIX A

TABLES

Table 3

TNO Device Parameters

Jsc (mA/cm ²)	$V_{\infty}\left(V ight)$	FF	PCE (%)
58.43	0.18	0.246	4.47

Table 4

MoS₂ Device and Control Parameters

	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	PCE (%)
Full Device	0.005	0.04545	0.77	0.88
Control Device	0.01425	0.2778	0.22	0.22

Table 5

Pulsed Laser Deposition Parameters

Parameter	Details		
krF exciplex laser	Wavelength =248 nm		
	Pulse duration =30 ns		
	Frequency =10 Hz		
Targets	Titanium Nitride (TiN)		
Base vacuum	~1.0 x 10 ⁻⁶ Torr		
Target- Substrate	4 cm		
Distance			
Laser fluence	3.5 J/cm ²		
Aperture	15 cm x 5 cm		
Background gas	Ultra High Purity		
	Oxygen gas		
Flow rate of	40 sccm.		
Nitrogen gas			

Table 6

Thickness Measurement of TNO Thin Film

Feature		
Name	Length(nm)	Class Name
L1	175.0985	Class 1
L2	188.3862	Class 1
L3	197.102	Class 1
L4	207.4826	Class 1
L5	175.0984	Class 1
L6	169.6153	Class 1
L7	194.4204	Class 1
L8	162.0167	Class 1
L9	183.301	Class 1
L10	201.8397	Class 1
L11	110.3622	Class 1
L12	168.9953	Class 1
L13	201.319	Class 1
L14	156.7465	Class 1
Mean value	177.9846	0
Standard		
Deviation	24.20462	0
Minimum	110.3622	0
Maximum	207.4826	0
Range	97.12034	0
Sum	2491.784	0
Index of Minimum	11	0
Index of		
Maximum	4	0
Number of Elements	14	14

Feature	Length(n	Class	
Name	m)	Name	
L1	100.6153	Class 1	
L2	100.1541	Class 1	
L3	88.88879	Class 1	
L4	77.7771	Class 1	
L5	100.1541	Class 1	
L6	89.06249	Class 1	
L7	89.06248	Class 1	
L8	99.99988	Class 1	
L9	99.99988	Class 1	
L10	100.6153	Class 1	
L11	94.44446	Class 1	
L12	105.7016	Class 1	
L13	105.7016	Class 1	
L14	127.8984	Class 1	
L15	111.2499	Class 1	
L16	122.2222	Class 1	
Mean			
value	100.8468	(0
Standard			
Deviation	12.0946	(0
Minimum	77.7771	(0
Maximum	127.8984	(0
Range	50.12071	(0
Sum	1613.548	(0
Index of			
Minimum	4	(0
Index of			
Maximum	14	(0
Number			
of			_
Elements	16	10	6



Figure 19. Thin Film Architecture for Photoactive TiNO design



Figure 20. Thin Film Design for Incorporating MoS₂



Figure 21. Pulsed Laser Deposition Chamber and Features



Figure 22. Conduction and Valence Band Changes through Oxidation (Bandgap Creation) and Nitridation (Bandgap Reduction)



Figure 23. Bandgap Diagram Representing Molybdenum Disulfide as an Electron Transport Layer (ETL)



Figure 24. TiNO Thin Film Depositions Using Pulsed Laser Deposition



Figure 25. P3HT Thin Films Deposited on ITO Using Spin Coating



Figure 26. Mask Utilized During Electrode Deposition



Figure 27. Current-Voltage Curves of TNO System



Figure 28. Double Bandgap Photovoltaic Configuration



Figure 29. XRD Results Identifying Presence of ITO, Cu, and TiN



Figure 30. XPS Data Show Signature Peaks of O1s, Ti2p, and N1s



Figure 31. Compositional Profile Determined through Depth Profiling. This Shows Proper Doping Took Place throughout the Thin Film



Figure 32. UV-vis Spectra and TAUC Plot Generated to Determine the Bandgap



Figure 33. SEM Image of TiNO Deposit



Figure 34. Current-Voltage Curves for Molybdenum Based Device



Figure 35. Current-Voltage Curves for Control Device



Figure 36. UV-vis Spectrum for P3HT