

BACK SURFACE STUDIES OF Cu(In,Ga)Se₂
THIN FILM SOLAR CELLS

by

Hamed Simchi

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Materials Science and Engineering

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ABSTRACT

Cu(In,Ga)Se₂ thin film solar cells have attracted a lot of interest because they have shown the highest achieved efficiency (21%) among thin film photovoltaic materials, long-term stability, and straightforward optical bandgap engineering by changing relative amounts of present elements in the alloy. Still, there are several opportunities to further improve the performance of the Cu(In,Ga)Se₂ devices. The interfaces between layers significantly affect the device performance, and knowledge of their chemical and electronic structures is essential in identifying performance limiting factors. The main goal of this research is to understand the characteristics of the Cu(In,Ga)Se₂-back contact interface in order to design ohmic back contacts for Cu(In,Ga)Se₂-based solar cells with a range of band gaps and device configurations. The focus is on developing either an opaque or transparent ohmic back contact via surface modification or introduction of buffer layers in the back surface.

In this project, candidate back contact materials have been identified based on modeling of band alignments and surface chemical properties of the absorber layer and back contact. For the first time, MoO₃ and WO₃ transparent back contacts were successfully developed for Cu(In,Ga)Se₂ solar cells. The structural, optical, and surface properties of MoO₃ and WO₃ were optimized by controlling the oxygen partial pressure during reactive sputtering and post-deposition annealing. Valence band edge energies were also obtained by analysis of the XPS spectra and used to characterize the interface band offsets.

As a result, it became possible to illuminate of the device from the back, resulting in a recently developed “backwall superstrate” device structure that outperforms conventional substrate Cu(In,Ga)Se₂ devices in the absorber thickness

range 0.1-0.5 μm . Further enhancements were achieved by introducing moderate amounts of Ag into the $\text{Cu}(\text{In,Ga})\text{Se}_2$ lattice during the co-evaporation method resulting in a 9.7% cell (with 0.3 μm thickness) which has the highest efficiency reported for ultrathin CIGS solar cells to date.

In addition, sulfized back contacts including ITO-S and MoS_2 are compared. Interface properties of different contact layers with $(\text{Ag,Cu})(\text{In,Ga})\text{Se}_2$ absorber layers with various $\text{Ga}/(\text{Ga}+\text{In})$ and $\text{Ag}/(\text{Ag}+\text{Cu})$ ratios are discussed based on the XPS analysis and thermodynamics of reactions.

Chapter 1

INTRODUCTION

1.1 Thesis Statement

The main goal of this project is to develop a technology to reduce the manufacturing cost of the Cu(In,Ga)Se₂ thin film solar cells by lowering the absorber thickness. This leads to lower material usage and higher manufacturing throughput.

Nevertheless, the importance of back contact recombination would be higher in thinner cells and should be considered by appropriate choice of back-contact material or back surface modification. To do so, it is important to understand the characteristics of the absorber layer-back contact interface in order to design ohmic back contacts for Cu(In,Ga)Se₂-based solar cells with a broad range of band gaps and device configurations. In particular, development of the back contacts is being focused on the unique constraints that the superstrate configuration imposes for the absorber optimization, and back contact properties.

1.2 Motivation and Significance of Research

Energy affects nearly every aspect of our lives although current energy sources and patterns of energy use are unsustainable. Continuing to consume ever greater amounts of fossil fuels will cause too much damage to the environment, risk unprecedented climate change, and rapidly deplete petroleum resources. By emphasizing much greater energy efficiency and growing reliance on renewable

energy sources such as solar energy, wind power, and bio-energy, all of the problems associated with current energy patterns and trends can be mitigated. Renewable energy sources could provide all of the energy consumed in the world [1]. There is actually more than enough solar energy potential alone to meet projected global energy needs [1]. However, renewable energy (excluding hydropower) is still a relatively small portion of total energy supply (Fig. 1.1), though the installed global renewable energy capacity has more than quadrupled between 2000 and 2010 [2]. Concerning photovoltaics, certain challenges remain such as availability of mineral resources, their cost, and environmental issues that need to be addressed for greater adoption of the technology.

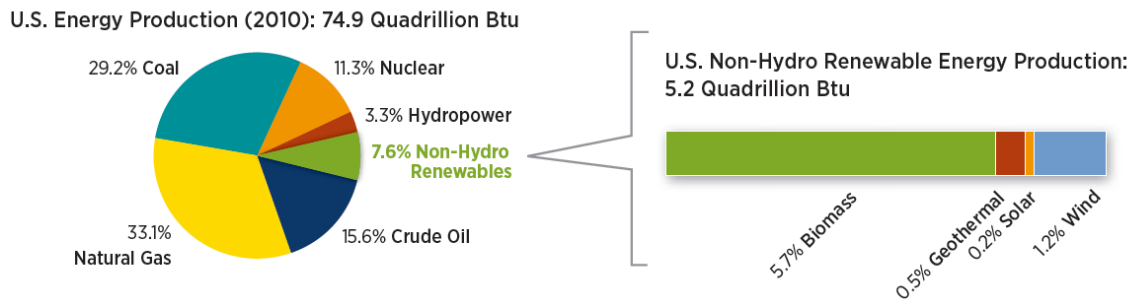


Figure 1.1: US energy production, reprinted from [1].

Thin film solar cells have the advantages over crystalline Si and GaAs solar cells since they can be deposited onto an inexpensive substrate at moderate temperatures, energy consumption would be lower, and module interconnection scribing will be easier in their production line. Three major thin film solar cells including amorphous silicon, CdTe, and Cu(In,Ga)Se₂ have revealed encouraging

potential for large scale productions. They have shown long-term stability and efficiencies of more than 20% have been reported for the Cu(In,Ga)Se₂-based cells [3]. The production cost of lower than \$1/W has been achieved for large-scale production. i.e. CdTe modules [4], which enables thin film solar cells to be competitive with conventional sources of energy.

1.3 Definition of the Critical Issues

The main goal of this project is to understand the characteristics of the Cu(In,Ga)Se₂-back contact interface in order to design ohmic back contacts for Cu(In,Ga)Se₂-based superstrate solar cells with a broad range of band gaps. Development of the back contacts is focused on the unique constraints that the superstrate configuration imposes for the absorber optimization, and back contact properties.

I have particularly studied the surface of the absorber layer and the interface between absorber layers and back contact to develop either an opaque or transparent back contact via surface modification or introduction of buffer layers in order to have ohmic contact in the back surface. Candidate materials have been identified based on modeling of band alignments and surface chemistry of the absorber layer and back contact. It is a part of an overall project for high performance superstrate Cu(In,Ga)Se₂-based solar cells.

1.4 Description of the Content

Background information and a current literature review on the Cu(In,Ga)Se₂ system is provided in Chapter 2.

Chapter 3 describes the experimental methods used for synthesis and characterization of Cu(In,Ga)Se₂ films and contact layers.

In Chapter 4, the effects of oxygen partial pressure and post processing on the structural, optical, and surface properties of the deposited MoO₃ films are explained. Evaluation of the MoO₃ electronic properties and back contact role in Cu(In,Ga)Se₂ thin film solar cells is also reported.

Chapter 5 addresses the properties of WO₃ thin films prepared by reactive rf sputtering. The effects of post processing on the structural, optical, and surface properties of the deposited films are described. Results are compared with MoO₃ films deposited by similar technique. Evaluation of the WO₃ electronic properties and back contact role in Cu(In,Ga)Se₂ thin film solar cells are also addressed.

In chapter 6, a backwall superstrate device structure that outperforms conventional substrate Cu(In,Ga)Se₂ devices for thin absorbers is demonstrated. The backwall structure (glass/ITO/MoO₃/Cu(In,Ga)Se₂/CdS/i-ZnO/Ag) utilizes MoO₃ transparent back contact to allow illumination of the device from the back.

In chapter 7, the surface properties of (Ag,Cu)(In,Ga)Se₂ films with a broad range of compositions are characterized using glancing incidence x-ray diffraction (GIXRD) and x-ray photoelectron spectroscopy (XPS) to elucidate the depth variation in composition and structure of films deposited by elemental co-evaporation. In addition, the interface properties of (Ag,Cu)(In,Ga)Se₂ films with MoO₃ and WO₃ contacts was studied using XPS. Effects of Ag-alloying on the valence band discontinuities are addressed since the valence band offset (ΔE_V) is equivalent to the barrier height for the back contact in devices.

1.5 List of Publications

The results of my research are also presented in the following publications:

- 1) **H. Simchi**, J.K. Larsen, Kihwan Kim, and W.N. Shafarman, “*Improved performance of for ultrathin Cu(In,Ga)Se₂ solar cells with a backwall superstrate configuration*”, IEEE Journal of Photovoltaics, accepted for publication.
- 2) **H. Simchi**, J.K. Larsen, and W.N. Shafarman, “*Transparent Back Contacts for Superstrate (Ag,Cu)(In,Ga)Se₂ Thin Film Solar Cells*”, IEEE Journal of Photovoltaics, under review.
- 3) **H. Simchi**, B.E. McCandless, T. Meng, and W.N. Shafarman, “*Structural, optical, and surface properties of WO₃ thin films*”, Journal of Alloys and Compounds, accepted for publication.
- 4) J. K. Larsen, **H. Simchi**, P. Xin, and W.N. Shafarman, “*Backwall superstrate configuration for ultrathin Cu(In,Ga)Se₂ solar cells*”, Applied Physics Letter, 104 (2014) 033901.
- 5) **H. Simchi**, B.E. McCandless, T. Meng, and W.N. Shafarman, “*Structure and interface chemistry of MoO₃ back contacts in Cu(In,Ga)Se₂ thin film solar cells*”, Journal of Applied Physics, 115 (2014) 033514.
- 6) **H. Simchi**, B.E. McCandless, T. Meng, J.H. Boyle, and W.N. Shafarman, “*Characterization of reactively sputtered MoO₃ films for solar cell application*”, Journal of Applied Physics, 114 (2013) 013503.
- 7) **H. Simchi**, B.E. McCandless, K. Kim, J.H. Boyle, and W.N. Shafarman, “*Effect of rapid thermal processing on the structural and device properties of (AgCu)(InGa)Se₂ thin film solar cells*”, Thin Solid Films, 535 (2013) 102-106.

- 8) **H. Simchi**, B.E. McCandless, K. Kim, J.H. Boyle, R.W. Birkmire, and W.N. Shafarman, An investigation of the surface properties of $(AgCu)(InGa)Se_2$ thin films”, IEEE Journal of Photovoltaics, 2 (2012) 519-523.

Conference proceedings

- 1) **H. Simchi**, J.K. Larsen, Kihwan Kim, and W.N. Shafarman, “*Improved performance of for ultrathin $Cu(In,Ga)Se_2$ solar cells with a backwall superstrate configuration*”, 40th IEEE photovoltaic specialists conference, June 2014, Denver, CO.
- 2) **H. Simchi**, J.K. Larsen, and W.N. Shafarman, “*Transparent Back Contacts for Superstrate $(Ag,Cu)(In,Ga)Se_2$ Thin Film Solar Cells*”, 40th IEEE photovoltaic specialists conference, June 2014, Denver, CO.
- 3) **H. Simchi**, B.E. McCandless, T. Meng, J.H. Boyle, and W.N. Shafarman, “ *MoO_3 back contact for $CuInSe_2$ -based thin film solar cells*”, Mater. Res. Soc. Symp. Proc. Vol. 1538, April 2013, San Francisco, CA.
- 4) **H. Simchi**, B.E. McCandless, W.N. Shafarman, K. Kim, J.H. Boyle, and R.W. Birkmire, “*Surface characterization of $(Ag,Cu)(In,Ga)Se_2$ thin films for solar cells*”, 37th IEEE photovoltaic specialists conference, June 2011, Seattle, Washington.

Chapter 2

BACKGROUND AND REVIEW

2.1 Cu(In,Ga)Se₂ Thin Film Solar Cells

Cu(In,Ga)Se₂ thin film solar cells have attracted a lot of interest because of their highest achieved efficiency among thin film photovoltaic materials and straightforward band gap engineering by changing the relative amounts of present elements in the alloy. Cu(In,Ga)Se₂ solar cells have the typical structure of glass/Mo/Cu(In,Ga)Se₂/CdS/ZnO/Grid. A scanning electron microscopy (SEM) cross section of this structure is shown in Figure 2.1a, which illustrates the polycrystalline structure of these materials. The most commonly used absorber preparation methods are: (i) *co-evaporation* where a chalcogenide film is formed during deposition and (ii) *precursor reaction* where a precursor film is deposited and then reacted with a Se and/or S containing atmosphere to form the chalcogenide film in a second step [5].

The Cu(In,Ga)Se₂ absorber layer has the chalcopyrite lattice which is based on the zinc blend lattice. The tetragonal unit cell of this structure is shown in Figure 2.1b. The tetragonal ratio of c/a is typically close to 2. Deviation from this value results from different cation and anion bonds lengths from elemental alloying.

CuInSe₂ alloys offer high optical absorption ($\alpha > 10^4 \text{ cm}^{-1}$) and a wide range of lattice constants and band gaps (Figure 2.2). The compounds can be alloyed to obtain a range of band gaps. The highest efficiency Cu(In,Ga)Se₂ cells have historically been produced with a band gap of 1.15 eV which corresponds to the Ga/(Ga+In) ratio of 0.25 [6,7].

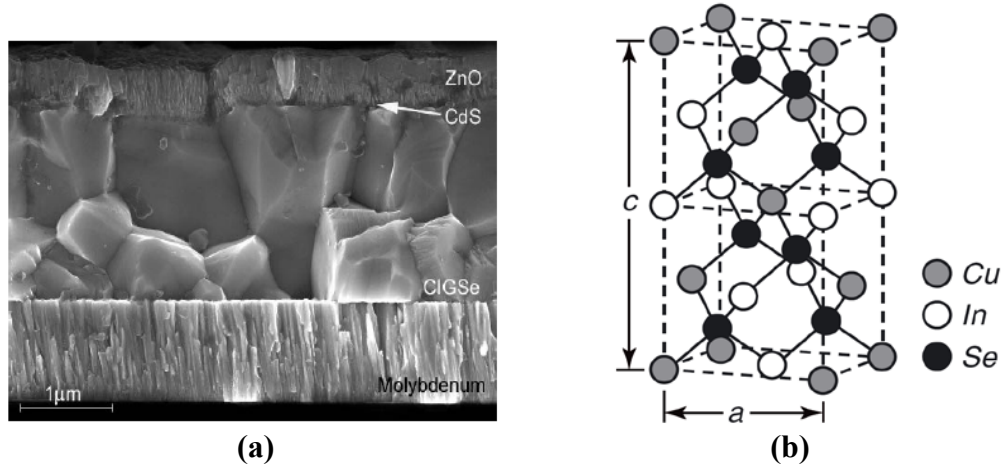


Figure 2.1: a) SEM cross-section of a Cu(In,Ga)Se₂ solar cell, taken from [8], and b) the unit cell of the chalcopyrite lattice structure, reprinted from [9].

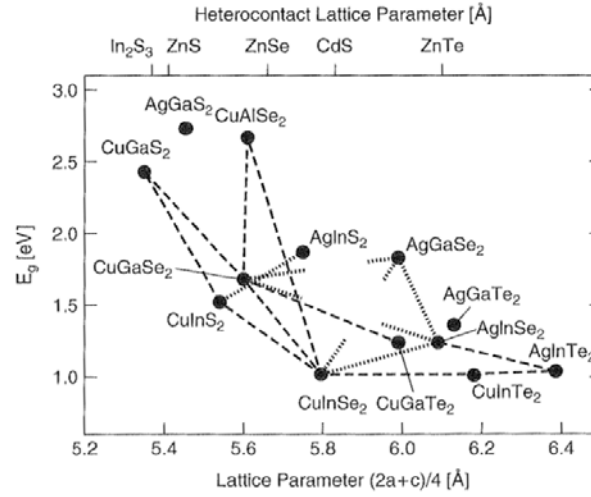


Figure 2.2: Band gaps and lattice constants of selected chalcopyrites, reprinted from [5].

It has been shown that surface of CuInSe₂ films have the composition different from the bulk, and close to the tie-line between Cu₂Se and In₂Se₃, defined in the ternary phase diagram [9]. In fact, ordered defect compounds (ODC) which have the

chalcopyrite structure with a structurally ordered insertion of intrinsic defects are present close to the surface. The creation of such defect phases accommodates the group I deficiency in CuInSe₂-based films through modification of crystallographic ordering [10]. Various ODC phases such as Cu₂In₄Se₇, CuIn₃Se₅, and CuIn₅Se₈ were predicted for the CuInSe₂ system [11].

2.1.1 Cu(In,Ga)Se₂ Cell Operation

Cu(In,Ga)Se₂ solar cells are working based on a heterojunction between the p-type absorber layer and n-type buffer layer making the charge separation possible. CdS is the most commonly used material for the n-type layer, but other compounds such as ZnS, ZnSe, In₂S₃, In₂Se₃, and Cd(OH)₂ have also been used by different groups [5,12]. The schematic band structure of Cu(In,Ga)Se₂/CdS heterojunction is shown in Fig. 2.3. Selected electronic properties of CuInSe₂ materials are summarized in Table 2.1.

When photons with energy $E > E_g$ hit the absorber layer, electrons will be excited to the conduction band leaving holes in the valence band. However, any electron in the conduction band is in a metastable state willing to stabilize by going to a lower energy state. As a result, the electron removes a hole from the valence band, and the process is called recombination. In practice, recombination losses may occur at the surface, in the bulk, or in the depletion region and can reduce both the current and the voltage of the solar cell.

The current-voltage (J-V) behavior of Cu(In,Ga)Se₂/CdS devices can be defined by the diode equation [9]:

$$J = J_D - J_L = J_0 \exp \left[\frac{q}{AKT} (V - R_S J) \right] + G(V - R_S J) - J_L \quad (2.1)$$

Where J_D is the dark current, J_L the light current, J_0 the diode current, A the ideality factor, K the Boltzmann constant, T the temperature, R_s the series resistance, G shunt conductance. The diode current J_0 is given by:

$$J_0 = J_{00} \exp\left(-\frac{\phi_b}{AKT}\right) \quad (2.2)$$

Where J_{00} is the prefactor, and ϕ_b the barrier height. Indeed, the values of A , ϕ_b , and J_{00} depend on the particular recombination mechanism that dominates the J_0 . On the other hand, series resistance R_s and shunt conductance G are due to losses occurring in series or parallel with the primary diode [9].

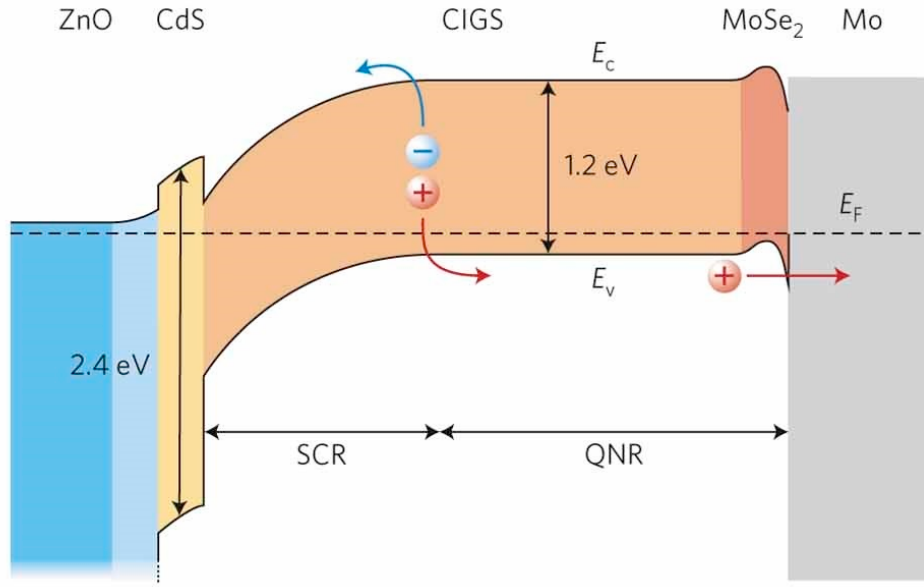


Figure 2.3: Schematic band diagram of a Cu(In,Ga)Se₂ solar cell at 0V, reprinted from [13]. The conduction band energy E_C , valence band energy E_V , Fermi level E_F , space charge region (SCR), and quasi-neutral region (QNR) are also shown.

Table 2.1: Selected electronic properties of high efficiency Cu(In,Ga)Se₂ devices [14,15].

Optical bandgap (eV)	Carrier concentration (cm ⁻³)	Hole Mobility (cm ² /Vs)	Carrier life time (ns)
1.2-1.3	10 ¹⁵ -10 ¹⁶	15-200	10-250

The device operation can be studied by identifying loss mechanisms which can be divided into three categories [9]:

- Optical losses that limit generation of carriers and therefore the short-circuit photocurrent (J_{SC}).
- Recombination losses that limit the open-circuit voltage (V_{OC}) and fill factor (FF).
- Parasitic losses, such as series resistance, shunt conductance, and voltage-dependent current collection, which are most evident by their effect on FF but can also reduce J_{SC} and V_{OC} .

The best performance has been achieved by depositing a 20-50 nm CdS layer on a 2-3 μm Cu(In,Ga)Se₂ absorber layer [16,17]. Reducing the thickness of the absorber layer has the potential advantage of reducing the manufacturing cost, due to lower material consumption and higher manufacturing throughput [18].

On the other hand, when the absorber thickness is reduced below 1 μm , the performance of Cu(In,Ga)Se₂ devices begins to deteriorate due to incomplete optical absorption leading to lower J_{SC} [19].

In addition, the importance of back surface recombination would be higher in thinner cells in which the minority-carrier diffusion length is comparable with the Cu(In,Ga)Se₂ thickness, and more minority carriers reach and recombine at the back

contact reducing the V_{OC} . Nevertheless, Kim et al. [20] have recently shown that V_{OC} and FF can be maintained high even for thicknesses below $0.5\ \mu\text{m}$. This might be due to presence of MoSe_2 at the back surface reflecting the minority carriers, thus preventing the back surface recombination (see Fig. 2.3). Therefore, in the case of thin absorber layers, an appropriate choice of back-contact material, surface modifications, or inclusion of a Ga grading to give a bandgap gradient [21] should be considered to reduce back surface recombination.

Figure 2.4 shows the modeled effect of a back contact barrier on the cell parameters with different absorber thicknesses [5]. For the thick absorbers V_{OC} is only slightly influenced by the back contact barrier. But, for thinner cells, $\phi_b^p \geq 0.3\ \text{eV}$ results in some loss in V_{OC} and the cell performance. The presence of a back contact barrier increases the slope of the quasi Fermi level toward the back surface which leads to greater minority carrier transport to the back contact, and thus higher recombination [22]. For the very thin devices, absorber thickness become smaller than the space charge region, and device would be fully depleted [21]. In this case, free-carrier concentration shouldn't have any effect on the built-in potential between front and back contacts, and device parameters depend only on the film thickness [21].

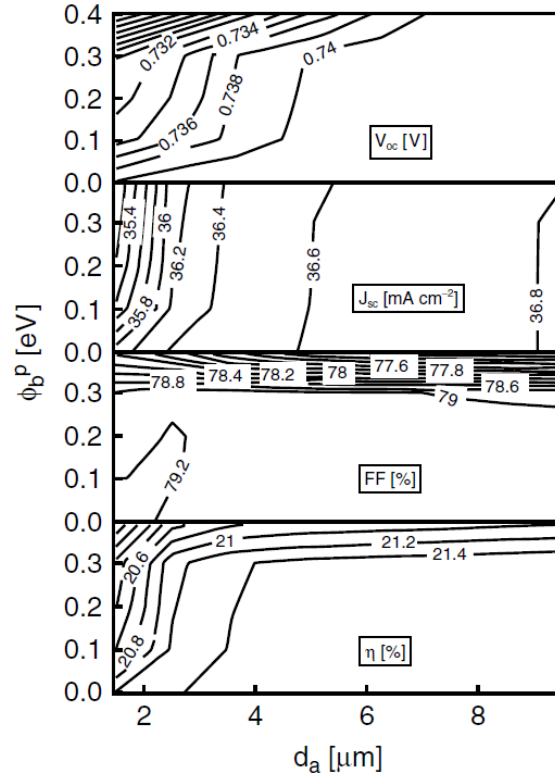


Figure 2.4: The effect of back contact barrier ϕ_b^P on the solar cell parameters with different absorber thickness d_a , reprinted from [5].

2.2 Configurations for Cu(In,Ga)Se₂ Solar Cells

2.2.1 Substrate Configuration

Thin film solar cells with Cu(In,Ga)Se₂ absorber layers are mostly grown in the substrate configuration (Fig. 2.5a). The substrate is usually soda lime glass with a sputter deposited Mo layer as a back contact. The Cu(In,Ga)Se₂ absorber layer is then deposited on the Mo layer, and then the p-n junction is formed by deposition of a very thin buffer layer of CdS using chemical bath and/or physical vapor deposition. Afterwards a high-resistance (HR) ZnO layer and a transparent conducting oxide, typically doped ZnO or indium tin oxide (ITO), are deposited, usually by sputtering or

chemical vapor deposition. Depositing a current collecting grid completes the solar cell's structure.

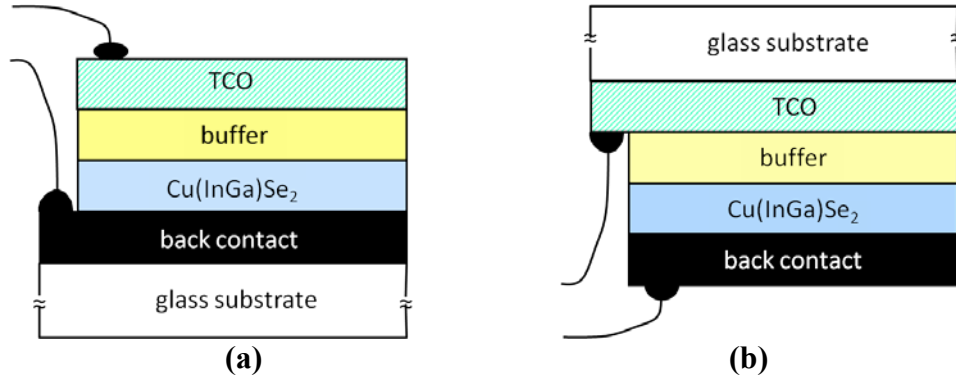


Figure 2.5: The schematic of a) substrate and b) superstrate Cu(In,Ga)Se₂ solar cell.

2.2.2 Superstrate Configuration

The superstrate solar cell refers to a configuration where the light shines through the glass substrate (Fig. 2.5b). This configuration is commonly used for solar cells based on CdTe and a-Si absorber layers. The superstrate configuration has the following potential advantages over the typical substrate solar cells:

Low cost: The glass itself acts as the encapsulant material which results in a lighter weight module with lower overall fabrication cost. It has been shown that the electronic materials have almost the same price as of the glass plates [23,24]. Therefore the superstrate cell have lower overall fabrication cost compared to substrate solar cells. Use of low-cost back sheet materials, similar to Si modules, will be possible in this configuration.

High deposition temperature: Since the TCO layer is being deposited before the Cu(In,Ga)Se₂, it is feasible to use high temperature (300-500 °C) during the

deposition of TCO and buffer layers in order to improve optical and electrical properties of materials. Films deposited at high temperature are typically more stable, producing more stable cells, and relaxing requirements for encapsulation. The buffer-CIGS interdiffusion is plausible during the high temperature treatment and should be prevented by choosing proper materials and processes.

Tandem cell: The superstrate structure has the potential to be used as the top cell in monolithically interconnected tandem cells. It would be the wide band gap cell absorbing the short wavelength portion of the spectrum.

Thin absorber: It simplifies incorporation of optical enhancement using light scattering with textured TCO layers and improved back contact reflectance.

Development of high efficiency Cu(In,Ga)Se₂ solar cells in the superstrate configuration presents several critical issues different from the substrate configuration which have limited the performance. These will be discussed in the followings.

Table 2.2 shows some notable results of superstrate CuInSe₂-based cells. The first CuInSe₂ superstrate cells were made in 1986 by Duchemin, et al. [25] via a spray pyrolysis method. They found that the main restrictive factor is the inter-diffusion of CdS and CuInSe₂ which happens during the deposition of absorber layer. Lower deposition temperatures and more stable buffer layers improved the efficiency up to 5% [26]. Later on, Yoshida et al. [27] confirmed that the limiting factor is the inter-diffusion of the CdS/CuInSe₂ interface which necessitates low CuInSe₂ deposition temperatures. Superstrate cell efficiencies of 8.1% [28] were reported using deposition temperatures of 400 to 450°C.

Table 2.2: Superstrate Cu(In,Ga)Se₂ cell results

Window layer	Buffer	Absorber	Back contact	Eff. (%)	Ref.
ITO	CdS	CuInSe ₂	NA	3.0	[25]
ITO	CdS	CuInSe ₂	Pt	6.6	[27]
ITO	In ₂ Se ₃	CuInSe ₂	Au	3.6	[29]
ZnO:Al	ZnO	CuInGaSe ₂	Au	10.2	[30]
ZnO:Al	ZnO	CuInGaSe ₂	Au	12.8	[31]
FTO	CdS	CuInGaSe ₂	Au	2.4	[32]
FTO	In ₂ S ₃	CuInSe ₂	NA	2.8	[33]

Replacing CdS with ZnO resulted in an increase in efficiency of superstrate Cu(In,Ga)Se₂ solar cells [30]. Those 10.2% efficient cells were made by depositing the Cu(In,Ga)Se₂ directly on an un-doped ZnO layer. Further improvements (12.8% efficiency) was accomplished by grading the absorber layer and introducing Na by means of co-evaporated Na₂Se during the initial step of the absorber layer growth [31]. These cells are the highest efficiency superstrate Cu(In,Ga)Se₂ cells reported to date. Recent studies on superstrate Cu(In,Ga)Se₂ cells made by low-cost electro-deposition [32] and spray-pyrolysis [33] methods couldn't exceed 3% efficiency.

Since the ZnO layer restricts the diffusion of Na from the glass into the absorber layer, it's necessary to add Na source during the evaporation of Cu(In,Ga)Se₂ layer. Otherwise the carrier density, open circuit voltage (V_{OC}) and fill factor (FF) would be low [34]. However, light soaked superstrate cells with the efficiency of 11.2% were attained without Na incorporation [35]. This is found to be true for most of the superstrate solar cells [36] and has been attributed to increase of carrier density which causes the saturation of defect states [35].

2.2.3 Backwall Superstrate Configuration

As mentioned above, one of the main restrictive factors limiting the performance of superstrate CuInSe₂-based thin film solar cells is the inter-diffusion of CdS and CuInSe₂ due to the elevated temperature deposition of Cu(In,Ga)Se₂ [37,38]. In order to overcome that issue, one approach would be implementing a “backwall superstrate structure” that we have proposed recently [39]. Fig. 2.6 shows the backwall superstrate structure in comparison with substrate and frontwall superstrate structures.

The backwall superstrate configuration is preferred over the frontwall superstrate configuration, since the p-n junction is formed after Cu(In,Ga)Se₂ deposition and the critical buffer-absorber inter-diffusion is prevented. In addition, light trapping can be obtained by texturing of the TCO layer before absorber deposition and a front reflector after Cu(In,Ga)Se₂ deposition can be added after all other device processing. The parasitic absorption in the CdS layer is also avoided.

The main difference of the backwall superstrate cell compared to the conventional substrate structure (Figure 2.6) is that light is absorbed primarily at the back of the absorber layer and not at the p-n junction. The blue light (~500 nm) will be almost completely absorbed in first 0.2 μm Cu(In,Ga)Se₂, whereas longer wavelength light, ~900 nm, is completely absorbed in 1 μm [9]. Since the minority carrier lifetimes and diffusion length are relatively short in Cu(In,Ga)Se₂ devices, it is necessary to use thin absorbers to ensure collection of the short wavelength generated carriers. Thickness reduction is also favorable for the large scale manufacturing of the Cu(In,Ga)Se₂ solar cells. This leads to lower material usage, which may become increasingly important due to the scarcity and cost of In [40]. Thickness reduction also

can enable increased manufacturing throughout, since the deposition time can be reduced.

On the other hand, when the absorber thickness is reduced below 1 μm , the performance of $\text{Cu}(\text{In,Ga})\text{Se}_2$ devices begins to deteriorate due to incomplete optical absorption leading to lower J_{SC} [19]. This can be mitigated by adding a front reflector after all other device processing.

Another potential issue is the increased importance of back contact recombination for the low thickness [21]. The magnitude of this effect can be reduced by appropriate choice of back-contact material, surface modifications, or inclusion of a Ga grading [21].

In the backwall superstrate configuration, illumination is from the back surface hence a wide band gap transparent back contact is needed in the structure. The criteria to be considered in choosing back contacts for $\text{Cu}(\text{In,Ga})\text{Se}_2$ devices, in general, and transparent back contacts, in particular, will be discussed in the following sections.

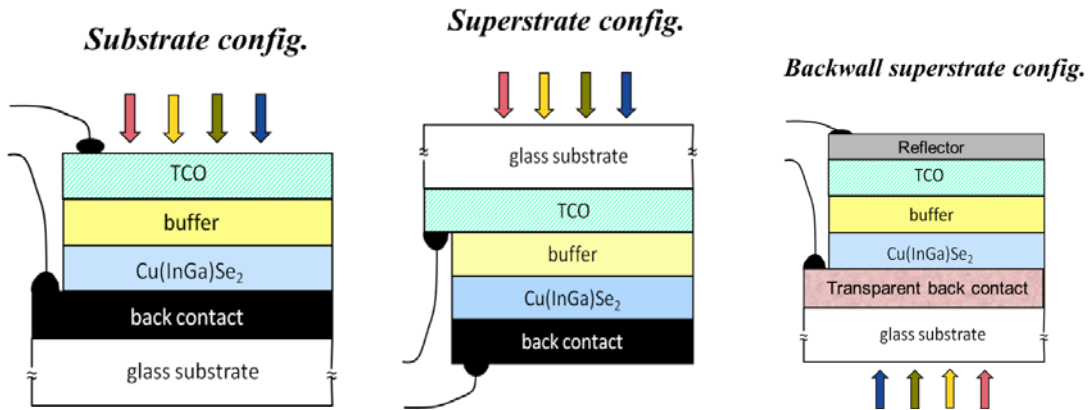


Figure 2.6: Schematic illustration of different configuration proposed for $\text{Cu}(\text{In,Ga})\text{Se}_2$ solar cells.

2.3 Back Contacts for Cu(In,Ga)Se₂ Solar Cells

Fig. 2.7a shows the band diagram of a p-type semiconductor and a metal contact before being brought in contact. The Schottky model of the metal-semiconductor barrier [41] predicts that the barrier height (ϕ_b) depends on the work function of the metal (ϕ_m), the band gap (E_g) of the p-type semiconductor, and the electron affinity (χ) of the p-type semiconductor:

$$\phi_{bp} = E_g + \chi - \phi_m \quad (2.3)$$

This will be modified to the following equation if the primary contact is a semiconductor, with the band gap and electron affinity of E_g^{SC} and χ^{SC} , respectively (Fig. 2.7b):

$$\Phi_{bp} = E_g^A + \chi^A - (E_g^{SC,B} + \chi^{SC,B}) \quad (2.4)$$

Ohmic contacts are metal–semiconductor junctions that do not rectify current. They have linear or quasi-linear current-voltage characteristics resulting from a small barrier between the two layers. Therefore, it is necessary to use a high work function metal contact or well-aligned buffer (semiconductor) layer in order to reduce Φ_b . Modeling has shown that barrier height at the back contact of the absorber should be less than 0.3 eV in order to not impede the cell performance [5]. Since the CuInSe₂ and CuGaSe₂ alloys have electron affinities (bandgaps) of 4.6 eV (1.04 eV) and 4.1 eV (1.68 eV), respectively [42], it's necessary to use a material with a work function > 5 eV for the back contact or well-aligned buffer layer in order to have the minimum barrier height at the junction.

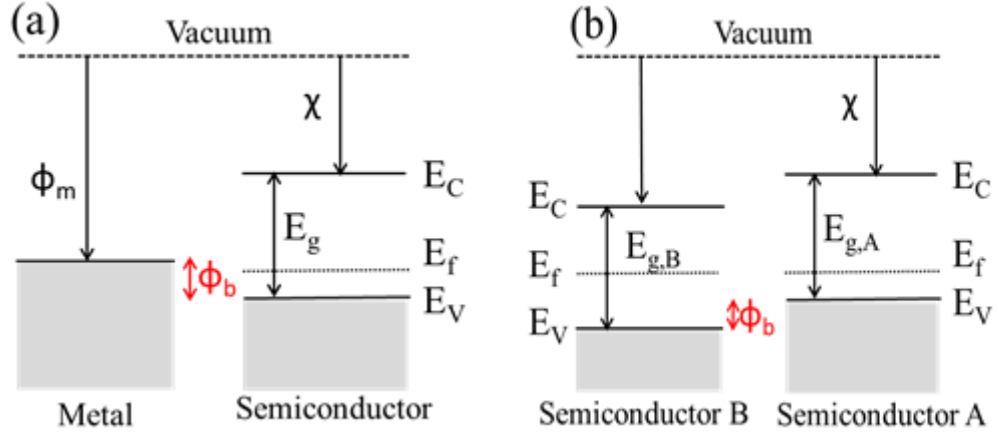


Figure 2.7: Band diagram of a p-type semiconductor and (a) a metal, and (b) a semiconductor contact layer.

In reality, the barrier height in most cases doesn't follow the simple Schottky model, and in some cases is even independent of the work function of the metal. Bardeen [43] was the first who pointed out the importance of surface states in behavior of metal-semiconductor contacts. The degree of dependence of barrier height on choice of metal is found to be dependent upon the semiconductor, the nature of its surface before contact formation, and the interfacial chemistry [44]. Rhoderick [45] has shown that for p-type semiconductors the barrier height can be calculated using the following equation:

$$\phi_b^p = \gamma(E_g + \chi_s - \phi_m) + (1 - \gamma)\phi_0 \quad (2.5)$$

Where ϕ_b^p is the barrier height of a p-type semiconductor, ϕ_0 is the energy of surface states, and γ is defined as:

$$\gamma \equiv 1 / \left(1 + \frac{qtN_{ss}}{K_i\epsilon_0} \right) \quad (2.6)$$

Here q is the electron charge, t is the interfacial layer thickness, N_{ss} is the density of surface states, K_i is the dielectric constant of the interfacial layer, and ϵ_0 is the dielectric constant of that layer. Clearly, for $N_{ss} = 0$, $\gamma = 1$ which results in the Schottky limit (Eq. 2.3). For $N_{ss} \rightarrow \infty$, $\gamma \rightarrow 0$, and the Bardeen limit happens in which the barrier height is constant and independent of the metal work function. This indicates that extrinsic factors such as crystal quality and surface treatment have a large effect on barrier heights [46].

Table 2.3 gives the work function values for a list of metals/compounds. Previous studies on Cu(In,Ga)Se₂ solar cells [30,47,48] have suggested the use of some of these metals/compounds for both substrate and superstrate configurations. Mo, the most widely used material for the base electrode in CuInSe₂ thin film solar cells, creates a blocking contact with a barrier height of ~ 0.8 eV [49] but a MoSe₂ layer forms during the deposition of CuInSe₂ layer [49–52], and gives ohmic characteristics to the contact. This is not the case in the superstrate configuration since the metal contact is deposited after the absorber layer.

Table 2.3: Work function of selected elements/compounds

Element	Work function (eV)	Element	Work function (eV)	Compound	Work function (eV)
Ag	4.5-4.7	Ir	5.0-5.7	ITO	4.8
Au	5.1-5.5	Mo	4.4-4.9	FTO	4.4
Be	4.9	Ni	5.0-5.4	ZnO	4.7
Co	5.0	Pt	5.1-5.9	MoSe ₂	5.7
Cu	4.5-5.1	Te	4.9	MoO ₃	5.5

All of the studied CuInSe₂-based superstrate cells (Table 2.2) have used high work function metals, i.e. Pt or Au, as the back contact which are not viable candidates for commercial applications. Therefore, one must develop either an opaque or transparent back contact via surface modification or introduction of buffer layers (e.g. MoSe₂) in order to have an ohmic contact at the back surface.

Previous studies on CuInSe₂ film structure have shown the presence of different ordered defect compounds (ODC) phases which typically segregate near the surface [10,53–55]. These have chalcopyrite structure with a structurally ordered insertion of intrinsic defects [11]. In fact, ODC phases such as Cu(In_{1-x}Ga_x)₃Se₅ and Cu(In_{1-x}Ga_x)₅Se₈ which have a bandgap of 0.2 eV higher than that of the corresponding Cu(In_{1-x}Ga_x)Se₂ alloy [56–58], may result in a higher barrier height.

Figure 2.8 shows the effect of γ (surface quality factor) and bandgap variation on the barrier height of Au contacts on Cu(In_{0.7}Ga_{0.3})Se₂ and Cu(In_{0.2}Ga_{0.8})Se₂ films, based on Eq. (2.5). The Au work function is assumed to be constant at 5.31 eV [42]. At any given surface condition, increasing the bandgap will increase the barrier height. Therefore, ohmic contacts can only be obtained in certain conditions. The effect of surface defects is less significant at higher band gaps.

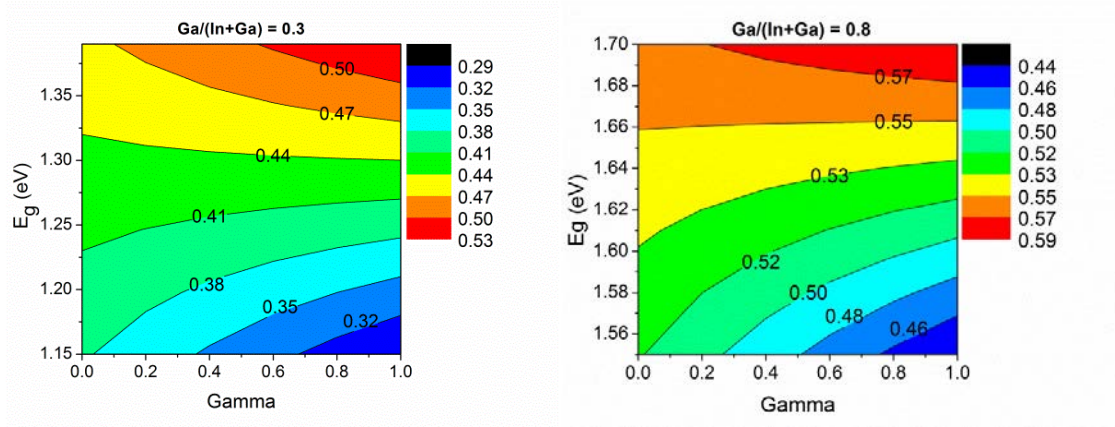


Figure 2.8: Effect of bandgap and surface condition (γ) on the barrier height of the Au-Cu(In_{1-x}Ga_x)Se₂ contact, based on the Rhoderick model [45]. Color codes are representing different barrier height values; units are in eV.

2.3.1 Current Transport Mechanism

The current transport mechanism for the metal-semiconductor contacts can be defined in three different regimes [44]:

- I) Thermionic emission for $kT \gg qE_{00}$
 - II) Thermionic-field emission for $kT \approx qE_{00}$
 - III) Field emission (tunneling) for $kT \ll qE_{00}$
- (2.6)

Where k is the Boltzmann's constant, T the absolute temperature, q the electron charge and E_{00} the characteristic energy of semiconductors which is given by:

$$E_{00} = \frac{h}{4\pi} \left(\frac{N}{m\varepsilon} \right)^{1/2} \quad (2.7)$$

Here h is Planck's constant, N the semiconductor net carrier concentration, m the effective mass, and ε the semiconductor dielectric constant. Therefore the ratio of kT/E_{00} is a measure of the relative importance of the thermionic process in relation to the field emission (tunneling) process. Table 2.4 shows typical values for the

electronic properties of CuInSe₂ films [14]. Therefore, calculating the values of $E_{00} \approx 0.059$ (for heavy holes) and 2.82 (for light holes) and $kT \approx 0.026$ (at room temperature), either field emission or thermionic field emission would be the dominant current transport mechanism between CuInSe₂ alloys and metal/transparent contacts.

Table 2.4: Selected electronic properties of CuInSe₂ and CuGaSe₂ [14,15].

Parameter	N (cm ⁻³)	ϵ	m (m _{e0})		E ₀₀ (eV)	
			Light hole	Heavy hole	Light hole	Heavy hole
CuInSe ₂	10 ¹⁵ -10 ¹⁶	13.6	0.09	0.72	0.059	2.82
CuGaSe ₂	10 ¹⁵ -10 ¹⁶	11.0	0.14	1.2	0.052	2.43

The contact resistivity ρ_c , which is an important factor in ohmic contacts, is defined as [44]:

$$\rho_c \equiv \left(\frac{\partial J}{\partial V} \right)_{V=0}^{-1} \quad (2.8)$$

The value of $\rho_c < 0.06 \Omega\text{-cm}^2$ has been reported as a criterion for a low resistance back contact for a typical CuInSe₂ cell [59]. Specific contact resistance is a function of the barrier height, net carrier concentration, and temperature [44,60]:

$$\text{when } kT \gg qE_{00} \quad \rho_c \propto \exp\left(\frac{q\phi_b}{kT}\right) \quad (2.9)$$

$$\text{when } kT \approx qE_{00} \quad \rho_c \propto \exp\left(\frac{q\phi_b}{E_{00} \coth\left(\frac{E_{00}}{kT}\right)}\right)$$

$$\text{when } kT \ll qE_{00} \quad \rho_c \propto \exp\left(\frac{q\phi_b}{E_{00}}\right)$$

Qualitative dependence on the above-mentioned parameters is shown in Fig. 2.9 for a fixed semiconductor material. In thermionic emission, contact resistance is independent of carrier concentration and depends only on the barrier height (ϕ_b). In the case of thermionic field and field emission, contact resistance has a dependence on both ϕ_b and N . Hence one requires low barrier heights (ϕ_b) and a high carrier concentration (N) to produce low resistance ohmic contacts.

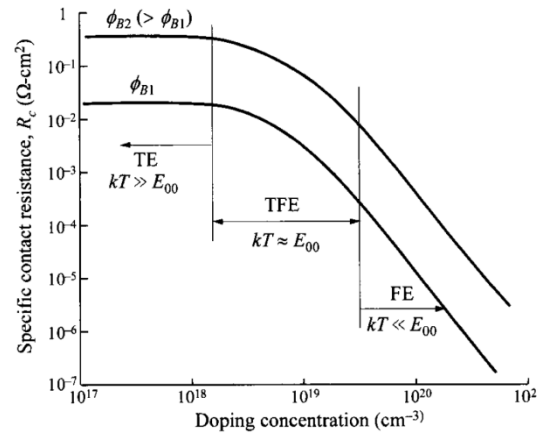


Figure 2.9: Specific contact resistance as a function of net carrier concentration (and E_{00}), barrier height, and temperature, reprinted from [60].

In practice, the contact resistance can be highly affected by a number of other factors that influence conduction, e.g. interface layers due to oxide formation or contamination, surface damage, minority carrier injection, energetically deep lying impurity levels, or traps [61]. For example, Moons, et al. [62] have reported that surface etching of CuInSe₂ crystals with a 0.5% solution of Br₂ in methanol for 30 sec at room temperature decreases the resistance of Au/CuInSe₂ ohmic contacts, but

increases the resistance of In-Ga contacts. Rabinal, et al. [63] have found that the Br₂/methanol treatment resulted in lower resistance of Au contacts compared to a KOH+KCN+H₂O treatment.

2.3.2 Transparent Back Contacts

While substrate-type devices usually employ metallic Mo back electrodes, making it impossible for light to pass through the metal electrode layer, a transparent back contact is required in the backwall superstrate configuration allowing illumination from the back of the device, as discussed in section 2.2.3. In addition, transparent back contacts can be used in frontwall superstrate or substrate solar cells where they can potentially be used as the top cell of tandem devices, with wide bandgap $E_g \geq 1.6$ eV [64]. Besides, such semitransparent cells have potential applications as bifacial devices and solar windows.

Several groups have employed transparent back contacts for both substrate and superstrate configurations of CuInSe₂-based solar cells. Table 2.5 shows a list of potential transparent compounds to be considered as the primary back contacts for Cu(In,Ga)Se₂ solar cells. In the first row, selected properties of Cu(In,Ga)Se₂ films are also shown for comparison.

For the backwall superstrate cells or substrate cells, back contact candidates should be thermodynamically stable under Cu(In,Ga)Se₂ growth conditions with Se vapor. In addition, there should be a low barrier height at the junction, forming an ohmic contact with Cu(In,Ga)Se₂ layer. MoSe₂ can be formed during the Cu(In,Ga)Se₂ deposition and is reported to have ohmic characteristics as the contact [50]. But, it would block a notable portion of the spectrum due its low bandgap value

of ~ 1.4 eV, and therefore is not an ideal candidate for the backwall superstrate structure.

Table 2.5: Electronic properties of selected transparent compounds, and their calculated band offsets compared to Cu(In,Ga)Se₂ alloy. Gibbs energy of formation values at 550 °C are also shown.

Compound	Band gap (eV)	Work function (eV)	Electron affinity (eV)	Valence band offset (eV)	Conduction band offset (eV)	ΔG at 550°C (kcal/mol)
Cu(In,Ga)Se ₂	1.15	5.3	4.4	---	---	
MoSe ₂	1.4	4.4	4.2	0.05	0.1	-59.9
MoO ₃	3.2	5.4	2.2	-0.15	-1.9	-198.3
WO ₃	3.0	5.1-6.2	3.3	0.35	-0.8	-222.6
ZnTe	2.3	5.3	3.5	0.25	-0.9	NA
Cu ₂ O	2.2	4.7	3.2	-0.15	-1.2	-64.0
ZnO	3.4	5.2	4.6	2.45	0.2	-95.7
SnO ₂	3.6	4.9	4.5	2.55	0.1	-153.8
In ₂ O ₃	3.7	4.8	4.4	2.55	0.0	-250.2
V ₂ O ₅	2.3	4.7	5.4	2.15	1.0	-507.2
TiO ₂	3.0	4.2	3.9	1.35	-0.5	-240.8
Cd ₂ SnO ₄	3.0	NA	3.8	1.25	-0.6	NA

Based on the values summarized in Table 2.52.5, all of the well-known TCO compounds such as ZnO, In₂O₃, SnO₂, Cd₂SnO₄, V₂O₅ and TiO₂ have a large Gibbs energy of formation, and thus are stable under at Cu(In,Ga)Se₂ growth condition at

550 °C. Still, formation of Ga_2O_3 phase ($\Delta G = 285 \text{ kcal/mol}$) is likely at the oxides- Cu(In,Ga)Se_2 interface.

On the other hand, they would have a valence band offset $> 1 \text{ eV}$ relative to the Cu(In,Ga)Se_2 layer, making a blocking barrier for the carriers transport through the back contact. However, as discussed in the previous section, based on Rhoderick [45] model, the actual barrier height depends the nature of the surface before contact formation, and the interfacial chemistry [44]. Therefore, extrinsic factors such as crystal quality and surface treatment would have a large effect on barrier heights [46].

Previous studies have used these wide band gap materials i.e. ITO [37,65], ZnO:Al [37], $\text{SnO}_2\text{:F}$ [37], ZnO:Al/MoSe_2 [66] with varying degrees of success. However, it was found that the Cu(In,Ga)Se_2 film should be deposited at low temperature ($< 500 \text{ }^\circ\text{C}$) with these materials to prevent the diffusion of F, in the case of $\text{SnO}_2\text{:F}$ [67], or the formation of Ga_2O_3 at the interface [67–69], and thus limiting their potential application in Cu(In,Ga)Se_2 based devices. Some notable results reported using these transparent contacts are discussed in the following.

Nakada, et al. [37] reported that the performance of cells made with $\text{SnO}_2\text{:F}$ and ITO back contacts is almost the same as that of conventional Cu(In,Ga)Se_2 thin film solar cells fabricated using Mo back contacts. Almost no intermixing at the $\text{Cu(In,Ga)Se}_2/\text{ITO}$ interface was observed by secondary ion mass spectrometry [70] and an efficiency of 12.6% for the bifacial Cu(In,Ga)Se_2 cells using the transparent conductive oxide (TCO) back contacts was reported [37].

In another study, Woods, et al. [71] showed that while TCO layers such as ITO can be proper back contact candidates for low band gap devices, non-ideal band alignment and lack of sufficient interface states or mid-gap states in the TCO for

tunneling necessitates use of an interface layer for wide band gap ($E_g > 1.35$ eV) Al-alloyed CuInSe_2 devices.

The TCO back contacts have also been employed for tandem devices where Nishiwaki, et al. [65] achieved an efficiency of 7.8% with a V_{OC} of 1.18 V using an ITO back contact for the top layer of a stacked tandem cell. The transparency loss, which might be caused by the formation of oxygen vacancies, opaque and highly resistive sub-oxides in the ITO layer, and or surface selenization of the ITO layer, must be prevented for high efficiency superstrate and tandem devices [65].

Nakada, et al. [37] and Nishiwaki, et al.[65] found that $\text{Cu(In,Ga)Se}_2/\text{TCO}$ contacts exhibit ohmic characteristics probably due to: a) direct recombination of holes in the valence band of Cu(In,Ga)Se_2 and electrons in the conduction band of the n^+ -TCO, or b) trap-assisted tunneling in the presence of the barrier at the $p\text{-Cu(In,Ga)Se}_2/n^+\text{-TCO}$ interface. However, direct tunneling through the barrier may be difficult since the carrier concentration of Cu(In,Ga)Se_2 is usually too low to form a very thin depletion layer or barrier inside of the $p\text{-Cu(In,Ga)Se}_2$.

Table 2.5 shows that Cu_2O and ZnTe , with moderate bandgap values of ~ 2.3 eV, can also be considered as transparent back contacts. Their band structure relative to the Cu(In,Ga)Se_2 layer would also be desired due to low valence band offset (< 0.3 eV) at the back contact interface. Nevertheless, they are not stable under the Cu(In,Ga)Se_2 growth condition, and a noticeable amount of inter-diffusion is likely because of high diffusion coefficient of Cu [72,73] and Zn [74,75] atoms at high temperature deposition of the Cu(In,Ga)Se_2 . Therefore, Cu_2O and ZnTe cannot be viable back contact candidates for the either substrate or backwall superstrate Cu(In,Ga)Se_2 solar cells.

Table 2.5 shows that V_2O_5 doesn't provide a desired band alignment with $Cu(In,Ga)Se_2$ and hence will not be considered for further investigation. Instead, MoO_3 and WO_3 have a low valence band offset with $Cu(In,Ga)Se_2$ layer and can be potential candidates to be considered as the primary back contact of $Cu(In,Ga)Se_2$ thin film solar cells. The choice of MoO_3 and WO_3 as a contact layer was inspired by work in the field of organic electronics [76–78] where it has been well established that transition metal oxides, such as V_2O_5 [76], WO_3 [79], and MoO_3 [76,80–82], are efficient hole injection materials for organic devices, being placed between an anode electrode and a hole-transport layer [83–85]. Such buffer layers can enhance the performance of organic photovoltaic cells by preventing undesired recombination of photo generated-carriers [86], by keeping excitons away from electrodes, or by modifying surface properties to promote a higher degree of ordering or to tune the effective work function of electrodes [87,88].

Hori et al. [89] have shown that the insertion of a MoO_3 layer as a cathode buffer layer enhances the performance of the organic solar cells. Kinoshita et al. [81] have also found that inserting a thin MoO_3 on ITO substrate layer improves the open circuit voltage (V_{OC}) of organic solar cells without affecting short-circuit current density and fill factor, resulting in an increased power conversion efficiency of the device.

The increase in V_{OC} is attributed to enhancement in built-in potential generated by the difference in the work function of electrodes. According to the metal-insulator-metal model, V_{OC} depends on the difference of work function of electrodes [90,91]. Higher V_{OC} has been achieved in organic solar cell by varying the work function of the cathode electrode [90,92] or anode electrode [91]. Detailed photoemission studies

[83,93] have shown that the effective work function of these transition metal oxides on a conductive surface such as ITO can be very high due to the presence of an interfacial dipole between the oxide and the conductive surface.

Recently, a MoO_3 back contact buffer has also been successfully employed for CdS/CdTe solar cells [94–96]. Lin et al. [94,95] have confirmed the ohmic characteristics of MoO_3 back contacts for CdS/CdTe solar cells. With contacts such as MoO_3/Ni and MoO_3/Al , cell efficiencies comparable to those with conventional back contacts have been produced. Again, the usefulness of MoO_3 is attributed to its high work function which is needed to match that of p-type CdTe in producing contacts with low resistance. In addition, the MoO_3 buffer acts as a diffusion barrier to minimize the interaction between the metal electrode and CdTe [95].

The highest reported work function value for MoO_3 is 6.86 eV [83], obtained for a near stoichiometric MoO_3 film. On the other hand, lower work function values of about 5.3 eV have also been reported for the MoO_3 [76]. The discrepancy arises due to the nature of MoO_3 being very sensitive to processing conditions. MoO_3 is reported to have crystal structures of monoclinic (β) or orthorhombic (α) with the space groups of $P2_1/c$ and $Pbnm$, respectively [97]. However, oxygen deficiency may lead to the formation of sub-stoichiometric phases of Mo_9O_{24} , Mo_8O_{23} , and Mo_4O_{11} which have been presented in the Mo-O phase diagram (Fig. 2.10 [98]).

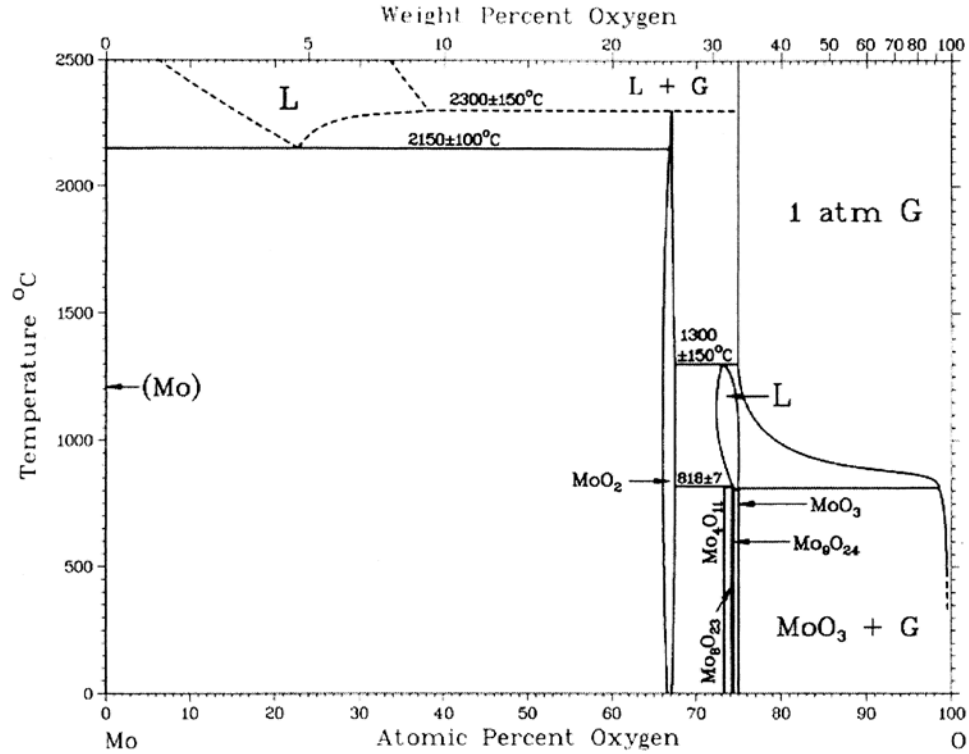


Figure 2.10: Phase diagram of Mo and O, reprinted from [99].

Zhang et al. [77] reported that the work function of MoO_{3-x} is highly dependent on the deposition method, air exposure and composition of the MoO_{3-x} film. Scanlon et al. [100] based their study on a combination of theoretical DFT calculations and XPS measurements. They have shown that the Fermi level is close to the conduction band in the semiconductor MoO_{3-x}. However, when x is increased to 1 the bandgap is filled with states and the material acts as a metal. This demonstrates the dramatic change of properties of MoO_{3-x}, by variation of x from 0 to 1. A slightly oxygen deficient MoO₃ film can therefore behave very differently than a stoichiometric film.

Analogously, WO_3 films with a wide bandgap (2.5-3.2 eV) [101–103] and high work function (> 6 eV) [104] can be considered as a potential candidate for the primary back contact of Cu(In,Ga)Se_2 thin film solar cells. Table 2.5 shows the theoretical valence band offset value of 0.35 eV between WO_3 and Cu(In,Ga)Se_2 layer. WO_3 films have also been widely used in bulk-hetero-junction [105–107], and dye-sensitized solar cells [105,106].

Han et al. [108] have shown that introducing a thin WO_3 buffer layer can enhance the performance of P3HT:PCBM-60 bulk heterojunction cells made on transparent anodes. They have related the observed improvement to the relatively large shunt resistance of WO_3 -based cells under illumination that is linked to a low carrier recombination resulting in high fill factor and open-circuit voltage. In another study, Janssen et al. [109] have employed a WO_3 transparent as the interconnecting layer and could enhance the performance of organic tandem solar cells.

In a recent study by Li et al. [110] a semitransparent inverted polymer solar cell was demonstrated using transparent $\text{MoO}_3/\text{Ag}/\text{WO}_3$ anodes. This structure has solved the low transmittance and high series resistance issues of conventional anodes used in tandem structures [111,112]. The MoO_3 buffer layer improves the hole collection, while the WO_3 layer enhances the optical transmittance of the photovoltaic device. The series resistance of the cell has also been reduced due to the very thin Ag layer.

Table 2.5 shows that MoO_3 and WO_3 have a low valence band offset with Cu(In,Ga)Se_2 layer and can be potential candidates to be considered as the primary back contact of Cu(In,Ga)Se_2 thin film solar cells. In particular, their stability at high temperatures [113], high transparency ($>80\%$ in the visible and near IR range) and

wide bandgap of MoO₃ (3.0-3.8 eV) [114–116] and WO₃ (2.5-3.2eV) [101–103,117] make them ideal transparent back contact candidates for the superstrate devices. Their Fermi level and density of states can potentially be tuned by controlling the oxygen stoichiometry during the deposition and/or post processing. To do so, we need an in-depth understanding of the structural, optical and surface properties of the MoO₃ and WO₃ films, which will be discussed in the following chapters in details. Since the electrical resistivity of the MoO₃ and WO₃ films are $> 10^6 \Omega\text{-cm}$ [115,118–121], only very thin layers were considered in this study to prevent high series resistance in the device.

Chapter 3

EXPERIMENTAL

3.1 Sputtering

Sputtering is a process in which bombardment of a target material with high energy ions results in ejection of its atoms. This takes place only if the kinetic energy of the incoming ions is much higher than conventional thermal energies of atoms ($\gg 1$ eV) [122]. The sputtering process has been widely utilized in a variety of applications such as thin films deposition, analytical techniques (e.g., Secondary Ion Mass Spectroscopy and X-ray Photoelectron Spectroscopy), surface treatment etc. [122–124].

The ratio between the numbers of atoms ejected from the target to the numbers of incident ions is defined as the sputtering yield (S) [125]. The currently accepted theory for the sputtering yield from collision cascade is based on the Sigmund model [126] and predicts that

$$S = \frac{3\alpha}{4\pi^2} \frac{4M_1M_2}{(M_1+M_2)^2} \frac{E_1}{E_b} \quad (\text{for } E_1 < 1 \text{ keV}) \quad (3.1)$$

And

$$S = 3.56\alpha \frac{Z_1Z_2}{Z_1^{2/3}+Z_2^{2/3}} \left(\frac{M_1}{M_1+M_2} \right) \frac{S_n(E)}{E_b} \quad (\text{for } E_1 > 1 \text{ keV}) \quad (3.2)$$

Where α is a measure of the efficiency of the momentum transfer in collision, M_1 and M_2 are the atomic weight of the atoms, E_1 is the energy of incident ion, E_b is the surface binding energy, Z_1 and Z_2 are the atomic numbers, and $S_n(E)$ is a measure of the energy loss per unit length due to nuclear collisions. Previous studies have shown

the effect of incident energy on the sputtering yield of monoatomic and multicomponent solids [127,128]. At high energy S is relatively constant because $S_n(E)$ tends to be independent of energy [125]. Typically, S is in the range of 0.1 to 10, depending on the target material and incident ion energy.

Fig. 3.1 explains two possible mechanisms that may happen during the sputtering process. If the heavy ions hit the surface, their energy will be dissipated near the surface making a collision cascade. As a result, atoms will be ejected from the surface of the target (mechanism I) [126]. Alternatively, if light ions such as H^+ and D^+ hit the surface, their low energy cannot produce a collision cascade near the surface. Therefore, those ions will be reflected from inside the target material and hit near-surface atoms. This may result in ejection of surface atoms in case the collision energy is sufficient to overcome the surface barrier (mechanism II) [129,130].

In practice, the sputtering mechanism shift from mechanisms I to II by decreasing the mass of incident ions, and both mechanisms contribute to the sputtering yield of ions with intermediate mass, such as Ar^+ .

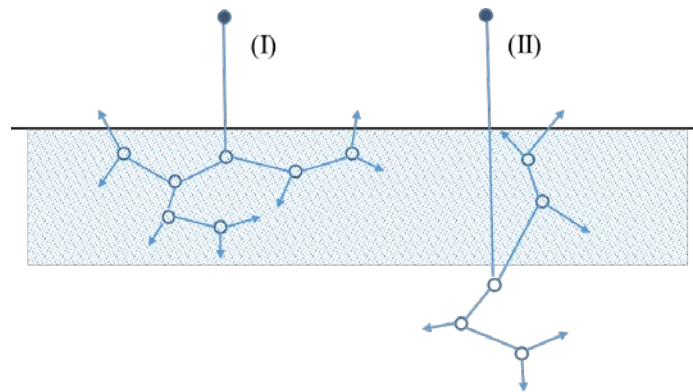


Figure 3.1: Schematic diagram of the sputtering mechanisms. Sputtering mechanism for (I) heavy-ion bombardment, and (II) light-ion bombardment [125].

3.1.1 Reactive Sputtering

Sputtering is normally carried out in an argon ambient, and either pure single metal targets or metal alloys can be sputtered, making it possible to deposit complex coatings. By adding a reactive gas to the sputtering process, *reactive sputtering*, it is possible to form a compound between sputtered metal atoms and reactive gas molecules. In this way, different forms of oxides, nitrides, borides, and carbides can be made [123]. Figure 3.2 illustrates a schematic of a typical reactive sputtering system. It should be noted that the addition of the reactive gas significantly changes the behavior of the sputtering process. The deposition rate as well as the composition of the film will be influenced by the flow of the reactive gas, and should be considered in practice [131,132]. The partial pressure (P) of the reactive gas is an important parameter in the reactive sputtering process. In fact, a uniform partial pressure P of the reactive gas will cause a uniform flux of reactive molecules F (molecules/unit area and time) to the cathode. Based on the gas kinetic model [133], the relation between flux of molecules (F) and the partial pressure (P) can be derived as:

$$F = \frac{P}{\sqrt{2kT\pi m}} \quad (3.3)$$

where k is a Boltzmann's constant, T is the absolute temperature, and m is the mass of the gas molecule.

When the supply of the reactive gas is too low the sputtering rate is high, but deposited films will have a sub-stoichiometric composition. On the other hand, high supply of the reactive gas results in a stoichiometric composition although the deposition rate is reduced due to poisoning of the target surface. Therefore, there are optimum processing conditions in which both high rate and stoichiometric film composition may be obtained.

In comparison with the sputtering from oxide targets, reactive sputtering produces films with a better uniformity as a result of better plasma density caused by the high conductivity of elemental targets [123].

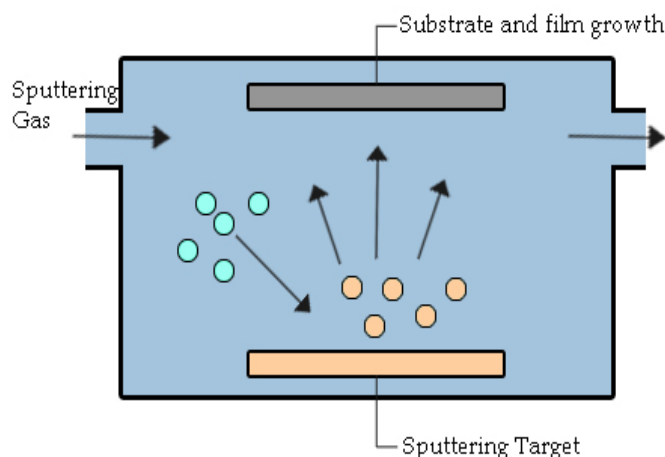


Figure 3.2: Schematic of a typical reactive sputtering system.

3.1.2 Reactive RF Sputtering of MoO_3 and WO_3 Films

For this project, Molybdenum oxide and Tungsten oxide films were deposited on different substrates by reactive rf sputtering from a 5cm diameter Mo target or a 10 cm diameter W target (99.95% purity), respectively. The sputter chamber was pumped to a base pressure of $\sim 10^{-7}$ Torr. The substrate was positioned parallel to the target with a distance of 1.8 cm and substrate heating was provided by a halogen lamp heater on the back side of the substrate. The sputtering gases were a mixture of argon (Ar) and oxygen (O_2), with oxygen content $\text{O}_2/(\text{O}_2+\text{Ar})$ varying between 0 and 1. The sputtering pressure was fixed at 10 mTorr and rf power was 250 W for both MoO_3 and WO_3 . For each run, the target was pre-sputtered for 30 minutes to clean and condition

the surface. Film thickness after deposition was determined using a Dektak mechanical step profilometer. Post-processing of the films was performed by annealing at temperatures of 300-500 °C, for 1 h in an air atmosphere, in a 6 cm diameter quartz-lined tube furnace.

3.2 (Ag,Cu)(In,Ga)Se₂ Growth

(Ag_wCu_{1-w})(In_{1-x}Ga_x)Se₂ films were deposited on different substrates using multi-source elemental evaporation and Figure 3.3 shows the schematic of the evaporation system. Films were deposited at 550 °C with constant fluxes over time so that they have no intentional through-film composition gradients. The ratios $x = \text{Ga}/(\text{In}+\text{Ga})$ and $w = \text{Ag}/(\text{Ag}+\text{Cu})$ were varied between 0 and 1 in order to evaluate the effect of alloying elements on structural and surface properties of the films. All films have bulk compositions with I/III ratio $(\text{Ag}+\text{Cu})/(\text{In}+\text{Ga}) \approx 0.8-0.9$. Film thickness for the backwall superstrate cells varied between 0.1-1 µm in order to find the optimum condition and were 2 µm thick for substrate cells. The thickness of the absorber layers were adjusted by variation of the deposition time (5-60 minutes). The composition and thickness were measured by x-ray fluorescence (XRF) and thickness verified by scanning electron microscopy of sample cross-sections. The Se/Metal flux ratio was ~ 10 during the growth of all films.

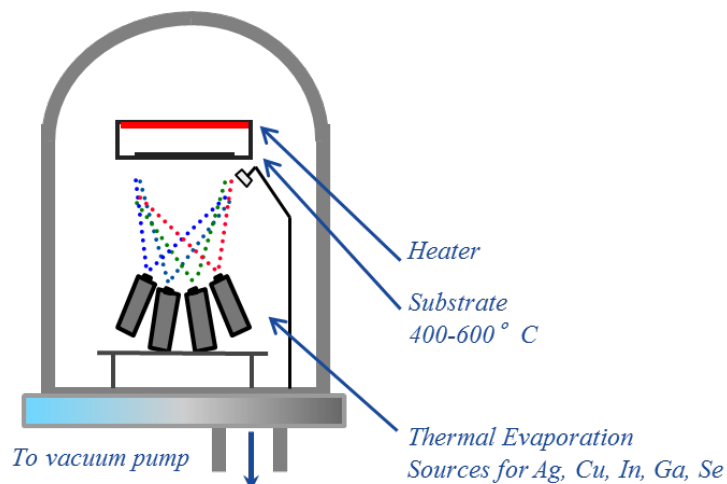


Figure 3.3: Schematic of the multi-source elemental evaporation system.

3.3 Structural Characterization

Structural properties of samples were characterized by symmetric x-ray diffraction (XRD) using a Philips/Norelco wide angle goniometer, and grazing incidence x-ray diffraction (GIXRD) using a Rigaku D/Max 2200, both with Cu K α radiation, and 0.02° step size. For the (Ag_wCu_{1-w})(In_{1-x}Ga_x)Se₂ films, GIXRD detailed scans were taken at 5 different incident angles ranging from 0.5° to 8°. This range of incident beam angles changes the sampling depth from 110 nm to 1770 nm in films with mid-compositions, Ag = 0.5 and In = 0.5. For the MoO₃ and WO₃ films, the incident angle was set to 0.5° corresponding to the sampling depth of ~ 250 nm.

The average composition of the absorber layers was determined by Energy-dispersive X-ray spectroscopy (EDS) using an Oxford Instruments Pentafet detector with an Amray 1810T electron microscope. The peak intensities were calibrated based on the counts obtained by analysis of a Cu sample. The EDS sampled depth is ~1400 nm at 20 kV. Interface properties and effect of different back contacts on the

(Ag_wCu_{1-w})(In_{1-x}Ga_x)Se₂ structure was studied using the JSM-7400F field emission scanning electron microscope (SEM) at 15 kV.

3.4 Surface Characterization

X-ray photoelectron spectroscopy (XPS) is the most widely used surface analytical technique in this project, and is therefore described here in more detail than the other techniques.

When a photon of energy $h\nu$ hits an electron located in a level with binding energy E_B (for example E_K of the K-shell in Figure 3.4), the photon energy will be transferred to the electron. As a result, a photoelectron with kinetic energy E_{kin} will be ejected:

$$E_{kin} = h\nu - E_B - \phi_s \quad (3.4)$$

where ϕ_s is the work-function of the instrument [134].

In the XPS analysis most attention is focused on the electrons ejected from the core levels, though electrons coming from the occupied portion of the valence band will be detected as well. Since each elements has its own characteristics set of electronic binding energies, it is possible to identify different elements by measuring the photoelectron kinetic energies. In addition, equation (3.4) suggests that any changes in E_B will cause a change in E_{kin} . Therefore, any changes in the chemical bonds of an atom can be identified by monitoring changes in the photoelectron energies.

When an electron with kinetic energy E moves through a solid matrix M, it has a probability of traveling a certain distance before losing all or part of its energy due to an inelastic collision. The average distance traveled before such a collision is known as the inelastic mean free path $\lambda_M(E)$ [135], which is only a function of M and of E .

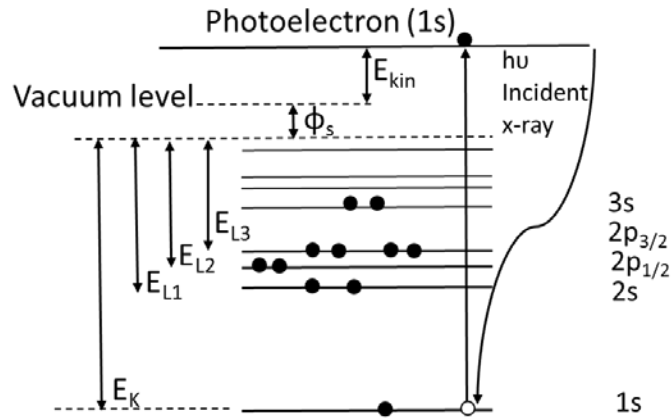


Figure 3.4: Schematic diagram of electron emission processes in solids [134]. In this example, a photon of energy $h\nu$ hits an electron located in a level with binding energy E_K . As a result, the photon energy is transferred to the electron, and a photoelectron with kinetic energy E_{kin} is ejected.

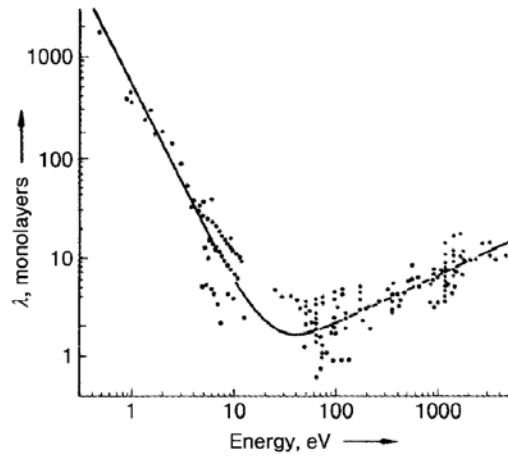


Figure 3.5: The inelastic mean free path as a function of electron kinetic energy, reprinted from [134].

Seah and Dench [122] have measured the variation of λ in terms of atomic monolayers as a function of kinetic energy, as shown in Figure 3.5. Since the energy ranges used in XPS analysis are typically 50 – 1200 eV, the values of λ are very small,

corresponding to only a few monolayers. So the photoelectrons must originate from atomic layers very close to surface to be detected. Therefore, the XPS technique is very surface-specific.

Figure 3.6a shows a wide-scan or survey XPS spectrum of a Mo foil recorded over a wide range of energies with the Al $K\alpha$ (1486.6 eV) radiation. Though such a spectrum reveals the major features, minor or more detailed features of the spectra will be revealed only if a better energy resolution is acquired over much more restricted energy ranges (narrow or fine scan spectra) which is shown in Fig. 3.6b. The peaks were fit by Gaussian-Lorentzian curves satisfying the following constraints: a) the $3d_{5/2}$ to $3d_{3/2}$ ratio is 3:2; b) each doublet has equal full width at half maximum (FWHM); and c) the spin orbit splitting of the Mo 3d doublets is 3.13 eV [136–138].

The shift in energy of the photoelectron peak observed in Fig. 3.6b is due to change in the chemical state of the element. When an atom makes a bond with another atom or group of atoms, the valence electron density changes resulting in an adjustment of the electrostatic potential affecting the core electrons [134]. Therefore, the binding energies of the core electrons change, and according to Equation 3.4, cause shifts in the corresponding photoelectron peaks. The shift can be positive or negative if the charge is accepted or donated, respectively, and can be used to identify unknown samples. A complete collection of such values can be found in the NIST X-ray photoelectron spectroscopy database [139]. In fact, XPS is the main the surface analytical technique used in identification of chemical states.

In many cases, besides the analytical information about the original surface, it is desired to collect information about the composition and chemical states of samples in a depth considerably greater than the inelastic mean free path. To do so, depth

profiling is performed by etching layer by layer and analyzing the surface afterwards. A noble gas such as Ar^+ is typically used to sputter etch the surface to minimize any chemical effects. However, preferential sputtering may result in a chemically modified surface, even if the primary ion from the ion gun is not chemically reactive and should be considered in the data analysis. The depth resolution achievable during profiling depends on many variables, such as roughness, crystalline structure, phase distribution, electrical conductivity, atomic mixing, preferential sputtering, compound reduction, diffusion, segregation, and sputter-induced topography which are discussed in detail in Refs [135,140].

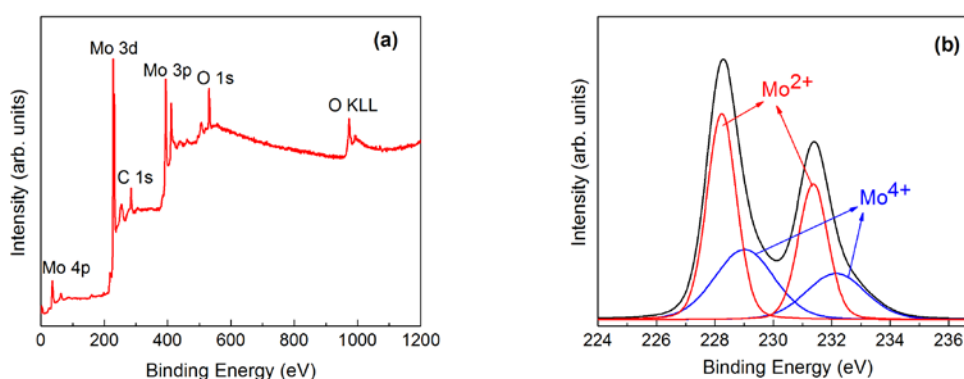


Figure 3.6: a) Wide scan spectrum, and b) fine scan spectrum of Mo3d doublet obtained by analysis of a Mo foil.

For this project, high resolution XPS measurements were performed with 0.05 eV step size to study the core level binding energy and oxidation states of different films. The instrument used was a Physical Electronics Model 5400, equipped with a multi-channel hemispherical analyzer, and a monochromatic Al $K\alpha$ x-ray excitation

under the applied voltage of 20 kV. An Ar⁺ ion gun (2 keV) was used to perform depth profiling by etching layer by layer and analyzing the surface afterwards. The first two minutes of sputter etching remove adsorbed contaminants such as oxygen and carbon and are not included in the analysis. The Ar⁺ ion etch rate was calibrated using a Ta₂O₅/Ta foil sample and found to be about 1 nm/min. For the film samples of this study this rate was applied as a depth etch rate. The error on the atomic concentrations depends on the element's counting statistics and was less than 1% for all the elements due to high number of counts measured. The XPS line of Ag 3d, Cu 2p, In 3d, Ga 2p, Ga 3d, Se 3d, Mo 3d, Mo 3p, W 4f, Sn 3d and O 1s were considered for the composition analysis. Charging offsets, which can be significant for the highly resistive samples, were corrected by calibrating the XPS spectrum based on the C 1s peak position (284.8 eV) [136].

Band discontinuities were obtained by analysis of the XPS spectra. The accuracy of the experimental measurements of band discontinuity is limited primarily by the determination of the valence band edge from the experimental spectra. A precise method would be based on the knowledge of the theoretical density of states in the valence band region [141,142]. However, these values were not available for the materials of this work; therefore, a more common approach to determine the valence band edge was used. For this study, the top of the valence band, E_V , was measured by linear extrapolation of the leading edge of the valence band spectrum back to the energy axis and defining the slope intercept as E_V [143,144]. The absolute value of the energies were corrected using the C 1s signal (C 1s = 284.8 eV) [136]. The effect of possible preferential sputtering, which can be significant for lighter elements, has not

been taken into account here so only relative differences in the band alignment of various samples are significant.

Fig. 3.7 shows the sample curves for the Mo-CIGS etched for 90 min. The valence band offsets were determined using the following equation [141,145,146]:

$$\Delta E_V = (E_{CL1} - E_{V1}) - (E_{CL2} - E_{V2}) - \Delta E_{CL} \quad (3.5)$$

Where E_{CLi} is the core level binding energy in the bulk, E_{Vi} is the valence band edge in the bulk, and ΔE_{CL} is the energy difference between the core levels at the interface.

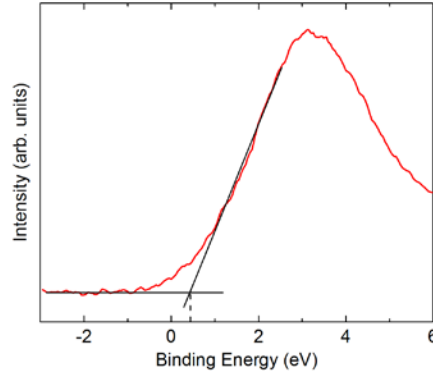


Figure 3.7: Valence band edge of Mo/Cu(In,Ga)Se₂ samples sputter etched for 90 min.

3.5 Optical Characterization

Optical properties of the samples were analyzed using a Perkin-Elmer UV/Vis/NIR spectrophotometer model Lambda 750 equipped with an integrating sphere. Figure 3.8 shows the instrument setup used for this study. Total transmission (T) and reflection (R) data were obtained from 300-1400 nm at 1 nm intervals.

The total absorption coefficient α was calculated from the T-R measurements using the following equation [147]:

$$\alpha = \frac{1}{d} \ln \frac{(1-R)^2}{T} \quad (3.6)$$

Where d is the thickness, T the transmittance, and R the reflectance of films. This equation is valid for highly absorbing materials with $\alpha d \gg 1$ [147].

For photon energies larger than the bandgap (E_g) the absorption coefficient α can be described by the following equation:

$$\alpha E \sim (E - E_g)^n \quad (3.7)$$

where E is the photon energy and the exponent n depends on the type of optical transition in the gap region. Specifically, n is 1/2, 3/2, and 2 for transitions being direct allowed, direct forbidden, and indirect allowed, respectively [147]. This assumes that there is no spectral dependence in the index of refraction, and thus the Tauc optical gap may be determined through a linear extrapolation of the spectral dependence of α^n vs E [148]. It should also be noted that for films with multiple transitions, the interpretation of band edge by a simple linear fit might be misleading. For example, it has been shown that in (Ag,Cu)(In,Ga)Se₂ alloys, changing the group I and group III cations varies the absorption edge shape by different transition states near the valence band, making the choice of the best fit very difficult [149].

In this study, linear fitting was performed for data above the principal inflection point, where the slope changes significantly. The best fit was determined based on the shape of the curves, statistical absolute error (ΔE_g), and coefficient of determination (r^2) indicating how well data fit a line.

The electronic structure calculation of MoO₃ indicated that valence band and conduction band are comprised of the p orbitals of oxygen ions and 4d state of molybdenum cation, respectively [150,151]. Previous studies have reported both direct

allowed [114,115,137,150,152,153] and indirect allowed [151,154] transitions for the bandgap of MoO₃.

Similarly, the electronic structure calculation of WO₃ indicated that valence band and conduction bands are comprised of the 2p orbitals of oxygen ions and 5d orbital of tungsten cation, respectively [155,156]. Again, both direct allowed [101,102,155] and indirect allowed [103,121] transition have been reported for the bandgap of WO₃. Therefore, both possibilities were examined here and the optical bandgaps (E_g) of the films were determined by plotting $(\alpha E)^2$ or $(\alpha E)^{1/2}$ versus $h\nu$ and performing a linear fit to the data, extrapolating to the x-axis (E). For both MoO₃ and WO₃ films, the indirect allowed transition gives a much better coefficient of determination (r^2), and is considered as the primary transition for the bandgap evaluation.

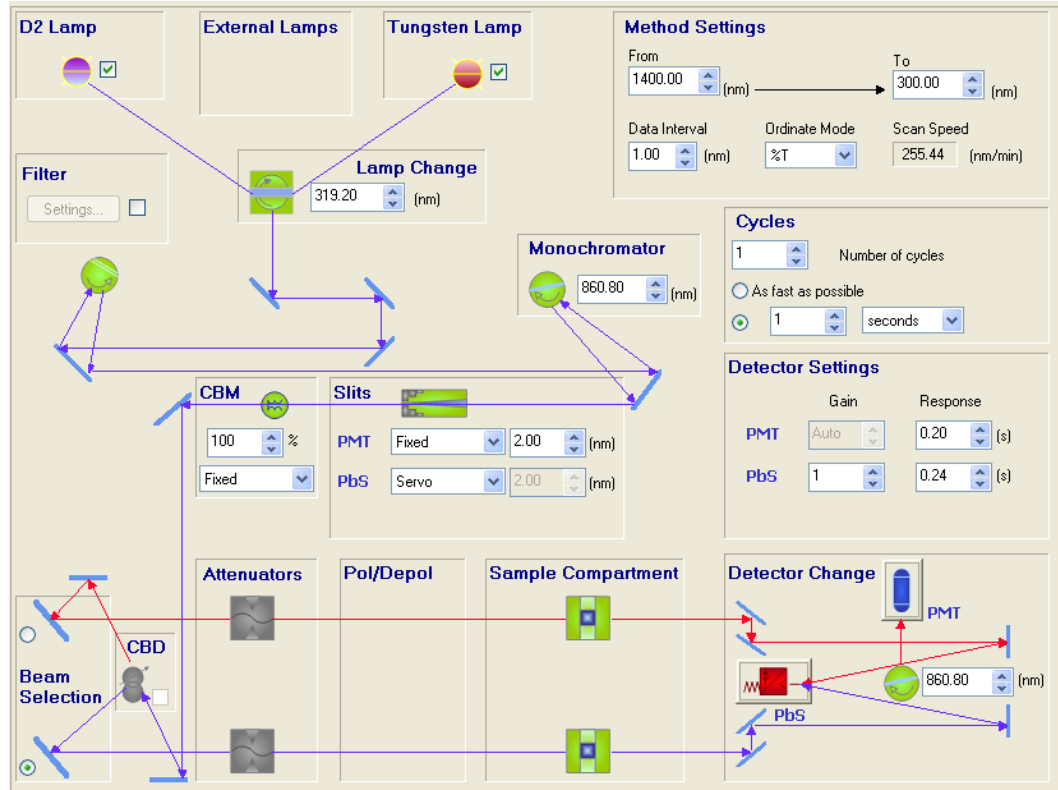


Figure 3.8: UV/Vis/NIR spectrophotometer set-up used for optical characterization.

3.6 Device Fabrication

Backwall superstrate cells were made with absorber thickness ranging from 0.1 μm to 1 μm . All devices were fabricated on soda lime glass (SLG). The layer thicknesses deposited for backwall devices are: SLG/ITO(300 nm)/MoO₃(10 nm)/Cu(In,Ga)Se₂ (0.1-1 μm)/CdS(100nm)/i-ZnO(50nm)/Ag(500nm). Control substrate devices, SLG/Mo(700 nm)/Cu(In,Ga)Se₂ (0.1-1 μm)/CdS(50nm)/ZnO(50nm)/ITO(150nm)/Ni-Al grid, were deposited in the same Cu(In,Ga)Se₂ runs as the backwall devices to allow for comparison of devices with the two different configurations produced under the same conditions. The ITO and ZnO layers are deposited by room temperature sputtering. The ITO layer, with sheet resistance around 15 $\Omega/\square$, used in backwall

devices was annealed at 550 °C for 15 min in an argon atmosphere to stabilize the layer before the subsequent processing steps. As Fig. 3.9 shows, Ar annealing didn't change the transparency of the ITO films, but caused in a shift in the absorption edge to higher energy range, increasing the bandgap due to the Burstein–Moss effect [157].

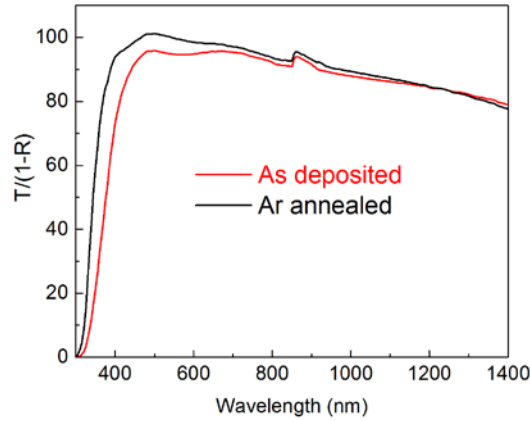


Figure 3.9: Normalized transmittance of ITO films before and after Ar annealing.

The MoO_3 layer is deposited at room temperature by reactive rf sputtering of Mo target at room temperature in an atmosphere with $\text{Ar}/(\text{Ar}+\text{O}_2)=35\%$ [116]. $\text{Cu}(\text{In,Ga})\text{Se}_2$ absorbers were deposited in a single stage co-evaporation process with constant fluxes of all elements and a substrate temperature of 550 °C. To terminate the $\text{Cu}(\text{In,Ga})\text{Se}_2$ growth the shutter was closed and the deposition followed by an in-situ annealing at 550 °C for 20 minutes. The shutter was reopened during the last 10 minutes of the annealing step to allow Se exposure. The thickness of the absorber layers were adjusted by variation of the deposition time from 5 to 48 minutes. All samples were grown under Cu-poor conditions and had final composition with

$[\text{Cu}]/([\text{In}]+[\text{Ga}]) = 0.85$ and $[\text{Ga}]/([\text{In}]+[\text{Ga}]) \approx 0.3$ and, therefore, a bandgap $E_g = 1.2$ eV. The composition and thickness were measured by x-ray fluorescence (XRF) and thickness verified by scanning electron microscopy of sample cross-sections. CdS was deposited onto the $\text{Cu}(\text{In,Ga})\text{Se}_2$ absorbers by chemical bath deposition. In order to prevent shunting, which tends to be problematic for thin $\text{Cu}(\text{In,Ga})\text{Se}_2$ layers [19], the samples were dipped twice in the CdS solution to double the layer thickness. To complete the devices Ni-Al grid metals for control samples or an Ag reflector for backwall devices were deposited by e-beam evaporation. The control samples and the backwall devices had device areas of 1 cm^2 and 0.4 cm^2 , respectively. The completed devices were analyzed by current-voltage (JV) under AM1.5G (100 mW/cm^2) illumination, and quantum efficiency (QE) measurements.

Chapter 4

MoO₃ TRANSPARENT BACK CONTACT

4.1 Introduction

Molybdenum oxide (MoO₃) is an emerging material with potential application in various fields such as selective oxidation catalysis [158], solid state micro batteries [159,160], electro-chromic devices [161,162], gas sensors [163], organic light-emitting diodes [82], and bulk-hetero-junction solar cells [76,89]. Different deposition methods including thermal evaporation [76], pulsed-laser deposition [159], chemical vapor deposition [164], sol-gel processing [165], spray pyrolysis [166], electron beam evaporation [167], and sputtering [168–170] have been employed to make MoO₃ films. Among them, reactive sputtering enables the use of a simple low-cost deposition system to produce insulating oxide films and the ability to control oxide formation by adjusting the oxygen concentration during growth [125]. MoO₃ is reported to have crystal structures of monoclinic (β) or orthorhombic (α) with the space groups of P21/c and Pbnm, respectively [97]. However, oxygen deficiency may lead to the formation of sub-stoichiometric phases of Mo₉O₂₄, Mo₈O₂₃, and Mo₄O₁₁ which have been presented in the Mo-O phase diagram [98].

As discussed in chapter 2, the Schottky model [41] indicates the need to use a high work function metal contact or well-aligned buffer layer in order to reduce barrier height ($\Phi_b < 0.3$ eV [5]) in the junction. Thus, MoO₃ films with a high work function (5.5 eV) [171] can be a potential candidate for the primary back contact of Cu(In,Ga)Se₂ thin film solar cells. In particular, high transparency (>80% in the

visible and near IR range) and wide bandgap (3.0-3.8 eV) [114,115] make MoO_3 a transparent back contact candidate for the superstrate and tandem devices. Its Fermi level and density of states can potentially be tuned by controlling the oxygen stoichiometry during the deposition and/or post processing [172].

In this chapter, the effects of oxygen partial pressure and post processing on the structural, optical, and surface properties of the deposited MoO_3 films were studied using glancing incidence x-ray diffraction (GIXRD), UV/Vis/NIR spectrophotometry, and x-ray photoelectron spectroscopy (XPS), respectively. Evaluation of the MoO_3 electronic properties and back contact role in Cu(In,Ga)Se_2 thin film solar cells is also reported.

4.2 Reactively Sputtered MoO_3 Films

4.2.1 Growth Rate

Fig. 4.1 shows the dependence of the deposition rate of molybdenum oxide films on the $\text{O}_2/(\text{O}_2+\text{Ar})$ ratio, at fixed deposition pressure = 10 m Torr. The deposition rate of the Mo film without O_2 was 40 nm/min. Increasing the oxygen partial pressure resulted in a lower deposition rate due to the chemical reaction of the Mo target with the oxygen gas and formation of an oxide layer on the surface of the target [138,173]. Nirupama et al. [114] used dc magnetron sputtering to make MoO_3 films and reported an initial increase of the deposition rate with the oxygen partial pressure due to an increase in power, followed by a gradual decrease with higher oxygen partial pressures. As can be seen in Fig 4.1, this wasn't observed here.

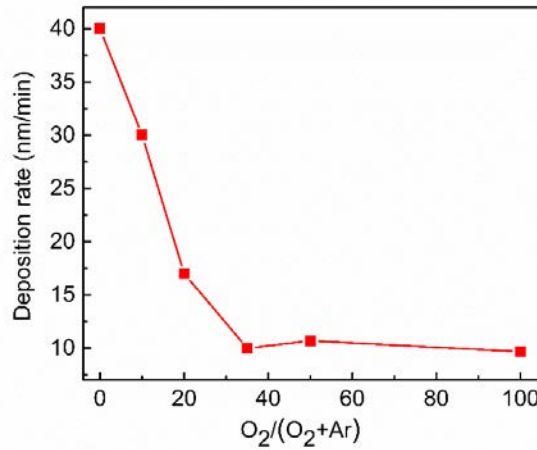


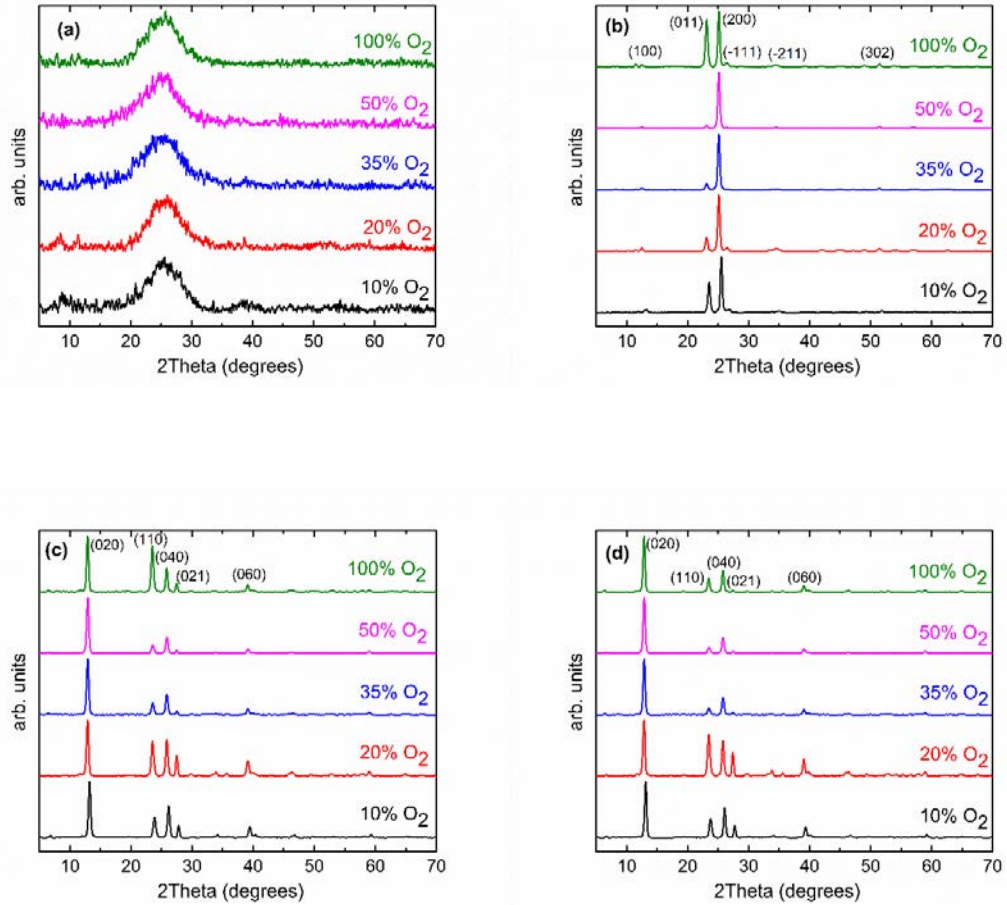
Figure 4.1: Effect of the oxygen partial pressure on the deposition rate of MoO_3 films.

4.2.2 Structural Properties

Fig. 4.2 shows the GIXRD patterns of reactive-sputtered MoO_3 films deposited at different oxygen partial pressures, and annealed at different temperatures. As-deposited films, independent of the oxygen partial pressures, show a broad peak centered at $\sim 26^\circ$ (Fig. 4.2a) indicating an amorphous structure with only short range order. Thus, low temperature deposition didn't provide sufficient energy for nucleation and growth of MoO_3 crystallites, in good agreement with Nirupama et al. [114]. Another study by Oka et al. [171] revealed that $O_2/(O_2+Ar) = 100\%$ was the only condition which resulted in polycrystalline MoO_3 films, with smaller $O_2/(O_2+Ar)$ ratios giving rise to an amorphous structure.

Annealing at $300^\circ C$ (Fig. 4.2b) resulted in crystallization of the molybdenum oxide films to the β - MoO_3 phase, which is the metastable form of the MoO_3 structure. Diffraction peaks at $2\theta = 12.49^\circ, 23.05^\circ, 25.1^\circ, 26.0^\circ, 34.0^\circ$, and 51.4° were identified as the (100), (011), (200), (-111), (-211), and (302) reflections of the monoclinic β -

MoO₃ phase, respectively [97]. The peak positions and d-spacings are listed in Table 4.1 along with standard values from the ICDD database.



4.2: Effect of oxygen partial pressure and annealing temperature on the GIXRD patterns of reactive-sputtered MoO₃ films; a) as-deposited, b) annealed at 300 °C, c) 400 °C, and d) 500 °C.

The slight shift in the peak positions compared to the ICDD card can be caused by the presence of internal/residual stress. In thin films, residual stresses of various

origin can be generated due to a) thermal stress; if the thermal expansion coefficients of the substrate and the film are different and if the growth/treatment is performed at a high temperature [125], and b) stress due to grain boundaries and impurities [174].

Samples annealed at 400 °C (Fig. 4.2c, and Table 4.2) showed reflections at 12.8°, 23.5°, 25.8°, 27.4°, 39.0° and 58.9° which were identified as the (020), (110), (040), (021), (060) and (081) reflections of the orthorhombic α -MoO₃ phase.

Symmetric XRD, not shown here, shows that these films exhibit (020) preferred orientation, in agreement with Sian et al. [137,175]. The strongest reflection expected for randomly oriented α -MoO₃ is the (021) at 12.8 degrees.

Fig. 4.2d and Table 4.3 show that samples annealed at 500 °C were also identified as α -MoO₃ phase with a (020) preferred orientation. These results are in good agreement with Fan et al. [115] who reported the crystallization of initially amorphous MoO₃ films to a monoclinic and then orthorhombic structure at substrate temperatures of 300 °C and 400 °C, respectively.

Table 4.1: The peak positions and d-spacing of MoO₃ film, deposited with O₂/(O₂+Ar) = 35% and annealed at 300 °C, in comparison with ICDD card 01-089-1554.

Peak position (2 θ)	d-spacing calculated	Peak position ICDD	d-spacing ICDD	Phase
12.49	7.080	12.42	7.118	β
23.10	3.847	23.01	3.862	β
25.12	3.543	25.00	3.559	β
26.00	3.373	25.96	3.430	β
34.00	2.600	33.80	2.650	β
51.43	1.775	51.45	1.775	β

Table 4.2: The peak positions and d-spacing of MoO₃ film, deposited with O₂/(O₂+Ar) = 35% and annealed at 400 °C, in comparison with ICDD card 00-005-0508.

Peak position (2θ)	d-spacing calculated	Peak position ICDD	d-spacing ICDD	Phase
12.87	6.874	12.76	6.930	α
23.51	3.780	23.32	3.810	α
25.80	3.450	25.70	3.463	α
27.44	3.248	27.33	3.260	α
39.00	2.305	38.97	2.309	α
58.91	1.566	58.80	1.569	α

Table 4.3: The peak positions and d-spacing of MoO₃ film, deposited with O₂/(O₂+Ar) = 35% and annealed at 500 °C, in comparison with ICDD card 00-005-0508.

Peak position (2θ)	d-spacing calculated	Peak position ICDD	d-spacing ICDD	Phase
12.86	6.877	12.76	6.930	α
23.48	3.787	23.32	3.810	α
25.79	3.451	25.70	3.463	α
27.39	3.253	27.33	3.260	α
39.07	2.304	38.97	2.309	α
58.91	1.566	58.80	1.569	α

Based on the GIXRD results, oxygen partial pressure during deposition, in the studied range, had no effect on the structure of the reactively rf sputtered MoO₃ films and no optimum or threshold oxygen partial pressure is needed. This contrasts with studies which reported the β to α phase transformation by increasing the oxygen

partial pressure during dc magnetron sputtering at 200°C [152], or pulsed-laser deposited MoO₃ films [176].

4.2.3 Surface Characterization

Fig. 4.3a shows the XPS survey scan of a MoO₃ film deposited at room temperature with O₂/(O₂+Ar) = 35% and the core levels for the major peaks are identified. This scan was typical for all MoO₃ films, independent of O₂/(O₂+Ar) ratios. The carbon peak (C 1s) observed at ~284 eV is due to the surface contamination of the film since they were exposed to atmosphere. Further small peaks related to other core energy levels were also identified and are recorded in Table 4.4.

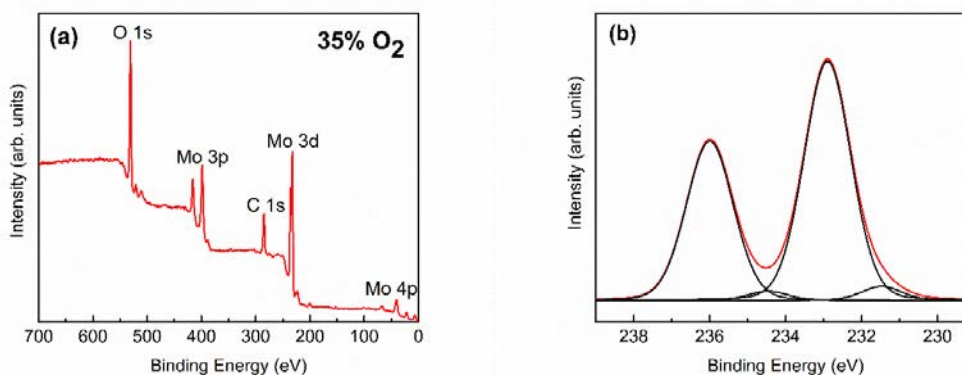


Figure 4.3: a) XPS survey spectrum, and b) high resolution scan of Mo 3d doublet core levels of MoO₃ film deposited at O₂/(O₂+Ar) = 35%.

High resolution scan of Mo 3d doublet core level, for the sample with O₂/(O₂+Ar) = 35%, is shown in Fig. 4.3b. The slight asymmetric line shape suggests the presence of mixed oxidation states of Mo. The peaks were fit by Gaussian-Lorentzian curves satisfying the following constraints: a) the 3d_{5/2} to 3d_{3/2} ratio is 3:2;

b) each doublet has equal FWHM; and c) the spin orbit splitting of the Mo 3d doublets is 3.13 eV [136,137,152].

Table 4.4: Core level binding energies of MoO₃ film, deposited at room temperature with O₂/(O₂+Ar) = 35%.

Core level	Binding energy (eV)	Core level	Binding energy (eV)
O 1s	530.81	Mo 3d _{3/2}	236.01
Mo 3p _{3/2}	398.02	Mo 3d _{5/2}	232.88
Mo 3p _{1/2}	416.09	Mo 4p	40.83
C 1s	284.83	O 2s	22.76

Figure 4.4 shows the high resolution scans of Mo 3d doublet core levels of MoO₃ films formed at different O₂/(O₂+Ar) ratios. The results are also summarized in Table 4.5. The peak fitting shown in Fig. 4.4 resolved that all of the as-deposited films contain two oxidation states of Mo⁶⁺ and Mo⁵⁺, corresponding to MoO₃ and Mo₄O₁₁ phases, respectively. The Mo⁴⁺ oxidation state would have lower core level bonding energies of 229-230 eV for Mo 3d_{5/2} and 232-233 eV for Mo 3d_{3/2} [136] and wasn't observed here. Increasing the oxygen partial pressure resulted in the slight shift of both Mo 3d_{5/2} and Mo 3d_{3/2} core levels to higher energy levels. As a result, the relative amount of MoO₃ phases (oxidation state of +6) determined by the peak areas increases by increasing the oxygen partial pressure, as shown in Fig. 4.5. The core level energy of oxygen (O 1s) decreased from 530.86 eV to 530.78 eV with increasing oxygen partial pressure.

Table 4.5: Core level binding energies of Molybdenum and Oxygen in as-deposited MoO₃ films.

O ₂ /(O ₂ +Ar) ratio	Binding energy (eV)				
	Mo ⁺⁶		Mo ⁺⁵		O 1s
	Mo 3d _{5/2}	Mo 3d _{3/2}	Mo 3d _{5/2}	Mo 3d _{3/2}	
10%	232.86	235.99	231.91	235.04	530.86
20%	232.76	235.89	231.84	234.97	530.90
35%	232.88	236.01	231.94	235.07	530.81
50%	232.85	235.98	231.92	235.05	530.79
100%	233.07	236.20	232.13	235.26	530.78

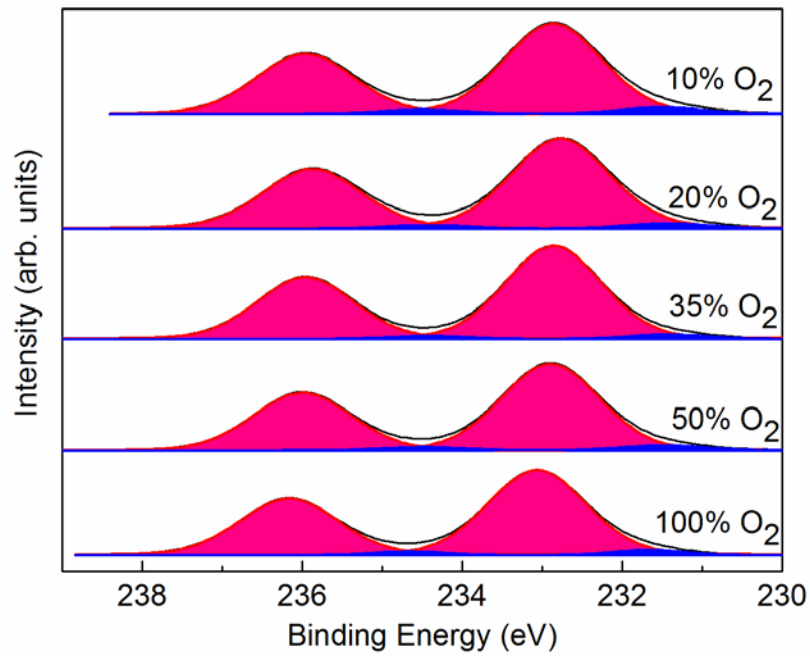


Figure 4.4: XPS core level binding energy of Mo 3d doublets of MoO₃ films deposited at room temperature at different oxygen partial pressures. Red and blue peaks represent the Mo⁺⁶ and Mo⁺⁵ doublets, respectively.

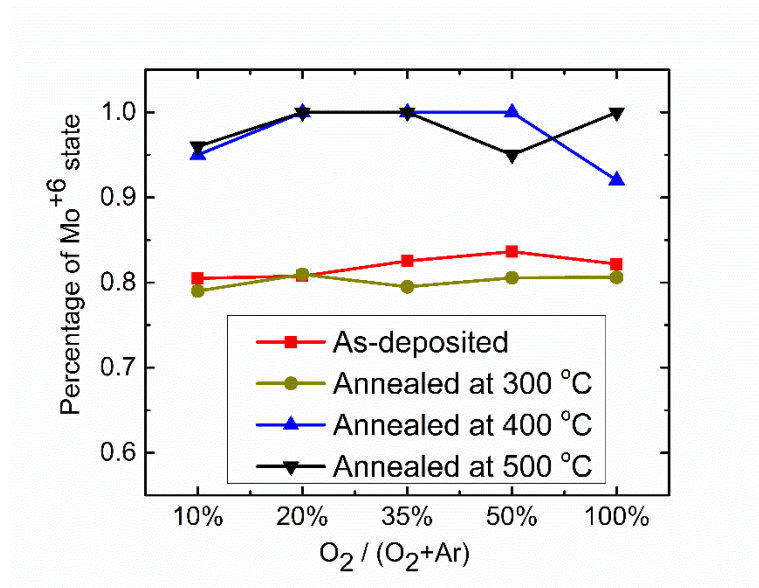


Figure 4.5: The percentage of the Mo⁺⁶ states presented in the MoO₃ films sputtered at different oxygen partial pressures, and different annealing temperatures.

Similar analysis was completed for samples annealed at 300, 400, and 500°C, for 1 h in air and the results are also shown in Fig. 4.5. Core level bonding energies of Mo⁶⁺ for samples annealed at 300 °C are in the range of 232.60-232.80 eV for Mo 3d_{5/2} and 235.73-235.93 eV for Mo 3d_{3/2}, which is ~0.2 eV lower than that of as-deposited films. This might be from the loss of oxygen resulting in an increase in the Mo⁵⁺ state (Mo₄O₁₁ phase). Consequently, the amount of the Mo⁶⁺ state decreases as shown in Fig. 4.5.

Higher temperature annealing at 400 and 500 °C resulted in a surface phase with composition very close to the MoO₃ stoichiometry. Therefore the Mo⁶⁺ state is the major state present in the high temperature annealed films.

Surface sensitive XPS bonding states are not fully correlated with the bulk GIXRD results. XPS results shows that both MoO₃ and Mo₄O₁₁ phases are present at

the surface of as-deposited and 300 °C-annealed films, while diffraction peaks of the Mo₄O₁₁ phase were below the GIXRD detection limit. This difference suggests a surface-limited oxygen deficiency in these films. However, there is a good agreement between the XPS and GIXRD results of samples annealed at higher temperatures (400 and 500 °C) where a crystalline α -MoO₃ phase observed associated with the Mo⁶⁺ surface state.

4.2.4 Optical Properties

As-deposited films appear uniformly smooth. Fig. 4.6 shows the transmittance of the MoO₃ films deposited at different O₂/(O₂+Ar) ratios. The film thickness, measured by Dektak mechanical step profilometer, for the 10%, 20%, 35%, 50%, and 100% ratio films were 600 nm, 510 nm, 300 nm, 320 nm, and 580 nm, respectively. All films show high transmittance in the visible range, indicating low concentration of oxygen ion vacancies [177]. The transmittance values drop steeply at $\lambda \approx 400$ nm indicating a strong band-to-band absorption. While increasing the oxygen partial pressure didn't affect the total transmittance it did cause a shift in the absorption edges to higher energies.

The total absorption coefficient α was calculated from the T-R measurements using the following equation [147]:

$$\alpha = \frac{1}{d} \ln \frac{(1-R)^2}{T} \quad (4.1)$$

where d is the thickness, T the transmittance, and R the reflectance of MoO₃ films.

For photon energies larger than the bandgap (E_g) the absorption coefficient α can be described by the following equation:

$$\alpha E \sim (E - E_g)^n \quad (4.2)$$

where $E = h\nu$ is the photon energy and the exponent n depends on the type of optical transition in the gap region. Specifically, n is $1/2$, $3/2$, and 2 for transitions being direct allowed, direct forbidden, and indirect allowed, respectively [147].

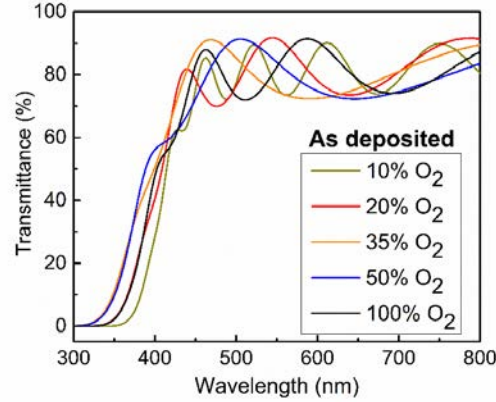


Figure 4.6: Transmittance plot of the MoO₃ films deposited at different O₂/(O₂+Ar) ratios.

The electronic structure calculation of MoO₃ indicated that valence band and conduction band are comprised of the p orbitals of oxygen ions and 4d state of the molybdenum cation, respectively [150,151]. Previous studies have reported both direct allowed [114,115,137,150,152,153] and indirect allowed [151,154] transitions for the bandgap of MoO₃. Therefore, both possibilities were examined here and the optical bandgaps (E_g) of the films were determined by plotting $(\alpha E)^2$ or $(\alpha E)^{1/2}$ versus E and performing a linear fit to the data, extrapolating to the x-axis (E). Sample curves are shown in Fig. 4.7 for the film deposited with O₂/(O₂+Ar) = 35%.

Linear fitting was performed for data above the principal inflection point. Then, a series of fit ranges from 5 to 100 points were considered to perform the linear

fit. The best fit was determined based on the shape of the curves, statistical absolute error (ΔE_g), and coefficient of determination (r^2). As Fig. 4.7 shows, for both as-deposited and annealed films, the indirect allowed transition gives a much better coefficient of determination (r^2), and is considered as the primary transition for the bandgap evaluation.

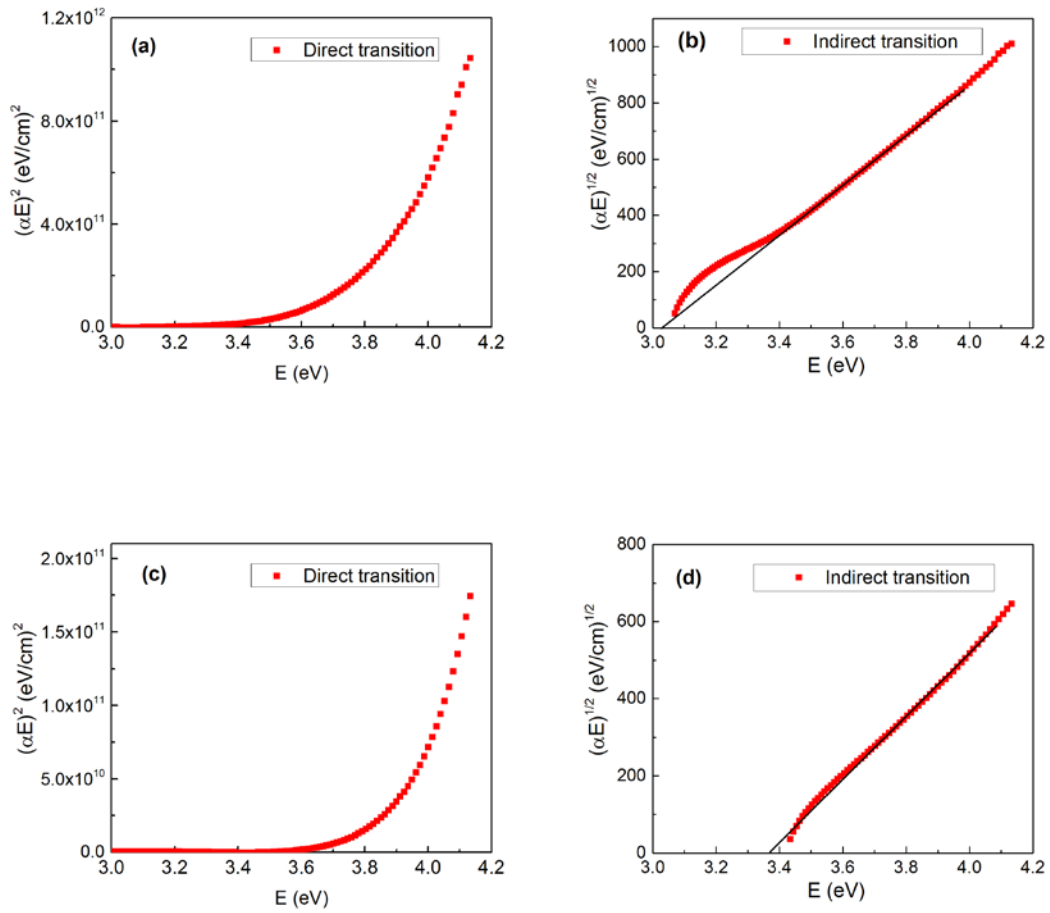


Figure 4.7: Direct and indirect transitions for the as-deposited (a and b) and 500 °C-annealed (c and d) MoO_3 films grown at $\text{O}_2/(\text{O}_2+\text{Ar}) = 35\%$.

Fig. 4.8 shows the variation of E_g , extracted from the best fitted curves for an indirect transition for the samples deposited at various $O_2/(O_2+Ar)$ ratios and annealed at different temperatures of 300-500 °C. There is a general trend that the bandgap of the MoO_3 films widened with increasing $O_2/(O_2+Ar)$ up to 50%, and then decreased for the films deposited with pure oxygen $O_2/(O_2+Ar) = 100\%$.

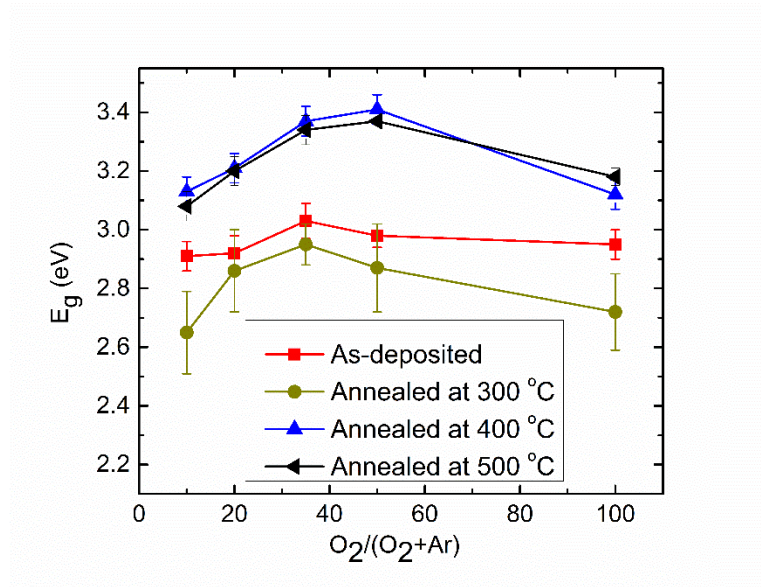


Figure 4.8: Variation of optical bandgap as a function of $O_2/(O_2+Ar)$ ratio and annealing temperature.

The optical bandgaps for the as-deposited films range from 2.6 to 2.9 eV, in good agreement with previously reported indirect bandgap values of MoO_3 [178]. Low bandgap values of MoO_3 films deposited at $O_2/(O_2+Ar) = 10\%$ may be due to the formation of sub-stoichiometric films. In fact, the impurity energy state induced by oxygen deficiency might lead to a decrease in the bandgap of MoO_3 films[114,138]. Widening E_g with increasing oxygen partial pressure can be attributed to the reduction

of oxygen deficiency and near-stoichiometry of the films [170]. Lower bandgap values of films deposited in a pure oxygen atmosphere may be due to a kinetically favored formation of sub-stoichiometric MoO_3 films at such atmosphere.

Annealing the films visibly roughened the surface due to crystallization and grain growth. Annealing at 300 °C had a small effect on the optical properties of the MoO_3 films, and they behave similarly to the as-deposited films (Fig. 4.8). The 300 °C annealed films were β phase, as shown in section 4.1. Lower bandgap values of β - MoO_3 compared to the α - MoO_3 phase had been reported previously [118,179].

Samples annealed at 400 and 500°C had wider bandgaps, in the range of 3.1 to 3.4 eV, compared to the as-deposited samples (Fig.4.8). These films have the α - MoO_3 phase, which is the stable form of the MoO_3 structure. This has a lower density of impurity states induced primarily by oxygen deficiency, and hence a wider bandgap [168]. MoO_3 films deposited at $\text{O}_2/(\text{O}_2+\text{Ar})$ ratios of 35% and 50% have the highest gain in bandgap by annealing temperature.

Hence, two sample groups can be identified from the optical analysis (Fig. 4.8). First, as-deposited and low temperature (300 °C) annealed samples which have bandgap values affected by a β -phase structure containing sub-stoichiometric phases with higher density of oxygen deficiencies. Second, high temperature (400-500 °C) annealed films have the α - MoO_3 phase with reduced sub-stoichiometric phases and wider bandgap.

4.3 Interface Chemistry and Device Properties of Films Made on MoO_3

In the previous sections, the effects of oxygen partial pressure and post-deposition annealing on the structural, optical, and surface properties of molybdenum oxide thin films deposited on glass by rf reactive sputtering were presented [116].

For this section, MoO₃ films were deposited on Mo or ITO-coated soda lime glass substrates with two different thicknesses of 10 and 30 nm. Higher thicknesses will result in a high through-film resistance due to the resistivity $> 10^6 \Omega\text{-cm}$ of the MoO₃ [115,118,119], and therefore were not considered here. Cu(In,Ga)Se₂ films were then deposited on different back contact structures incorporating MoO₃ films. The effects of MoO₃ back layers on the elemental distribution, structural properties and device performance of the Cu(In,Ga)Se₂ devices were studied using secondary ion mass spectroscopy (SIMS), x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD), scanning electron microscopy (SEM), and current-voltage analysis of complete solar cells. Films for structural characterization and devices were 2 μm thick, while for SIMS and XPS depth profiling 100 nm thick films were used to reduce sputter etch time and improve depth resolution at the back interface.

4.3.1 Interface Properties

4.3.1.1 SIMS Analysis

SIMS depth profile analysis was performed in order to find the elemental distribution in the Cu(In,Ga)Se₂ films made on different back contacts. For this purpose, 100 nm thick Cu(In,Ga)Se₂ films were deposited on Mo, Mo-MoO₃, ITO, and ITO-MoO₃ back contacts. Fig. 4.9 shows the SIMS depth profiles of the Cu(In,Ga)Se₂ films on different back layers plotted versus film thickness. For the Mo/Cu(In,Ga)Se₂ sample (Figure 4.9a) the profile shows the concentrations of Cu, In, and Ga drop rapidly at the interface after 100 nm. However, the Se concentration stays high and overlaps the Mo. This suggests the formation of a MoSe₂ layer at the interface, as has been reported previously [50–52].

For the Cu(In,Ga)Se₂ on Mo/MoO₃ sample, the Se signal in Figure 4.9b drops rapidly at the interface. There is no apparent Se accumulation at the interface and, therefore, no evident formation of MoSe₂. On the other hand, there is an observed accumulation of Ga at the interface on MoO₃ (Figure 4.9b), which can be attributed to the high affinity between Ga and O atoms [113]. In particular, formation of a thin Ga₂O₃ layer at the interface is thermodynamically favorable (Table 4.6).

The SIMS depth profile of the ITO/Cu(In,Ga)Se₂ stack is shown in Figure 4.9c. Again, there is an accumulation of Ga suggesting formation of Ga₂O₃ at the ITO/Cu(In,Ga)Se₂ interface.

Figure 4.9d shows the SIMS depth profile of the ITO/MoO₃/Cu(In,Ga)Se₂ stack. The Se concentration drops rapidly at the interface, while the Mo and O concentrations rise, suggesting there is no MoSe₂ formation at the interface.

Figure 4.10 compares the elemental distribution of different stacks in order to have a better understanding on the effect of oxide layers. Figure 4.10a shows that Ga profile was uniform for the control sample made on Mo; however, Ga has been accumulated towards the back surface for all films made on oxide layers. On the other hand, while Se is piled up at the interface of Mo/Cu(In,Ga)Se₂ sample, forming MoSe₂, it drops rapidly at the interface of films made on oxide layers. Therefore, MoSe₂ phase was not formed there (Fig. 4.10b).

Figure 4.10c shows the Na profile of different stacks. It can be seen that presence of oxide layers didn't act as a barrier for Na diffusion from the soda lime glass substrate to the Cu(In,Ga)Se₂ layer. Instead, Na concentration in the Cu(In,Ga)Se₂ layer is even higher compared to the control Mo/Cu(In,Ga)Se₂ sample. Alternatively, K diffusion is reduced by a few times for the films made on oxide layers

(Figure 4.10d). Recent studies have shown that K incorporation has a large effect on improving the junction quality of Cu(In,Ga)Se₂ solar cells resulting in an enhanced device performance [16]. Therefore, introducing moderate amounts of K could be considered as a tool to enhance the performance of backwall superstrate devices further.

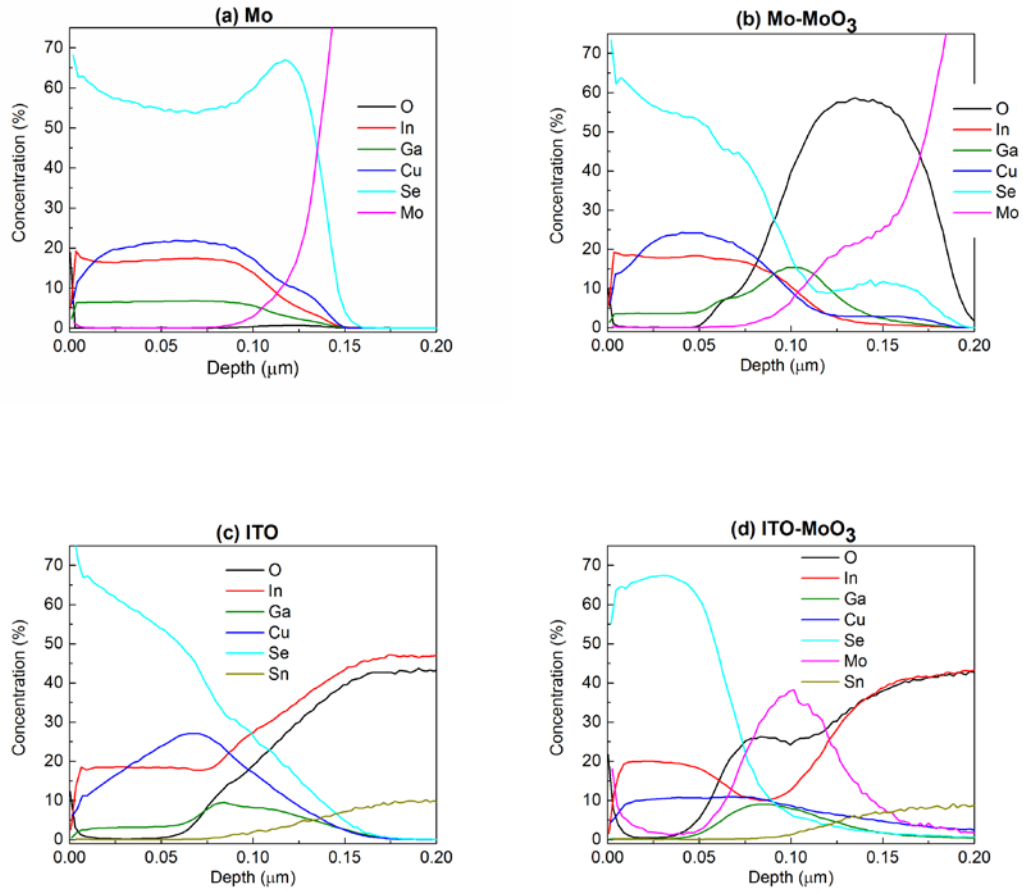


Figure 4.9: SIMS depth profile of a) Mo/Cu(In,Ga)Se₂, b) Mo/MoO₃/Cu(In,Ga)Se₂, c) ITO/Cu(In,Ga)Se₂, and d) ITO/MoO₃/Cu(In,Ga)Se₂.

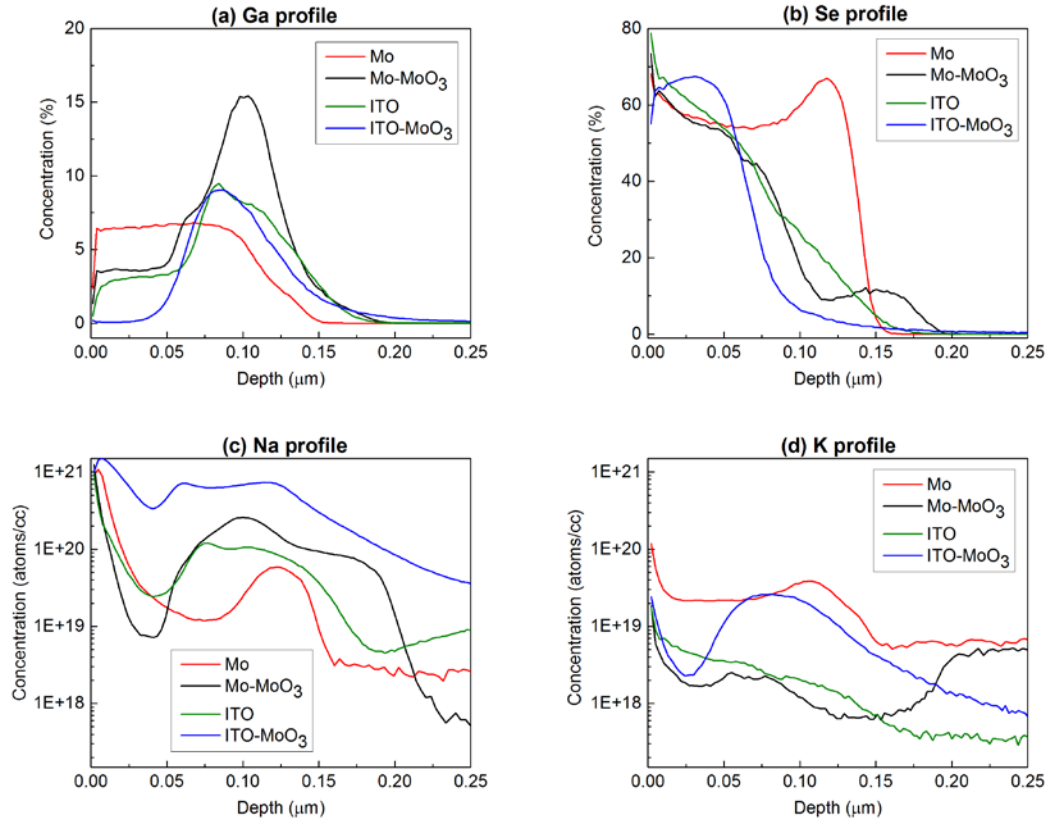


Figure 4.10: Compared SIMS depth profile of samples showing the effect of back contact on the distribution of a) Ga, b) Se, c) Na, and d) K through the Cu(In,Ga)Se₂ films.

4.3.1.2 XPS Analysis

The interfaces between the Cu(In,Ga)Se₂ and the different back contacts were characterized by XPS measurements. Their interpretation was facilitated by considering the thermodynamics of potential reactions using bulk enthalpy and entropy for reactant and product phases at 550 °C. The Gibbs free energies for possible reactions of different species are listed in Table 4.6. Figure 4.11 shows the XPS depth profiles of the 100 nm thick Cu(In,Ga)Se₂ films on different back layers plotted versus etch time. For the Mo/Cu(In,Ga)Se₂ sample (Figure 4.11 a) the profile

shows the concentrations of Cu, In, and Ga, determined by their peak areas, to drop rapidly at the interface after 90 min etch time. However, the Se concentration only decreases after ~ 110 min etching and overlaps the Mo. This suggests the formation of a MoSe_2 layer at the interface, as has been reported previously [50–52] and is predicted by Table 4.6. The formation of molybdenum oxide and gallium oxide layers is also possible due to their negative energy of formation.

High resolution XPS scans of Mo 3d doublet core levels are shown in Fig. 4.12a for the sample on Mo. The results show a slight asymmetric line shape, suggesting the presence of mixed oxidation states of Mo. The peaks were fit by Gaussian-Lorentzian curves satisfying the following constraints: a) the $3d_{5/2}$ to $3d_{3/2}$ ratio is 3:2; b) each doublet has equal full width at half maximum (FWHM); and c) the spin orbit splitting of the Mo 3d doublets is 3.13 eV [136–138]. The fit suggests the presence of Mo^{4+} and Mo^{2+} oxidation states in the sample on Mo, corresponding to MoO_2 and Mo/MoSe₂ phases, respectively, though with the very similar binding energy values of Mo and MoSe₂ phases (~ 228 eV) [180] it is difficult to distinguish the interface phases. However, the presence of a detectable Se peak at the same etch depth as the Mo doublets supports the hypothesis of MoSe₂ formation at the interface. In addition, high resolution scans of the Ga 3d region (Figure 4.13a) shows a slight asymmetric line shape suggestive of the partial oxidation of Ga at the Cu(In,Ga)Se_2 / Mo interface.

Table 4.6: Gibbs free energy of potential reactions at the Cu(In,Ga)Se₂ / back contact interface [113].

Reactants	Reaction	Gibbs free energy (kcal/mol)
Se-O	$O_2 \rightarrow 2O$	+95.12
	$Se_2 \rightarrow 2Se_L$	-4.55
Mo-Se-O	$Mo + 2Se \rightarrow MoSe_2$	-29.41
	$Mo + O_2 \rightarrow MoO_2$	-104.20
	$Mo + 3/2 O_2 \rightarrow MoO_3$	-128.04
	$MoO_3 + 2Se \rightarrow MoSe_2 + 3/2 O_2$	+98.63
	$MoO_3 + 2Se \rightarrow MoO_2 + MoSe_2 + 1/2 O_2$	-13.09
ITO-Se-O	$2In + 3/2 O_2 \rightarrow In_2O_3$	-285.99
	$In_2O_3 + 3Se \rightarrow \beta-In_2O_3 + 3/2 O_2$	+90.65
	$SnO_2 + 2Se \rightarrow SnSe_2 + O_2$	+77.28
	$2SnO_2 + Se \rightarrow SnSe + SnO + 1/2 O_2$	+171.37
Ga-Mo-Se-O	$2Ga + 3Se \rightarrow Ga_2Se_3$	-82.99
	$Ga_2Se_3 + 3/2 O_2 \rightarrow Ga_2O_3 + 3Se$	-113.19
	$MoO_3 + 2Ga \rightarrow Ga_2O_3 + Mo$	-68.13
	$2MoO_3 + 2Ga \rightarrow Ga_2O_3 + 3/2 MoO_2 + 1/2 Mo$	-96.40

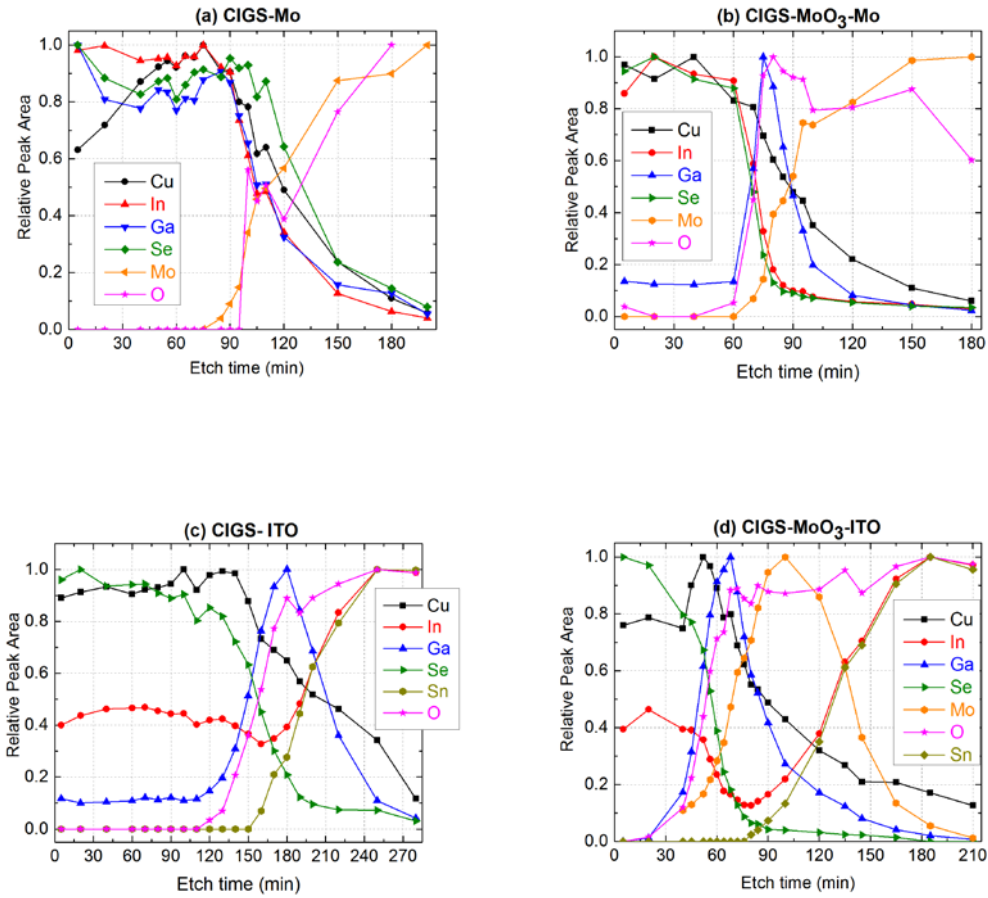


Figure 4.11: XPS depth profile of a) Mo/Cu(In,Ga)Se₂, b) Mo/MoO₃/Cu(In,Ga)Se₂, c) ITO/Cu(In,Ga)Se₂, and d) ITO/MoO₃/Cu(In,Ga)Se₂.

For the Cu(In,Ga)Se₂ on Mo/MoO₃ sample, the Se signal in Figure 4.11b closely follows the In profile, dropping rapidly at the interface. There is no apparent Se accumulation at the interface and, therefore, no evident formation of MoSe₂. Table 4.6 also confirms the reduction of MoO₃ with Se to form MoSe₂ is not favored. High resolution XPS analysis of the Mo 3d region for the Mo/MoO₃/Cu(In,Ga)Se₂ stack (Figure 4.12b) shows that both MoO₂ and MoO_{3-x} phases are present at the interface with negligible Se.

On the other hand, there is an observed accumulation of Ga at the interface on MoO₃ (Figure 4.13b), which can be attributed to the high affinity between Ga and O atoms [113]. In particular, formation of Ga₂O₃ at the interface is thermodynamically favorable (Table 4.6). High resolution scans of the Ga 3d region (Figure 4.13b) show a shoulder at high energy with its highest intensity at the Cu(In,Ga)Se₂/MoO₃ interface (75 min etch). Peak deconvolution of the Ga 3d area suggests that the satellite peak is due to the Ga₂O₃ phase [180] (Figure 4.13b). Formation of Ga₂O₃ at the interface of Cu(In,Ga)Se₂-TCO's has been reported previously [38,68,69]. The presence of a Ga₂O₃ phase, with bandgap ~4.5 eV [181], at the interface would be expected to create a large spike in the valence band alignment blocking hole transport. Good performance of devices made on MoO₃ layer (see section 4.3.2, Table 4.7) disagrees with such a band alignment. This contradiction may be caused by the very low thickness of the Ga₂O₃ phase formed at the interface enabling tunneling, presence of several intermediate states due to interface defects, or the possible formation of mixed oxides phases with In, Ga and Mo atoms present at the interface.

The XPS depth profile of the ITO/Cu(In,Ga)Se₂ stack is shown in Figure 4.11c. The Cu(In,Ga)Se₂/ITO interface can be characterized at ~150 min etching, where the Sn peak appears and Se and In peak intensities drop. Again, there is an accumulation of Ga and high resolution scans of the Ga 3d (Figure 4.13c) suggests formation of Ga₂O₃ at the ITO/Cu(In,Ga)Se₂ interface. Table 4.6 shows that any reaction of ITO with Se is not likely and ITO should be significantly more stable than other potential products in the ITO-Se-O system.

Finally, Figure 4.11d shows the XPS depth profile of the ITO/MoO₃/Cu(In,Ga)Se₂ stack. The Se concentration drops rapidly at the interface

(~60 min etch), while the Mo and O concentrations rise, suggesting there is no MoSe_2 formation at the interface. Table 4.6 also confirms that the likelihood of reducing MoO_3 with Se to form MoSe_2 is not favored due to the low Gibbs free energy of the reaction.

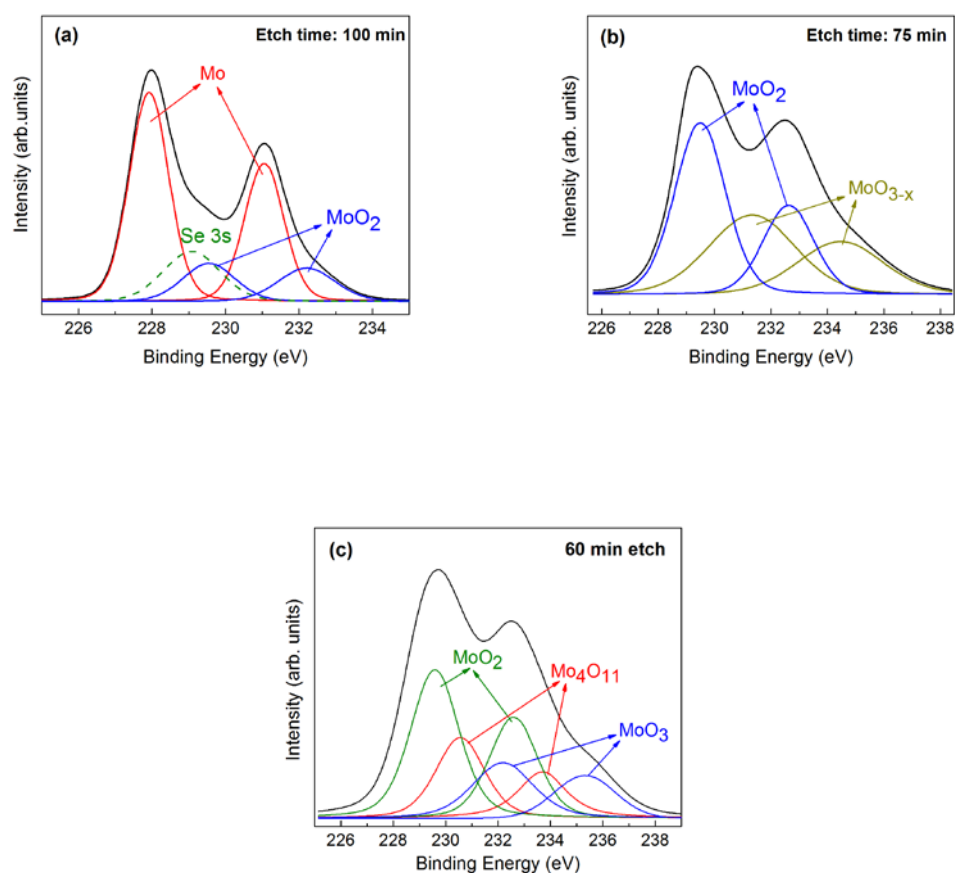


Figure 4.12: XPS analysis of the Mo 3d doublet at the interface of a) Mo/Cu(In,Ga)Se₂ and b) Mo/MoO₃/Cu(In,Ga)Se₂, and c) ITO/MoO₃/Cu(In,Ga)Se₂.

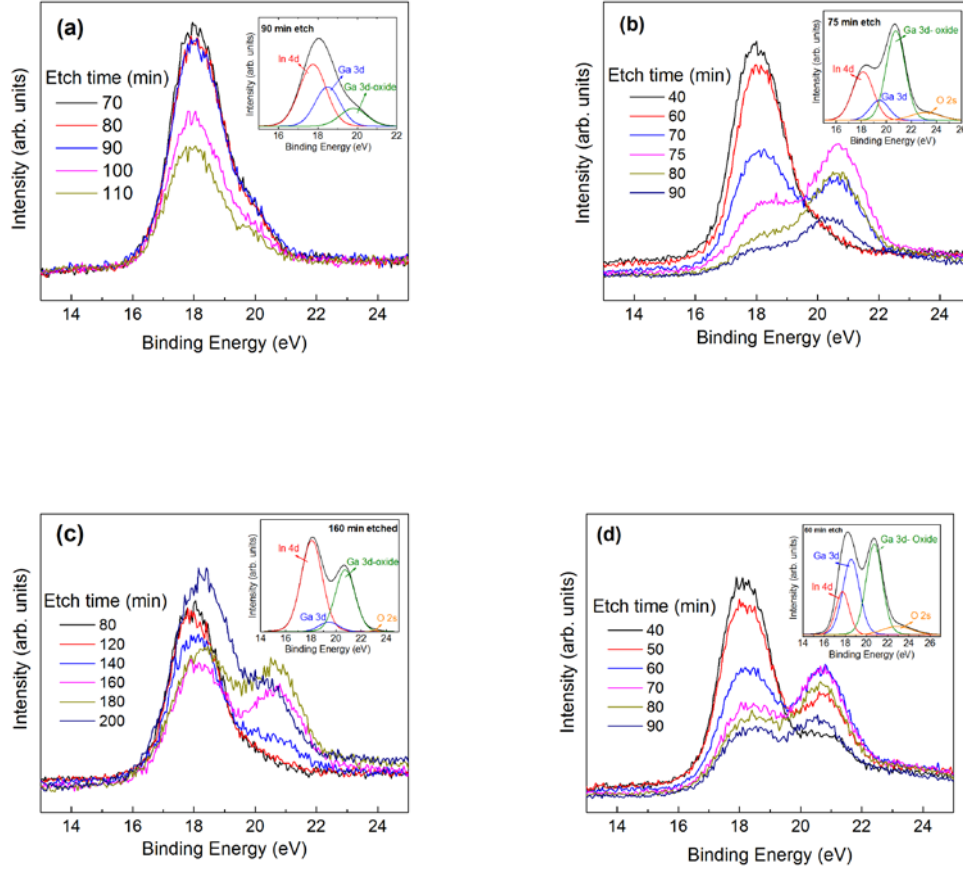


Figure 4.13: XPS analysis of Ga 3d peak of a) Mo/Cu(In,Ga)Se₂ , b) Mo/MoO₃/Cu(In,Ga)Se₂ , c) ITO/Cu(In,Ga)Se₂ , and d) ITO/MoO₃/Cu(In,Ga)Se₂.

A high resolution scan of the Mo 3d doublet (Figure 4.12c) shows the presence of oxidation states of Mo⁶⁺, Mo⁵⁺ and Mo⁴⁺, attributed to MoO₃, Mo₄O₁₁, and MoO₂ phases, respectively. However, it should be noted that preferential sputtering of oxygen atoms might have partially affected the oxidation states of Mo. Again, there is a Ga accumulation at the back surface of the Cu(In,Ga)Se₂ layer (Figure 4.13d), following the same trend of the oxygen distribution and apparent formation of Ga₂O₃.

Valence band edge energies were also obtained by analysis of the XPS spectra and used to characterize the interface band offsets, ΔE_V . Specifically, the valence band maximum, E_V , was measured by linear extrapolation of the leading edge of the valence band spectrum to the energy axis and defining the slope intercept as E_V [143,144]. The absolute value of the energies were corrected using the C 1s signal at 284.8 eV [136]. Figure 4.14 shows the data for the Mo/Cu(In,Ga)Se₂ sample after sputter etching for 90 min. The valence band offsets were determined using the following equation [141,145,146]:

$$\Delta E_V = (E_{CL1} - E_{V1}) - (E_{CL2} - E_{V2}) - \Delta E_{CL} \quad (4.3)$$

where E_{CL} is the core level binding energy in the bulk, E_V is the valence band edge in the bulk, and ΔE_C is the energy difference between the core levels at the interface. The Cu 2p, Mo 3d, and Sn 3d peaks were considered as the core peaks of the Cu(In,Ga)Se₂, MoO₃, and ITO layers, respectively.

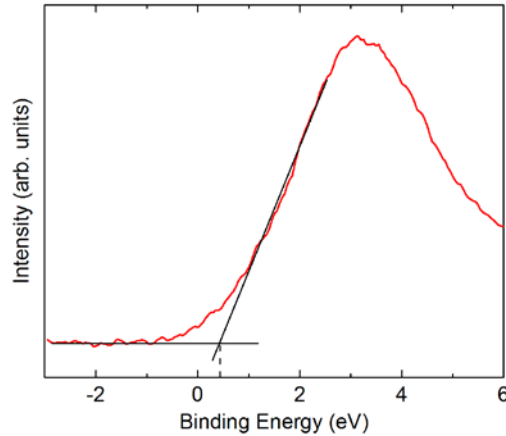


Figure 4.14: Valence band edge of Mo/Cu(In,Ga)Se₂ samples sputter etched for 90 min.

Figure 4.15 shows the energy band diagram of different samples using the valence band offsets measured by XPS. Bandgap values of 1.2 eV for Cu(InGa)Se₂, 1.4 eV for MoSe₂ [50], 2.9 eV for as-deposited MoO₃ and 3.2 for annealed MoO₃ [116], and 3.4 eV for ITO were assumed for the band structure illustration. It should be noted that no effect was observed in the J-V behavior in any of the samples due to a large valence band spike caused by Ga₂O₃ (with bandgap ~4.5 eV [181]) at the interface. Therefore, a Ga₂O₃ phase was not included in the energy band diagram plots. Figure 4.15a shows the band diagram of the control sample in which the MoSe₂ interlayer formed during the Cu(In,Ga)Se₂ deposition. It can be seen that Mo would be expected to create a blocking contact with a barrier height $\Phi_b \sim 0.8$ eV relative to the CIGS, in good agreement with previous studies [49]. A smaller valence band offset of ~ 0.2 eV was found between Cu(In,Ga)Se₂ and MoSe₂ layers consistent with the absence of a blocking contact as typically observed in devices. Adding the MoO₃ layer (Figure 4.15b) prevents the formation of MoSe₂ at the interface, with a small band offset of just ~ 0.1 eV between the Cu(In,Ga)Se₂ and MoO₃ layers.

Figure 4.15c shows the energy band diagram of the ITO/Cu(In,Ga)Se₂ stack. A valence band offset of ~ 0.9 eV was measured suggesting a blocking behavior for holes transporting to the ITO back contact. Introducing the MoO₃ layer at the ITO/Cu(In,Ga)Se₂ interface changes the energy band diagram (Figure 4.15d). As a result, the primary contact has a much lower valence band offset relative to the Cu(In,Ga)Se₂, ~ 0.1 eV, and cell performance would enhance (Table 4.7).

The energy band diagram of the ITO/MoO₃ annealed/Cu(In,Ga)Se₂ stack is shown in Figure 4.15e. Annealing the MoO₃ has increased its bandgap (see section

4.2.4), lowering the valence band edge of the film. As a result, a higher valence band offset of ~ 0.5 eV was found at the back surface.

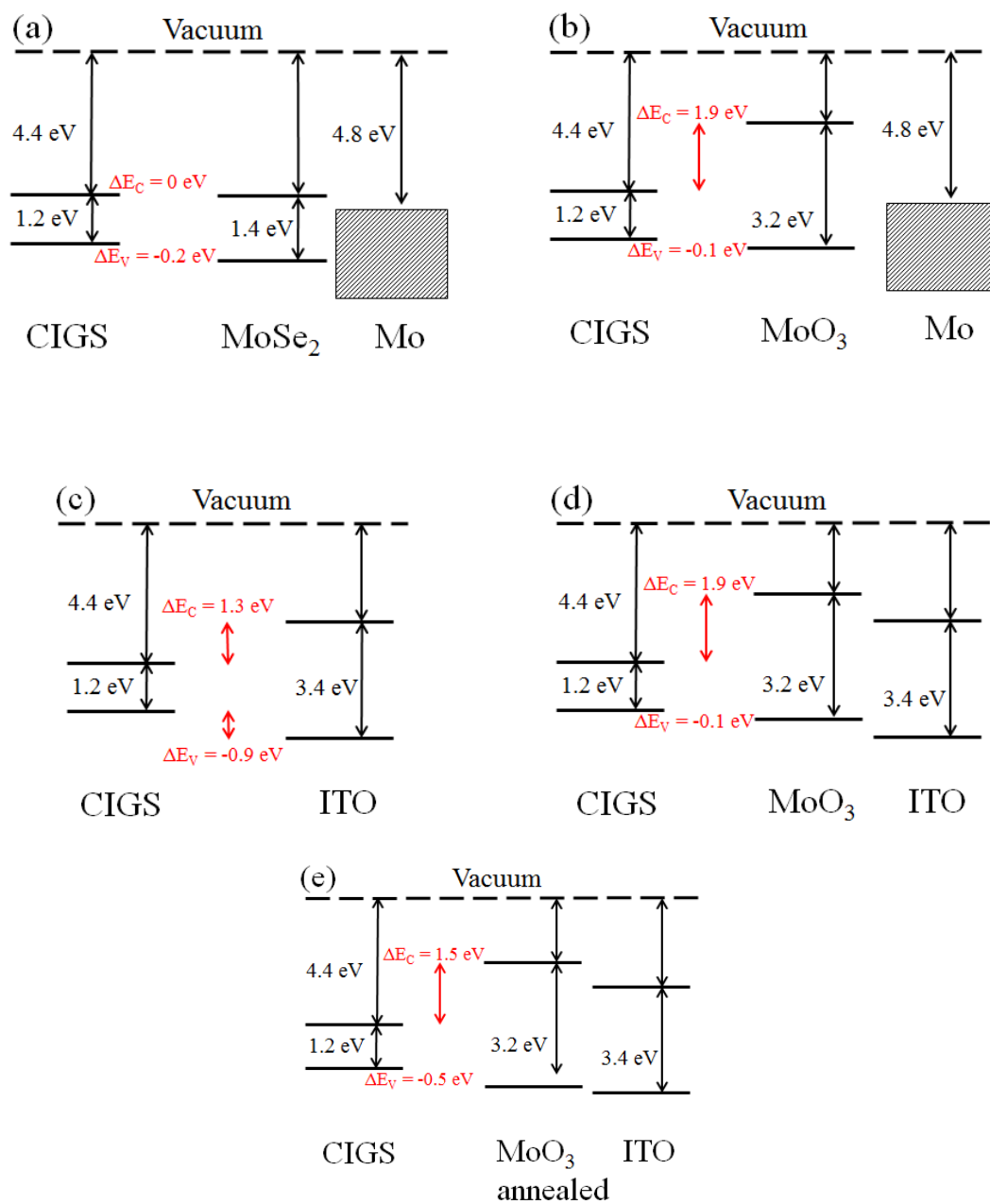


Figure 4.15: Band discontinuities between Cu(In,Ga)Se₂ and different back contacts determined from XPS analysis; a) Mo, b) Mo/MoO₃, c) ITO, d) ITO/MoO₃, and e) ITO/MoO₃-annealed back contacts.

4.3.2 Device Properties

Table 4.7 and Figure 4.16a show the J-V parameters of cells made on the Mo-MoO₃ stack with different thicknesses and treatment conditions. It can be seen that the device made on the 10 nm MoO₃ back layer (sample B) is comparable to the control sample on a Mo contact, with efficiency of ~14%. This is consistent with the good band alignment at the back surface of the cells made on Mo-MoO₃ back contact (Table 4.7 and Fig.4.15).

Cell made on the 30 nm MoO₃ back layer (sample C) have also a regular diode shape but with lower JV parameters compared to the control sample (Mo contact).

It was shown previously (Fig. 4.9) that such a thin MoO₃ layer didn't act a barrier for Na atoms diffusing from the soda lime glass substrate to the Cu(In,Ga)Se₂ layer. Instead, the K concentration has been reduced which might have affected the surface properties of Cu(In,Ga)Se₂ layer. The fill factor loss might also be partly due to higher series resistance of the cells made on 30 nm MoO₃. Series resistance values of 0.03, 0.06, and 0.3 $\Omega\cdot\text{cm}$ were calculated, by diode analysis, for the cells made on the Mo, Mo-MoO₃ (10 nm), and Mo-MoO₃ (30 nm) layers, respectively.

The efficiency of cells with an annealed Mo-MoO₃ stack was limited to 4.2%, showing a blocking diode behavior in the forward J-V profile (Fig. 4.16a, sample D). This may be caused by the presence of a large barrier between the valence bands of the Cu(In,Ga)Se₂ and MoO₃, due to the higher bandgap of the annealed MoO₃ films, as noted in section 4.3.1 (Fig.4.15).

Device properties of cells made on the ITO and ITO-MoO₃ stack are shown in Fig. 4.16b and also summarized in Table 4.7. The poor performance of the cells made on ITO may originate from the non-ideal band structure, though the J-V profiles do not show an obvious blocking barrier. The MoO₃ layer enhanced the cell performance

with the ITO back contact and improved V_{OC} to near that of the cells on just Mo. The efficiency of the device on ITO was limited to 8%, mainly due to low fill factor, however, the cell with the ITO/MoO₃ contact showed an improved efficiency of 11.9%. Device results show no V_{OC} loss with the use of MoO₃ due to insufficient Na in a Cu(In,Ga)Se₂ device [182]. Secondary ion mass spectroscopy analysis of samples (Figure 4.9) indicated that the 10 nm MoO₃ layer did not behave as a significant barrier to Na diffusion. The lower fill factor of cells made on ITO-MoO₃ can be attributed primarily to higher device series resistance. Series resistance values of 2.1, 0.41, and 0.71 $\Omega\cdot\text{cm}$ were found for the cells made on the ITO, ITO-MoO₃, and ITO-MoO₃ (annealed) layers, respectively.

Annealing the ITO-MoO₃ stack did not adversely affect cell performance, likely due to different nature of MoO₃ layer grown on ITO, and similar cell performance was obtained.

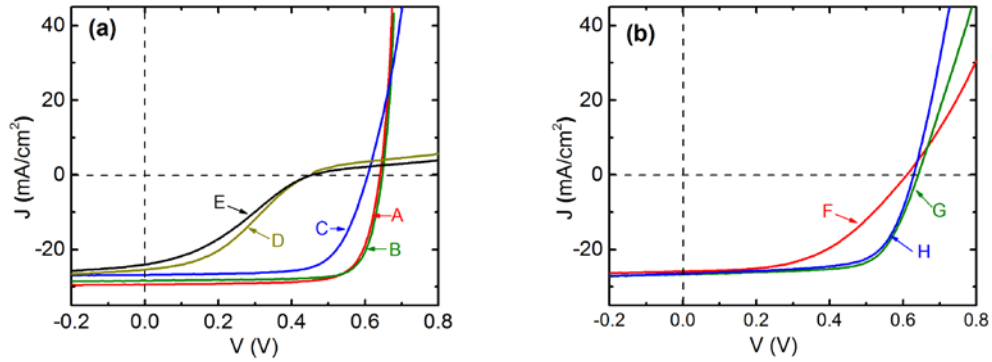


Figure 4.16: J-V profile of devices made on a) Mo and Mo-MoO₃ stacks and b) ITO and ITO-MoO₃ stacks. Samples are defined in Table 4.7.

Table 4.7: Cell properties of devices processed on the different back contacts. Valence band offsets (ΔE_V) at the back contact, determined by XPS analysis, are also presented for comparison.

Sample	Back contact	MoO ₃ thickness	MoO ₃ anneal (°C)	Eff. (%)	V _{OC} (mV)	J _{SC} (mA/cm ²)	FF (%)	ΔE_V (eV)
A	Mo	---	---	14.3	645	29.8	75.7	0.2
B	Mo+MoO ₃	10 nm	none	14.4	647	28.4	78.1	0.1
C	Mo+MoO ₃	30 nm	none	11.5	609	26.9	70.4	0.1
D	Mo+MoO ₃	10 nm	400	4.2	453	25.5	37.8	0.5
E	Mo+MoO ₃	30 nm	400	3.7	457	24.4	32.9	0.5
F	ITO	---	---	8.0	614	26.2	50.2	0.9
G	ITO+MoO ₃	10 nm	none	11.9	642	26.8	69.2	0.1
H	ITO+MoO ₃	10 nm	400	11.3	629	26.6	67.3	0.5

4.3.3 Structural Properties

As shown in the previous section, the best performance was obtained for cells made on the 10 nm as-deposited MoO₃ films. Therefore, this was considered as the optimum condition and further characterization was carried out.

Figure 4.17 shows the XRD patterns of 2 μ m thick Cu(In,Ga)Se₂ films deposited on the Mo, Mo-MoO₃, ITO, and ITO-MoO₃ back contact structures. In all cases, the chalcopyrite Cu(In,Ga)Se₂ phase was formed without any contribution from binary or ternary phases. However, the presence of oxide layers altered the crystallographic orientation of the Cu(In,Ga)Se₂ absorber layer. As a result, the intensity ratio between the (112) and (220)/(204) peaks reduced from ~10 for the control sample on Mo to 2.6, 1.9, and 2.1 for the Cu(In,Ga)Se₂ films deposited on Mo/MoO₃, ITO, and ITO/MoO₃ layers, respectively.

SEM cross sections of the devices made on different back contacts are shown in Figure 4.18. The different layers of back contact/Cu(In,Ga)Se₂/CdS/ZnO:Al device structure are noted in the figure. It can be seen that the film deposited on the Mo back contact (Figure 4.18a) has a large grain size, on the order of 0.5 μm . Introducing the MoO₃ interlayer reduced the Cu(In,Ga)Se₂ grain size (Figure 4.18b). Figs. 4.18c and 4.18d show that Cu(In,Ga)Se₂ films grown on ITO and ITO/MoO₃ back layers have a much smaller grain size than films made on the Mo substrate. This may be caused by different nucleation and growth mechanisms for Cu(In,Ga)Se₂ deposited on the oxide layers (ITO or MoO₃) [125]. However, no adhesion issues were observed in either case and there was no clear correlation between the grain size and the device properties.

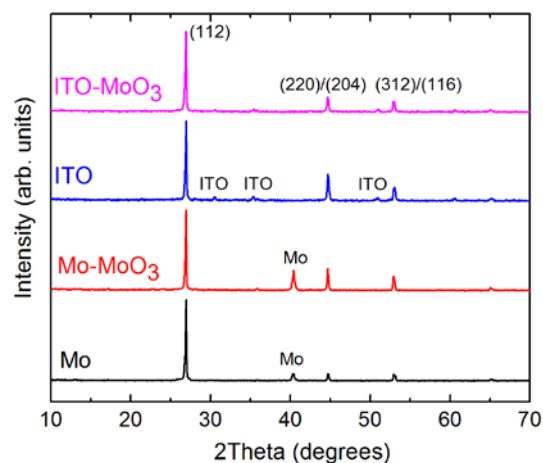


Figure 4.17: XRD pattern of the Cu(In,Ga)Se₂ deposited on Mo, Mo-MoO₃ stacks, ITO, and ITO-MoO₃ stacks. Indices of main diffracted planes of the Cu(In,Ga)Se₂ are also shown.

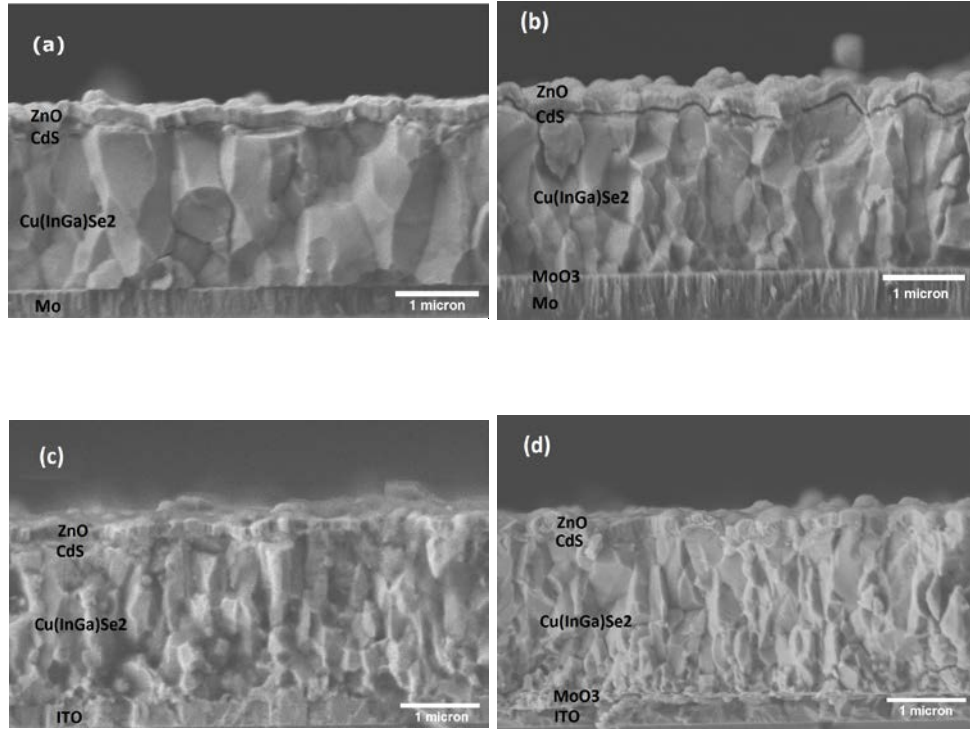


Figure 4.18: SEM cross-section of the cells made on the a) Mo, b) Mo-MoO₃, c) ITO, and d) ITO-MoO₃ back contacts.

Chapter 5

WO₃ TRANSPARENT BACK CONTACT

5.1 Introduction

In chapter 4, MoO₃ was proposed as a novel candidate for the primary back contact of Cu(In,Ga)Se₂ thin film solar cells [116,183]. 14% and 12% solar cell efficiencies have been achieved for the Mo-MoO₃ and ITO-MoO₃ back contacts, respectively [184].

Analogously, WO₃ films with a high work function (> 6 eV) [104] was considered as a potential candidate for the primary back contact of Cu(In,Ga)Se₂ thin film solar cells. In particular, high transparency ($>80\%$ in the visible and near IR range), and a wide bandgap (2.5-3.2eV) [101–103], of WO₃ make it a good back contact candidate for the bifacial and tandem devices. Its Fermi level and density of states can be potentially tuned by controlling the oxygen stoichiometry during the deposition and or post processing. To do so, we need an in-depth understanding of the structural, optical and surface properties of WO₃ films.

WO₃ has been used in various applications such as gas sensors [185], high temperature superconductivity [186,187], electro-chromic devices, windows, and displays [188,189], photo-electrochemical cells for solar energy conversion [101,190], and bulk-hetero-junction solar cells [105–107].

WO₃ is reported to have different crystal structures as a function of temperature: low- temperature monoclinic structure from -140 to -50 °C, triclinic structure from -50 to 17 °C, room temperature monoclinic structure from 17 to 330 °C,

orthorhombic structure from 330 to 740 °C and a tetragonal structure above 740 °C [191–194]. The room temperature monoclinic structure is the most stable form of WO₃ with the space group of P21/n [193]. However, oxygen deficiency may lead to the formation of sub-stoichiometric phases of W_nO_{3n-1} and W_nO_{3n-2} (such as W₁₈O₄₉ and W₂₀O₅₈) which are indicated in the W-O phase diagram [195].

This chapter addresses the properties of WO₃ thin films prepared by reactive rf sputtering in Ar + O₂ ambient with O₂/(O₂+Ar) = 50%. The effects of post processing on the structural, optical, and surface properties of the deposited films were studied using x-ray diffraction (XRD), UV/Vis/NIR spectrophotometry, and x-ray photoelectron spectroscopy (XPS), respectively. Results are compared with MoO₃ films deposited by the same technique. Evaluation of the WO₃ electronic properties and back contact role in Cu(In,Ga)Se₂ thin film solar cells are also addressed. Results are compared with MoO₃ films deposited by a similar technique.

5.2 Reactively Sputtered WO₃ Films

5.2.1 Structural Properties

Figure 5.1 shows the XRD pattern of the reactive-sputtered WO₃ films deposited on glass at O₂/(O₂+Ar) = 50% and annealed in Air at different temperatures. The as-deposited film shows a broad peak centered at ~ 24° (Fig. 5.1) indicating an amorphous structure with a short range order of the atoms in the crystal lattice. This feature may contain scattering from both the film and glass substrates. Annealing at 300 °C didn't produce any noticeable difference in the structure of WO₃ films. Thus, low temperature post-growth annealing (300 °C) doesn't provide sufficient energy for nucleation and growth of WO₃ crystallites.

Samples annealed at 400 °C became crystalline (Figure 5.1, and Table 5.1), with reflections at 23.18°, 23.58°, 24.38°, 26.60°, 28.94°, and 34.20° which were identified as the (002), (020), (200), (120), (-121), and (202) reflections of the monoclinic WO₃ phase [196], space group P21/n with $a_0 = 0.731$ nm, $b_0 = 0.754$ nm, $c_0 = 0.769$ nm, and $\beta = 90.8$ degrees. These films have a (200) preferred orientation. Figure 5.1 and Table 5.2 show that samples annealed at 500 °C were also identified as WO₃ phase, but with a (002) preferred orientation.

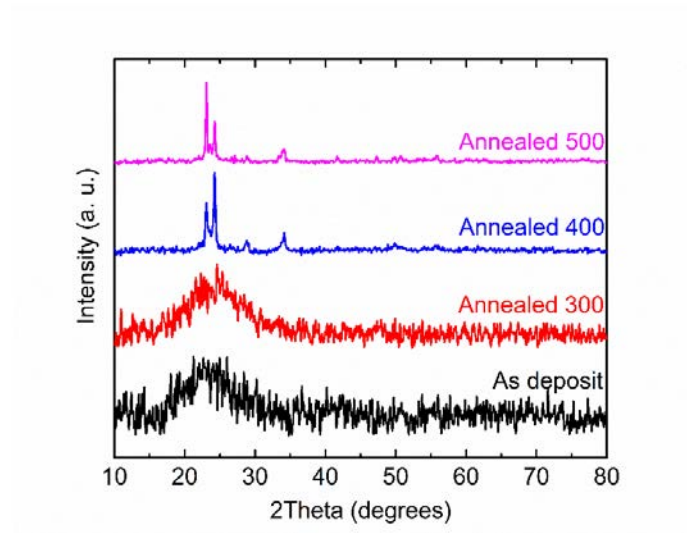


Figure 5.1: XRD pattern of WO₃ films annealed at different temperatures.

As mentioned above, monoclinic and orthorhombic structures are stable in the temperature range of 17-330 °C and 330-740 °C, respectively [26–29]. The monoclinic structure observed in this work might be formed because the very thin films did not experience the phase transition at 330 °C or because an orthorhombic

structure formed during annealing above 330 °C following a transformation to a monoclinic phase when the temperature decreases down to room temperature.

Preferential orientations of the films were determined using the fiber texture method proposed by Harris [197]. In this method, the texture coefficient (TC_{hkl}) of the crystals with the $\{hkl\}$ orientation compared to a randomly oriented sample can be determined using the following equation [198]:

$$TC_{hkl} = n \frac{I_{hkl}}{I_{r,hkl}} \sum \frac{I_{hkl}}{I_{r,hkl}} \quad (5.2)$$

where I_{hkl} is the integrated intensity of the hkl reflection, and n is the number of reflections. The r indices refer to the randomly oriented sample, which can be derived from the ICDD card of powders. The volume fraction (V_{hkl}) of crystals oriented along each hkl will then be determined as followed:

$$V_{hkl} = 100 \times \frac{TC_{hkl}}{\sum TC_{hkl}} \quad (5.3)$$

For the totally random samples such as powders, the TC numbers would be all equal to 1 with all the volume fractions (V_{hkl}) equally divided. For this study, 8 peaks with highest intensity were considered for the orientation analysis of films using the Harris method. The results for different hkl 's of the monoclinic unit cell are summarized in Tables 5.1 and 5.2. The sum of the TC's for these samples were about 7. It can be seen that films annealed at 400 °C have about 24 vol. % of crystallites oriented in the (200) direction. On the other hand, higher annealing temperature of 500°C shifts the orientation of WO_3 films, and 27 vol. % of crystallites are oriented in the (002) direction. For both cases, (-121) is the second preferred orientation of the annealed films.

Table 5.1: The peak positions (2θ), d-spacing (d), intensity (I), texture coefficient (TC), and volume fraction (V) of WO_3 film, deposited with $\text{O}_2/(\text{O}_2+\text{Ar}) = 50\%$ and annealed at $400\text{ }^\circ\text{C}$, in comparison with ICDD card 01-072-0677[196].

Measured						ICDD		
(2θ)	d (Å)	I	(hkl)	TC	V (%)	(2θ)	d (Å)	I
23.18	3.81	67	002	1.08	16.6	23.11	3.85	99.0
23.58	3.74	25	020	0.42	6.4	23.58	3.77	96.0
24.38	3.62	100	200	1.59	24.5	24.35	3.65	100.0
26.60	3.32	13	120	1.07	16.4	26.59	3.35	19.0
28.94	3.05	14	-121	1.38	21.1	28.91	3.08	16.0
34.20	2.58	35	202	0.98	15.1	34.15	2.62	56.0
49.88	1.77	8	400	0.88	13.5	49.89	1.83	22.0
55.90	1.58	8	420	1.08	16.6	55.89	1.64	15.0

Table 5.2: The peak positions (2θ), d-spacing (d), intensity (I), texture coefficient (TC), and volume fraction (V) of WO_3 film, deposited with $\text{O}_2/(\text{O}_2+\text{Ar}) = 50\%$ and annealed at $500\text{ }^\circ\text{C}$, in comparison with ICDD card 01-072-0677[196].

Measured						ICDD		
(2θ)	d (Å)	I	(hkl)	TC	V (%)	(2θ)	d (Å)	I
23.16	3.811	100	002	1.92	27.1	23.11	3.85	99.0
23.58	3.743	32	020	0.62	8.8	23.58	3.77	96.0
24.32	3.629	63	200	1.19	16.8	24.35	3.65	100.0
26.86	3.286	8	120	0.80	11.3	26.59	3.35	19.0
28.90	3.054	12	-121	1.45	20.5	28.91	3.08	16.0
33.26	2.654	9	022	0.44	6.2	34.15	2.69	56.0
34.16	2.584	20	202	0.66	9.4	49.89	2.62	22.0
55.88	1.580	7	420	0.93	13.1	55.89	1.64	15.0

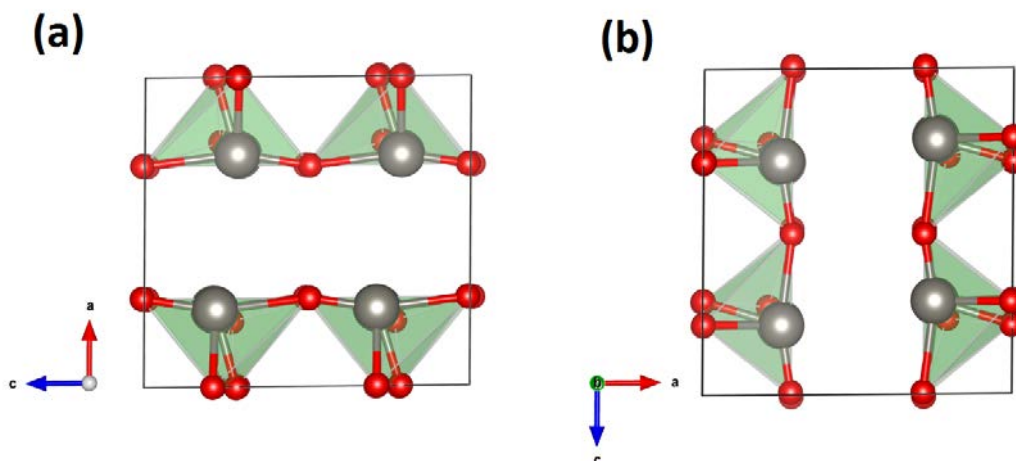


Figure 5.2: WO₃ monoclinic unit cell b-axis projection with (a) (h00) planes horizontal and (b) with (001) planes horizontal. Drawings made using VESTA [199]. Big (gray) and small (red) balls are representative of W and O atoms, respectively.

The preferred (h00) orientation in the 400 °C annealed films suggests a coordination between WO₃ planes containing maximum W atomic density in WO₃ and the terminating O atoms in SiO₂. In this closest-packing configuration, the W atoms lie exactly within planes parallel to the substrate (Fig. 5.2a). Line profile analysis of the (200) reflection profile indicates a Pearson VII distribution with significant nanocrystalline tail broadening. Scherrer analysis [200] of excess broadening indicates a coherency length of 50 nm. The SEM images (not shown here) didn't reveal any clear grain structures due to small grain size and high charging of resistive samples, even after coating with Au-Pt.

For 500 °C annealed films, (h00) texture is vanished, with lower (200) intensity and elimination of the (400) reflection. Preferred orientation shifts to (001) suggesting a loss of coordination with the substrate O atoms. In this c-axis

configuration, W atoms lie in 2 sets of parallel planes within the unit cell (Fig. 5.2b). Line profile analysis of the (002) reflection indicates a Pearson VII distribution with low nanocrystalline tail broadening and coherency length of 65 nm.

Besides, the impact of impurity diffusion from the glass cannot be ruled out as a factor influencing film recrystallization and orientation at high temperature annealing [201].

5.2.2 Optical Properties

Fig. 5.3 shows the optical transmittance and reflectance plots of the WO₃ films deposited on glass and annealed at different temperatures. The film thickness was 250 nm, determined by Dektak profilometer. All films show high transmittance in the visible range, indicating low concentration of oxygen ion vacancies [177,202]. The transmittance values drop steeply below the $\lambda \approx 400$ nm indicating a strong band-to-band absorption [147]. Increasing the annealing temperature did not significantly change the total transmittance of films but did cause a shift in the absorption edges to lower energy ranges, thus decreasing bandgaps.

The total absorption coefficient α was calculated from the T-R measurements using the following equation [39]:

$$\alpha = \frac{1}{d} \ln \frac{(1-R)^2}{T} \quad (4)$$

where d is the thickness, T the transmittance, and R the reflectance of WO₃ films. For photon energies slightly larger than E_g the absorption coefficient α can be described by the following equation:

$$\alpha E \sim (E - E_g)^n \quad (5)$$

where E is the photon energy and the exponent n depends on the type of optical transition in the gap region. Specifically, n equals $1/2$, $3/2$, and 2 for transitions being direct allowed, direct forbidden, and indirect allowed, respectively [39].

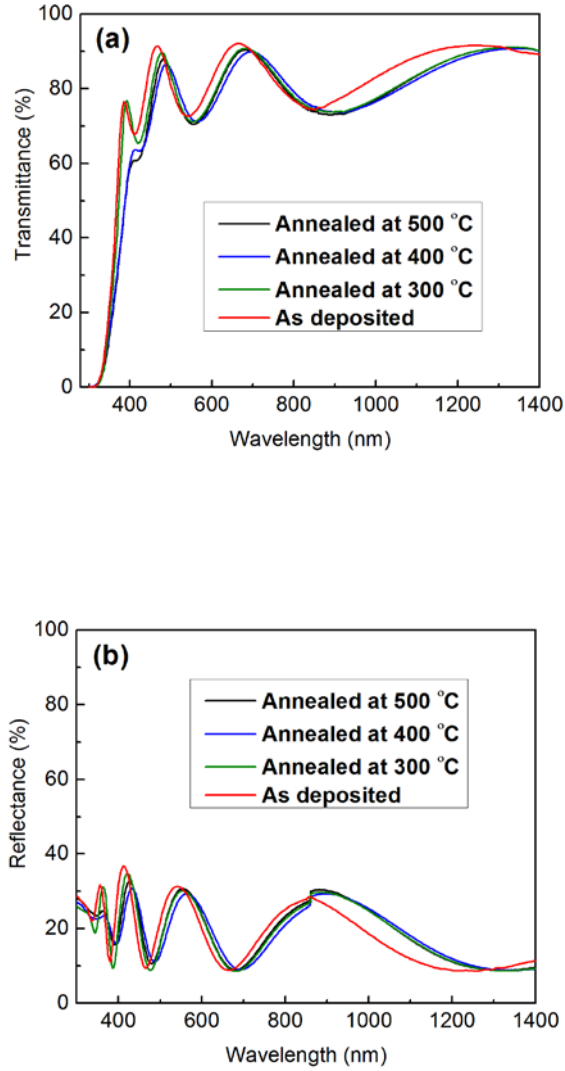


Figure 5.3: Transmittance and reflectance plots of the WO_3 films deposited at $O_2/(O_2+Ar) = 50\%$ and annealed at different temperatures.

Electronic structure calculations of WO_3 indicated that valence band and conduction band are comprised of the 2p orbitals of oxygen ions and the 5d orbital of tungsten cations, respectively [155,156]. Previous studies have reported both direct allowed [101,102,155] and indirect allowed [103,121] transitions for the bandgap of WO_3 . Therefore, both conditions were examined here and the optical bandgaps (E_g) of the films were determined by plotting $(\alpha E)^2$ or $(\alpha E)^{1/2}$ versus $h\nu$ and performing a linear fit to the data, extrapolating to the x-axis (E). Sample curves are shown in Figure 5.4 for the film deposited with $\text{O}_2/(\text{O}_2+\text{Ar}) = 50\%$, and annealed at different temperatures.

Linear fitting was performed for the data above the principal inflection point. Then, a series of fits were considered to perform the linear fit. The best fit was determined based on the shape of the curves, statistical absolute error (ΔE_g), and the coefficient of determination (r^2). As Figure 5.4 shows, none of the plots are well-matched with a linear fit. However, the indirect allowed transition gives a much better coefficient of determination (r^2) over the same number of points, and considered as the primary transition for the bandgap evaluation (Fig. 5.4b).

The bandgap values determined from the linear fit of the data above (for the same α range of 10^5 to 2×10^5) for the as-deposited, 300 °C annealed, 400 °C annealed, and 500 °C annealed films are shown in Figure 5.5. One can see that the annealing has reduced the bandgap values of reactive-sputtered WO_3 films. This is in agreement with the work of previous studies in which a drop in bandgap value was observed for the films annealed at high temperature, due to oxygen deficiency that occurs in WO_3 at higher annealing temperatures [43–45]. This is opposite behavior than what found for sputtered MoO_3 films [116] where E_g is increased after annealing.

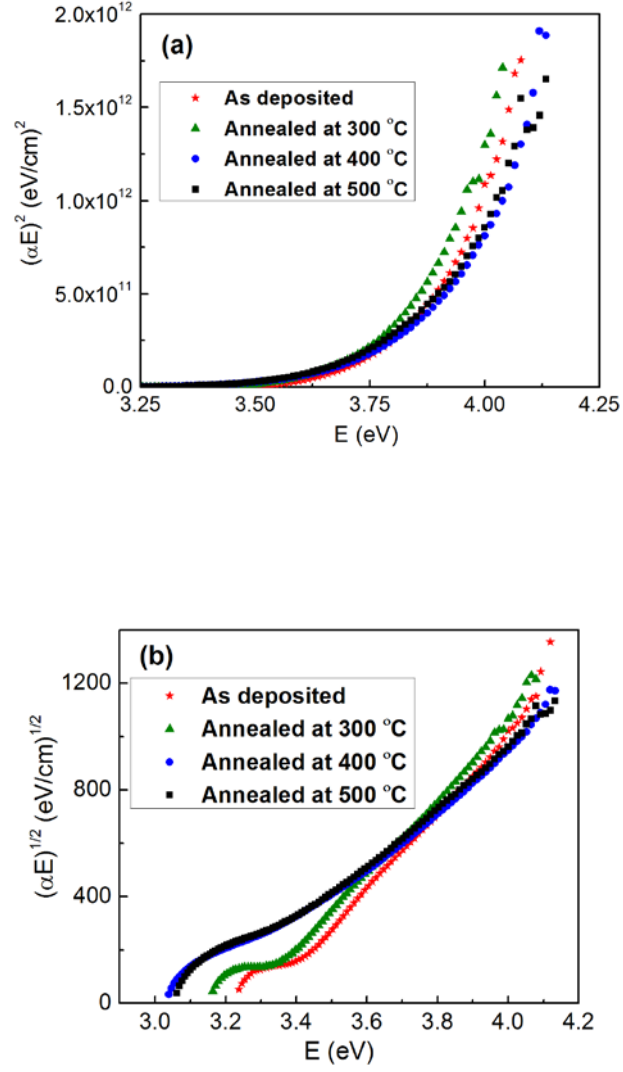


Figure 5.4: Tauc plots for WO_3 films deposited at $\text{O}_2/(\text{O}_2+\text{Ar}) = 50\%$ and annealed at different temperatures, assuming a) direct transition, and b) indirect transition.

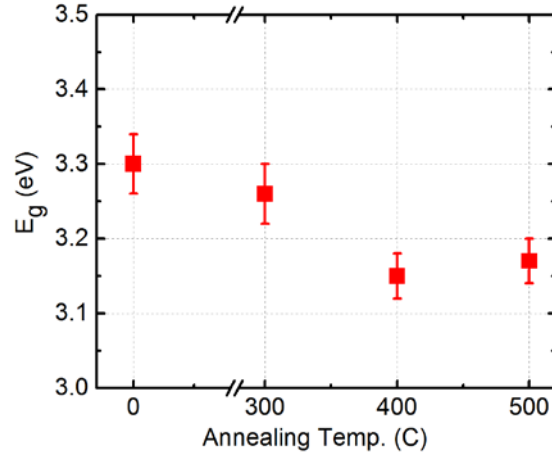


Figure 5.5: Variation of optical bandgap as a function of annealing temperature

5.2.3 Surface Properties

Fig. 5.6 shows the XPS survey scan of a WO_3 film deposited at room temperature with the major core level binding states indicated in the graph. This is a typical spectrum for all the WO_3 films independent of post treatment conditions. The carbon peak (C 1s) observed at ~ 284 eV is due to the surface contamination of the film since they were exposed to atmosphere.

High resolution scans of the W 4f doublet core levels are shown in Fig. 5.7. The peaks were fitted by Gaussian-Lorentzian curves satisfying the following constraints: a) the $3f_{7/2}$ to $3f_{5/2}$ ratio is 4:3; b) each doublet has equal FWHM; and c) the spin orbit splitting of the W 3d doublets is 2.18 eV [136].

The as-deposited film produces a symmetric line shape with no indication of mixed oxidation states. Peaks located at energies of 35.55 eV and 37.73 eV were identified as $3f_{7/2}$ and $3f_{5/2}$ peaks of WO_3 phase, respectively. The film annealed at 300 °C was also identified as the pure WO_3 phase with peaks positioned at 35.64 eV

and 37.76 eV, respectively. However, annealing at 400 °C resulted in a shift to lower binding energies of 35.11 eV (3f_{7/2}) and 37.29 eV (3f_{5/2}) due to the presence of single phase WO_{3-x} at the film surface.

Annealing at 500 °C leads to the formation of another set of peaks at 33.69 eV and 35.87 eV, probably corresponding to more oxygen deficient phases such as W₁₈O₄₉, W₂₄O₆₈, and/or WO₂ [180,195] besides the main WO_{3-x} doublet of 35.04 eV and 37.22 eV. The shift to a lower oxidation state indicates a loss of oxygen atoms at the surface after the 500 °C anneal. This result is in good agreement with the work done by Mahammad et al. [203] in which a WO_{3-x} phase (Magneli phase) in variable proportions was observed by a TEM study of WO₃ films annealed at 300-450 °C in air.

The change in the surface oxidation can be compared to the free energy (ΔG) and equilibrium constant (k) for the following reversible reaction at different temperatures [113]:



$$\Delta G^{300\text{C}} = +2.14 \text{ kcal/mol}; k^{300\text{C}} = 0.15$$

$$\Delta G^{400\text{C}} = +1.95 \text{ kcal/mol}; k^{400\text{C}} = 0.23$$

$$\Delta G^{500\text{C}} = +1.77 \text{ kcal/mol}; k^{500\text{C}} = 0.31$$

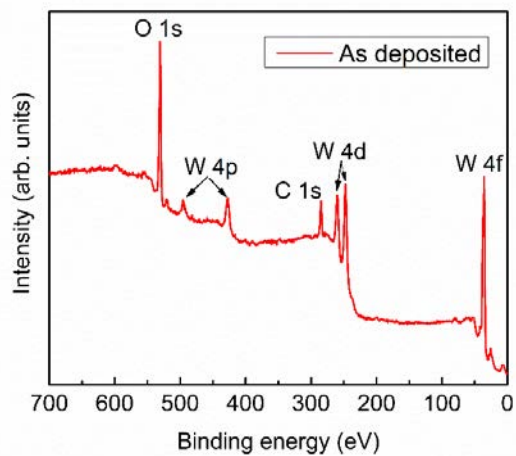


Figure 5.6: XPS spectrum of the WO_3 film deposited at room temperature at $\text{O}_2/(\text{O}_2+\text{Ar}) = 50\%$.

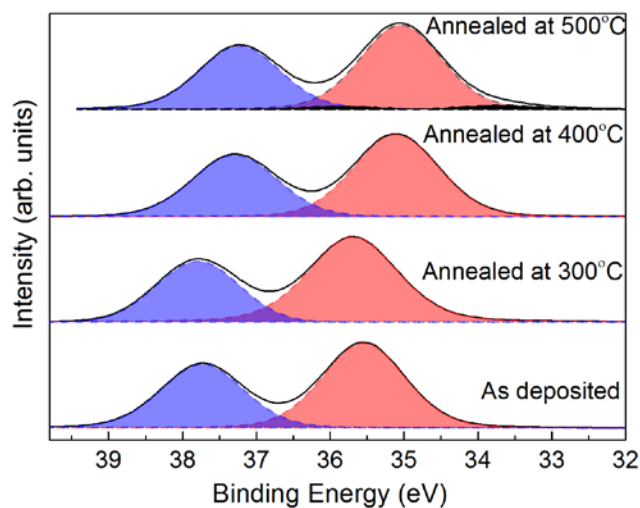


Figure 5.7: XPS core level binding energy of W 4f doublets of WO_3 films deposited at $\text{O}_2/(\text{O}_2+\text{Ar}) = 50\%$ and annealed at different temperatures.

While the reaction free energies to form the sub-oxide are positive in all cases the equilibrium constants give finite and relatively large product quantities. The addition of oxygen via air to the treatment environment will, through le Chatelier's principle, reduce these quantities such that at 'air' concentration, $[O_2] = 20\%$, the equilibrium constants are reduced to 0.03 at 400 °C and 0.11 at 500 °C. Since we do not know about the mass transfer limitation from the bulk to the surface region, this argument suggests that surface reduction can occur, even in the presence of air. The WO_{3-x} phase is not seen in the XRD analysis above indicating that it is confined to the film surface and below the XRD detection limit.

Nevertheless, XPS results are consistent with the optical properties where a shift in the absorption edge to lower energy ranges (decreasing bandgaps) is observed in the films annealed at 400-500 °C. Therefore, oxygen deficiency and the presence of lower oxidation states resulted in decreasing bandgaps of tungsten oxide films annealed at 400-500 °C. The optical modeling of the room temperature γ - WO_3 phase suggests a 0.50 eV drop in the energy gap if an oxygen vacancy is formed [204]. In another work, Gillet et.al [121] have also reported the lower bandgap of oxygen-deficient WO_3 films due to the presence of donor levels caused by oxygen vacancies at the surface. When the surface oxygen vacancy concentration increases, the donor orbitals overlap and lead to the formation of a band which lessens the gap [121]. The impurity energy state induced by oxygen deficiency might also lead to a decrease in the bandgap of WO_3 , similar to what has been reported for the MoO_3 films [114,138].

5.2.4 Comparing WO_3 and MoO_3 Films

Since Mo and W both belong to the group VI of transition metals, with the same number of electrons on the outer shell, analogous properties of their compounds

are expected. However, there are a couple of contradicting results in the structural, optical, and surface properties of reactively-sputtered and air-annealed MoO₃ and WO₃ films, which are addressed here.

As-deposited MoO₃ films have an amorphous structure. Annealing at 300 °C in air resulted in a crystallization of the molybdenum oxide films in the monoclinic β -MoO₃ phase. Samples annealed at 400 and 500 °C were both identified as pure orthorhombic α -MoO₃ phases with (020) preferred orientation [116]. For the WO₃ films, as-deposited films exhibit amorphous structure with no change detected after annealing at 300 °C. Samples annealed at 400 and 500 °C were crystallized and identified as pure monoclinic WO₃ phase with (200) and (002) preferred orientation, respectively.

UV/Vis/NIR spectrophotometry revealed a high optical transmittance (> 80%) in the visible range, with bandgaps in the range of 2.6 eV to 2.9 eV for the as-deposited MoO₃ films. Annealing at 300 °C had a negligible effect on the optical properties of the MoO₃ films, but samples annealed at 400 °C and 500 °C exhibited wider bandgaps within the range of 3.1-3.4 eV. In the case of WO₃ films, post processing had no significant effect on optical transmittance of the films, but it decreased the optical bandgap from ~3.30 eV for the as-deposited films to the ~3.15 eV for the films annealed at 400-500 °C.

High resolution XPS studies showed the presence of Mo⁶⁺ (MoO₃) and Mo⁵⁺ (Mo₄O₁₁) oxidation states at the surface of as-deposited and low temperature (300 °C) annealed films. Annealing at 400-500 °C suppressed the oxygen deficiency at the surface, resulting in films with a composition close to the stoichiometric phase. On the other hand, XPS studies of WO₃ films showed the presence of W⁶⁺ (WO₃)

oxidation states at the surface of as-deposited films and of films annealed at 300 °C. Annealing at 400-500 °C led to an oxygen deficient surface, resulting in films with higher sub-stoichiometric (WO_{3-x}) phases.

The differences observed in the properties of reactively-sputtered and air-annealed MoO_3 and WO_3 films can be explained by the difference in structural characteristics of these materials. For both MoO_3 and WO_3 , the metal atoms occupy the distorted octahedral sites, but differences in the connectivity of the octahedrons result in dissimilar structures. Consequently, the α - MoO_3 crystallizes with a layered structure (orthorhombic with space group Pbnm, see Fig. 5.8a), while the γ - WO_3 forms a ReO_3 -related structure (monoclinic with space group P21/c, see Fig. 5.8b) with a very different π -type overlap between the metal (d) and oxygen (2p) orbitals, similar to metastable β - MoO_3 phase with monoclinic structure [175,205]. Therefore, γ - WO_3 phase has properties similar to the metastable β - MoO_3 phase than that of α - MoO_3 phase.

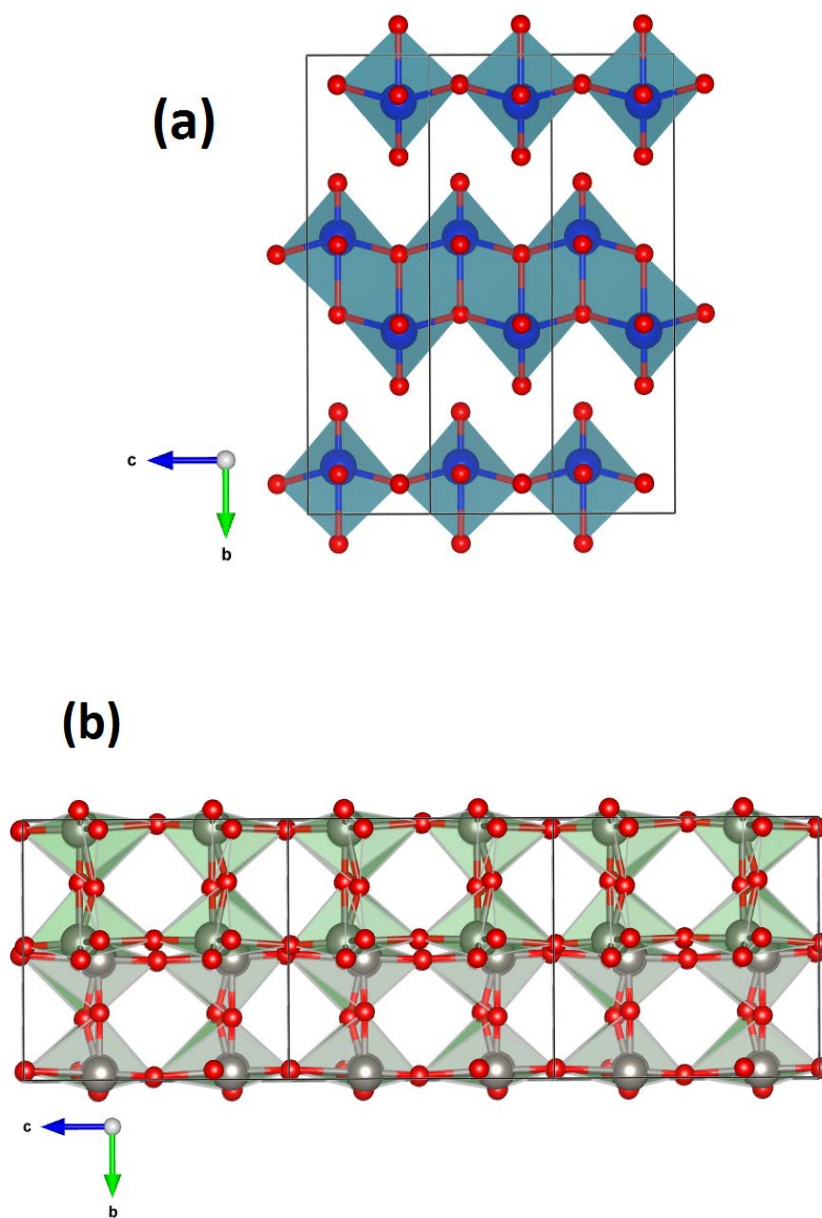


Figure 5.8: The structures of (a) orthorhombic α -MoO₃ and (b) monoclinic γ -WO₃ phases. Drawings made using VESTA [199].

5.3 Interface Chemistry and Device Properties of WO₃ Films

In the previous sections, the effects of oxygen partial pressure and post-deposition annealing on the structural, optical, and surface properties of WO₃ thin films deposited on glass by RF reactive sputtering were presented [116]. For this section, the interface chemistry and device properties of Cu(In,Ga)Se₂ solar cells made on WO₃ back contacts are discussed.

WO₃ films were deposited on the Mo/ITO coated glass substrates by reactive rf sputtering. Cu(In,Ga)Se₂ films were deposited on different back contact structures incorporating WO₃ films. The effects of WO₃ back layers on the elemental distribution, structural properties and device performance of the Cu(In,Ga)Se₂ films were studied using SIMS, XPS, XRD, SEM, and current-voltage analysis of complete solar cells. Films for structural characterization and devices were 2 μm thick, while for SIMS and XPS depth profiling 100 nm thick films were used to reduce sputter etch time and improve depth resolution at the back interface.

5.3.1 Interface Properties

5.3.1.1 SIMS Analysis

SIMS depth profile analysis was performed in order to find the elemental distribution, in the Cu(In,Ga)Se₂ films made on different back contacts. For this purpose, 100 nm thick Cu(In,Ga)Se₂ films were deposited on Mo, ITO, and ITO-WO₃ back contacts. Fig. 5.9 shows the SIMS depth profiles of the 100 nm thick Cu(In,Ga)Se₂ films on different back layers plotted versus film thickness. For the Mo/Cu(In,Ga)Se₂ sample (Figure 5.9a) the profile shows the concentrations of Cu, In, and Ga drop rapidly at the interface after 100 nm. However, the Se concentration stays

high and overlaps the Mo. This suggests the formation of a MoSe_2 layer at the interface, as has been reported previously [50–52].

The SIMS depth profile of the $\text{ITO}/\text{Cu}(\text{In,Ga})\text{Se}_2$ stack is shown in Figure 5.9b. There is an observed accumulation of Ga at the interface on MoO_3 (Figure 4.9b), which can be attributed to the high affinity between Ga and O atoms [113] suggesting formation of Ga_2O_3 at the $\text{ITO}/\text{Cu}(\text{In,Ga})\text{Se}_2$ interface.

Finally, Figure 5.9c shows the SIMS depth profile of the $\text{ITO}/\text{WO}_3/\text{Cu}(\text{In,Ga})\text{Se}_2$ stack. The Se concentration drops rapidly at the interface, while the W and O concentrations rise, suggesting there is no WSe_2 formation at the interface. Again, there is an accumulation of Ga suggesting formation of Ga_2O_3 at the $\text{ITO}/\text{WO}_3/\text{Cu}(\text{In,Ga})\text{Se}_2$ interface.

Figure 5.10 compares the elemental distribution of different stacks in order to have a better understanding on the effect of oxide layers. Figure 5.10 shows that Ga profile was uniform for the control sample made on Mo; however, Ga has been accumulated towards the back surface for all films made on oxide layers. On the other hand, while Se is piled up at the interface of $\text{Mo}/\text{Cu}(\text{In,Ga})\text{Se}_2$ sample, forming MoSe_2 , it drops rapidly at the interface of films made on oxide layers. Therefore, MoSe_2 phase was not formed there.

Figure 5.10c shows the Na profile of different stacks. It can be seen that presence of ITO and WO_3 layers didn't act as a barrier for Na diffusion from the soda lime glass substrate to the $\text{Cu}(\text{In,Ga})\text{Se}_2$ layer. Alternatively, K diffusion is reduced by one order of magnitude for the films made on ITO and WO_3 (Figure 5.10d). The main portion of Na and K accumulation at the back contact interface and front surface, due to high tendency between these elements and oxygen atoms [206].

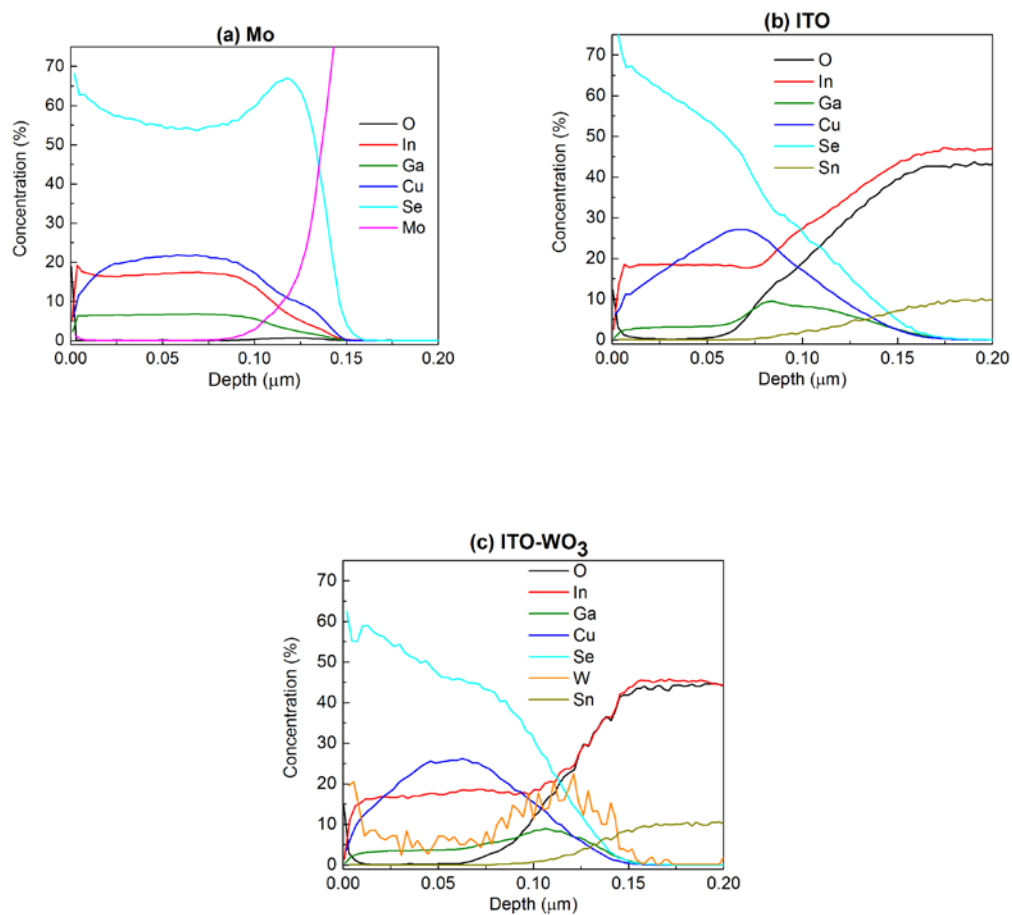


Figure 5.9: SIMS depth profile of a) Mo/Cu(In,Ga)Se₂, b) ITO/Cu(In,Ga)Se₂, and c) ITO/WO₃/Cu(In,Ga)Se₂.

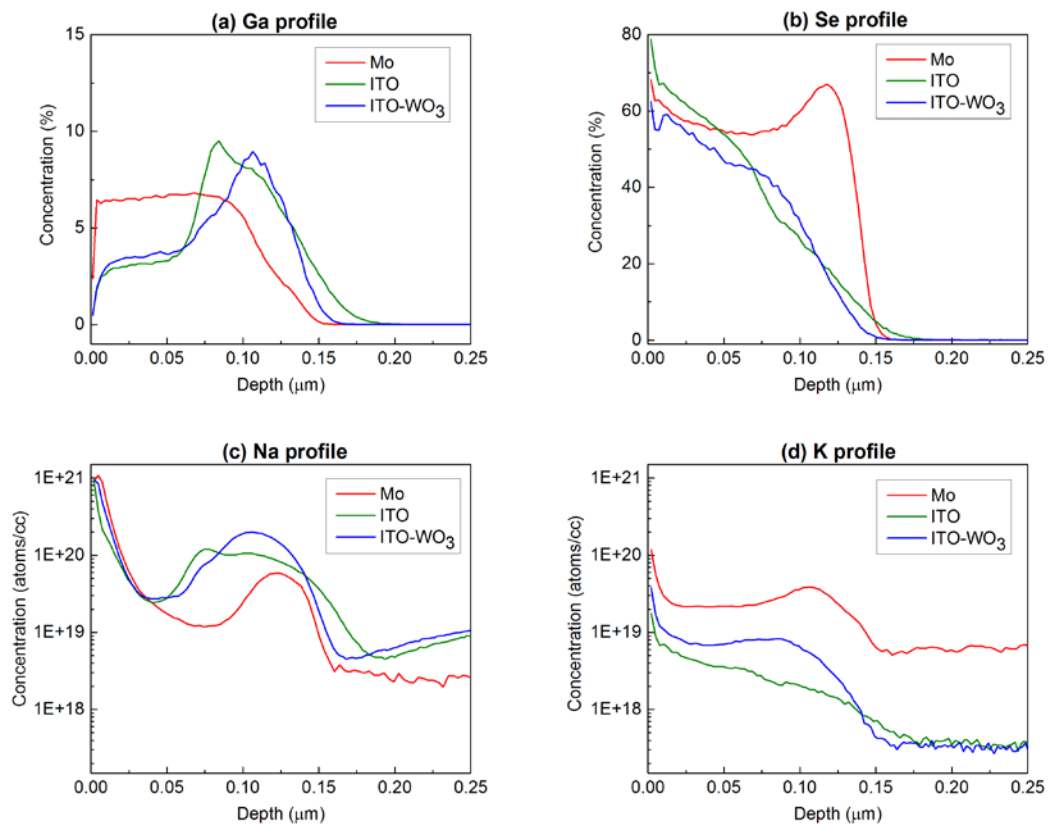


Figure 5.10: Effect of back contact on the distribution of a) Ga, b) Se, c) Na, and d) K through the Cu(In,Ga)Se₂ films.

5.3.1.2 XPS Analysis

The interfaces between the Cu(In,Ga)Se₂ and the different back contacts incorporating WO₃ were characterized by XPS measurements. Their interpretation was facilitated by considering the thermodynamics of potential reactions using bulk enthalpy and entropy for reactant and product phases at 550 °C. The Gibbs free energies for possible reactions of different species are listed in Table 5.3. Figure 5.11 shows the XPS depth profiles of the 100 nm thick Cu(In,Ga)Se₂ films on different back layers plotted versus etch time. The XPS analysis of Mo/Cu(In,Ga)Se₂ and

ITO/Cu(In,Ga)Se₂ samples was discussed in section 4.3; however, their plots are shown again here for comparison.

For the Mo/WO₃/Cu(In,Ga)Se₂ sample, (Figure 5.11b) the profile shows that the concentrations of Cu, In, Ga, and Se, determined by their peak areas, drop rapidly at the interface after 90 min etch time. There is no apparent Se accumulation at the interface and, therefore, no apparent formation of selenide phases such as WSe₂ at the interface. The Ga peak also drops rapidly at the interface in contrast with the Mo/WO₃/Cu(In,Ga)Se₂ sample discussed in section 4.3.3. Nevertheless, Table 5.3 suggests that the partial reduction of WO₃ with Se to form WSe₂, and formation Ga₂O₃ phase at the interface are likely.

High resolution scans of W 4f doublet core levels of WO₃ films after 100 min Ar etch are shown in Fig. 5.13. The peaks were fitted by Gaussian-Lorentzian curves satisfying the following constraints: a) the 3f_{7/2} to 3f_{5/2} ratio is 4:3; b) each doublet has equal FWHM; and c) the spin orbit splitting of the W 3d doublets is 2.18 eV [136]. The fit indicates the presence of WO₂ and WO_{3-x} phases at the interface of the WO₃/CIGS stack. No evidence of a WSe₂ phase with 3f_{7/2} and 3f_{5/2} doublets to be located 32.5 eV and 30.3, respectively [180], was observed. Therefore, partial reduction of the WO₃ phase might originate from preferential sputtering during the XPS depth profiling.

High resolution scans of the Ga 3d region are shown in Figure 5.12. The slight asymmetric line shape suggests the partial oxidation of Ga at the Mo/WO₃/Cu(In,Ga)Se₂ interface, very similar to the Mo/Cu(In,Ga)Se₂ sample. Therefore, only a small amount of Ga₂O₃ phase formed at the interface, though it was thermodynamically favorable (Table 5.3).

The XPS depth profile of the ITO/WO₃/Cu(In,Ga)Se₂ stack is shown in Figure 5.10d. It can be seen that there is an accumulation of Ga at the interface, similar to the Cu(In,Ga)Se₂/ITO (Figure 5.12c). High resolution scans of the Ga 3d region (Figure 5.11d) show a shoulder at high energy with its highest intensity at the Cu(In,Ga)Se₂/WO₃ interface (90 min etch). Peak deconvolution of the Ga 3d area suggests that the satellite peak is due to the Ga₂O₃ phase [180] (Figure 5.12d), in agreement with the results observed for ITO/MoO₃/Cu(In,Ga)Se₂ sample (section 4.3.3).

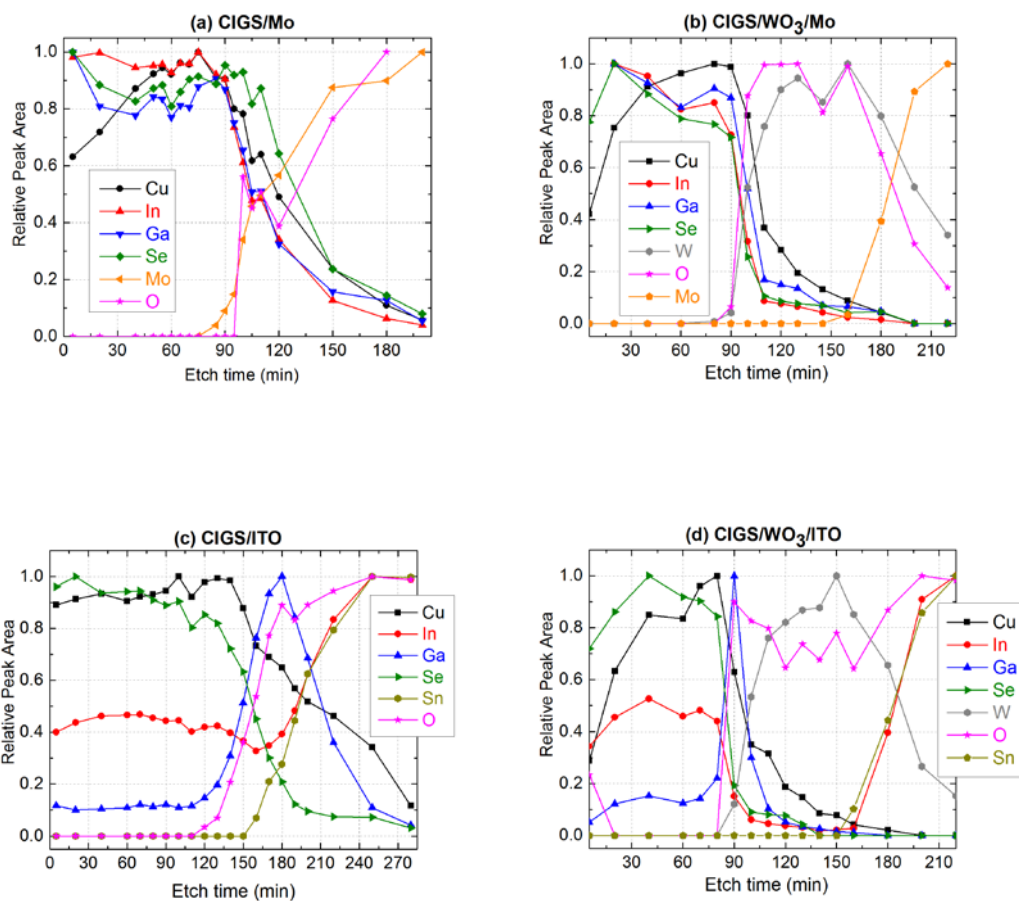


Figure 5.11: XPS depth profile of a) Mo/Cu(In,Ga)Se₂ , b) Mo/WO₃/Cu(In,Ga)Se₂ , c) ITO/Cu(In,Ga)Se₂ , and d) ITO/WO₃/Cu(In,Ga)Se₂.

Table 5.3: Gibbs free energy of potential reactions at the Cu(In,Ga)Se₂ / back contact interface, calculated at 550 °C [113].

Reactants	Reaction	Gibbs free energy (kcal/mol)
Se-O	$O_2 \rightarrow 2O$	+95.12
	$Se_2 \rightarrow 2Se_L$	-4.55
W-Se-O	$W + 2Se \rightarrow WSe_2$	-30.68
	$W + O_2 \rightarrow WO_2$	+13.74
	$W + 3/2 O_2 \rightarrow WO_3$	-150.49
	$WO_3 + 2Se \rightarrow WSe_2 + 3/2 O_2$	+119.71
	$WO_3 + 2Se \rightarrow WO_2 + WSe_2 + 1/2 O_2$	-35.93
ITO-Se-O	$2In + 3/2 O_2 \rightarrow In_2O_3$	-285.99
	$In_2O_3 + 3Se \rightarrow \beta-In_2O_3 + 3/2 O_2$	+90.65
	$SnO_2 + 2Se \rightarrow SnSe_2 + O_2$	+77.28
	$2SnO_2 + Se \rightarrow SnSe + SnO + 1/2 O_2$	+171.37
Ga-W-Se-O	$2Ga + 3Se \rightarrow Ga_2Se_3$	-82.99
	$Ga_2Se_3 + 3/2 O_2 \rightarrow Ga_2O_3 + 3Se$	-113.19
	$WO_3 + 2Ga \rightarrow Ga_2O_3 + W$	-45.92
	$2WO_3 + 2Ga \rightarrow Ga_2O_3 + 3/2 WO_2 + 1/2 W$	-52.58

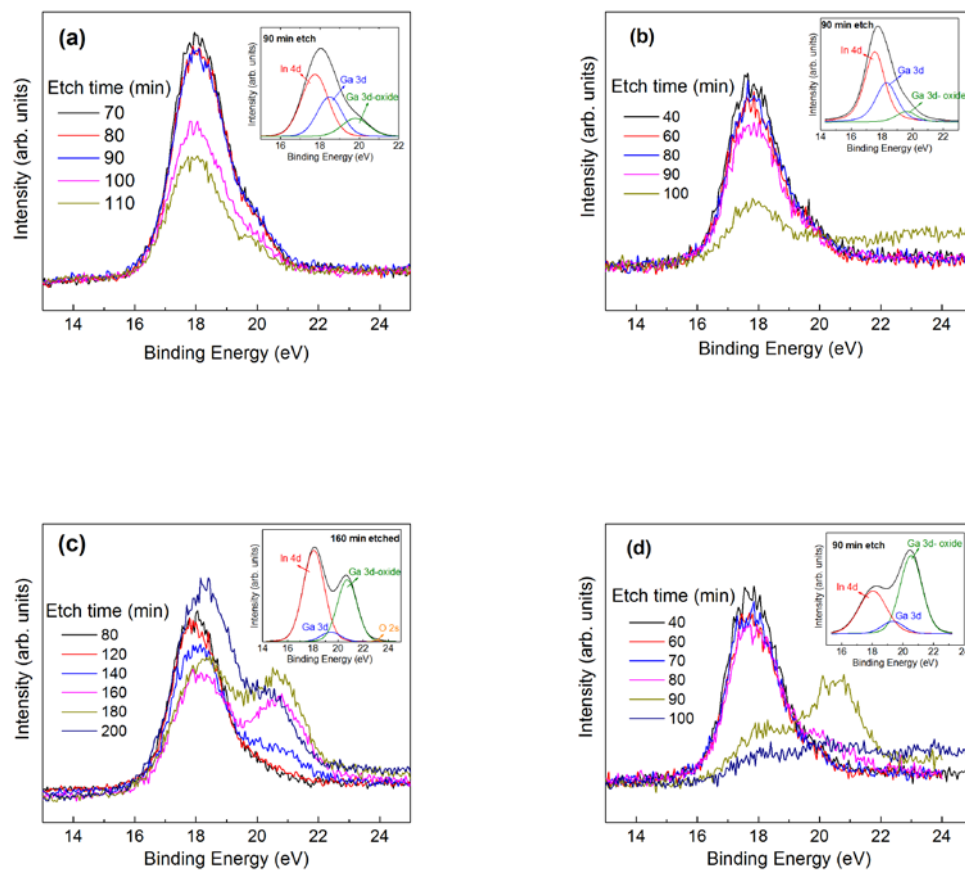


Figure 5.12: XPS analysis of Ga 3d peak of a) Mo/Cu(In,Ga)Se₂ , b) Mo/WO₃/Cu(In,Ga)Se₂ , c) ITO/Cu(In,Ga)Se₂ , and d) ITO/WO₃/Cu(In,Ga)Se₂.

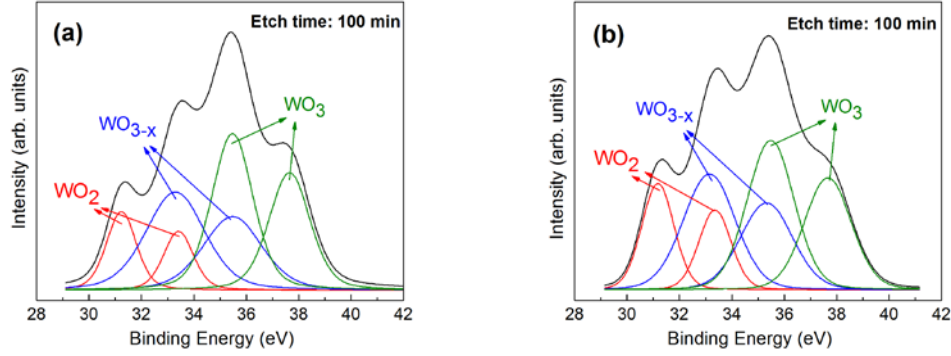


Figure 5.13: XPS analysis of W4f for a) Mo/WO₃/Cu(In,Ga)Se₂, and b) ITO/WO₃/Cu(In,Ga)Se₂.

Valence band edge energies were also obtained by analysis of the XPS spectra and used to characterize the interface band offsets, ΔE_v , using the method described in section 3.7. For this purpose, the Cu 2p, W 4f, and Sn 3d peaks were considered as the core peaks of the Cu(In,Ga)Se₂, WO₃, and ITO layers, respectively.

Figure 5.14 shows the energy band diagrams of different samples using the valence band offsets measured by XPS. The band structures of Mo/Cu(In,Ga)Se₂ and ITO/Cu(In,Ga)Se₂ samples were discussed in section 4.3; however, their plots are shown again here for comparison. Bandgap values of 1.2 eV for Cu(In,Ga)Se₂, 1.4 eV for MoSe₂ [50], 3.2 eV for WO₃ [117], and 3.4 eV for ITO were assumed for the band structure illustration. It should be noted that no effect was observed in the J-V behavior in any of the samples due to a large valence band spike caused by Ga₂O₃ (with bandgap $\sim$ 4.5 eV [181]) at the interface. Therefore, a Ga₂O₃ phase was not included in the energy band diagram plots.

For the control sample, a MoSe₂ interlayer formed during the Cu(In,Ga)Se₂ deposition, making a small valence band offset of 0.2 eV between Cu(In,Ga)Se₂ and

MoSe₂ layers consistent with the absence of a blocking contact as typically observed in devices. Adding the WO₃ layer (Figure 5.13b) prevents the formation of MoSe₂ at the interface, and a large band offset of 0.9 eV was found between the Cu(In,Ga)Se₂ and WO₃ layers. Therefore, it creates a blocking contact for the whole transport to the back electrode.

As discussed in section 4.3.3, the poor performance of the cells made on ITO may also originate from the non-ideal band structure, having a valence band offset of 0.9 eV at the ITO/Cu(In,Ga)Se₂ interface (Fig. 5.14c). Introducing the WO₃ layer at the ITO/Cu(In,Ga)Se₂ interface didn't make a noticeable change on the energy band diagram (Figure 5.14d). As a result, the primary contact still has a large valence band offset relative to the Cu(In,Ga)Se₂, and cannot improve the cell performance (Table 5.3). For the sample made on ITO-WO₃ annealed back contact, there is a valence band offset of 0.7 eV suggesting a blocking behavior for holes transporting to the back contact.

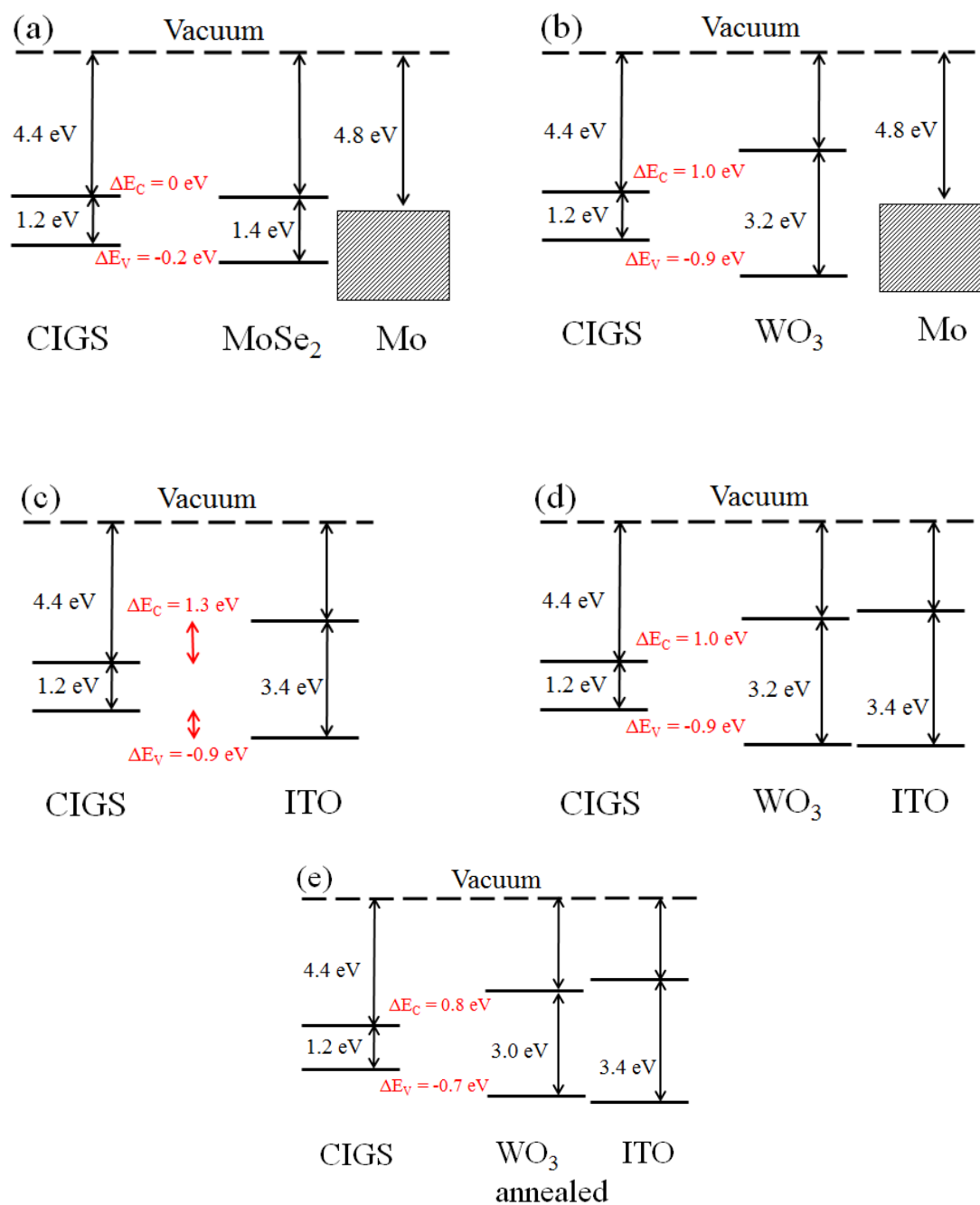


Figure 5.14: Band discontinuities between Cu(In,Ga)Se₂ and different back contacts determined from XPS analysis; a) Mo, b) Mo/WO₃, c) ITO, d) ITO/WO₃, and e) ITO/WO₃-annealed back contacts.

5.3.2 Device Properties

Fig. 5.15 shows the device properties of the cells made on the WO₃ back layers. It can be seen that the device made on the Mo-WO₃ (10nm) back layer, sample B, have a regular diode shape but with not as good as cell properties compared to the control sample made on Mo (sample A). This might be due to an undesired band alignment at the back surface ($\Delta E_V = 0.9$ eV), higher series resistance of this structure, and reduced concentration of K atoms diffusing from the soda lime glass substrate to the Cu(In,Ga)Se₂ layer. Nevertheless, the J-V profiles do not show an obvious blocking barrier.

Increasing the WO₃ thickness to 30 nm (Fig. 5.15, sample C) makes the above-mentioned issues more obvious, and a roll-over effect is seen in the J-V profile.

The efficiency of cells with an annealed WO₃ back contact was limited to ~4.5%, showing a blocking diode behavior in the forward J-V profile. This is caused by the presence of a large valence band offset of 0.7 eV at the back surface blocking the holes transport to the back contact. In addition, the inter-diffusion of ITO and WO₃ layers during the annealing might have formed new phases at the interface, deteriorating the device performance even further.

Device properties of cells made on the ITO-WO₃ stack are shown in Fig. 5.15b and also summarized in Table 5.4. The WO₃ layer couldn't enhance the cell performance with the ITO back contact. In all cases, device performance is very poor due the non-ideal band alignment at the back surface ($\Delta E_V = 0.9$ eV).

In conclusion, the device performance and band structure measurement of cells made on WO₃ suggest that it is not an ideal back contact candidate for substrate and backwall superstrate Cu(In,Ga)Se₂ solar cells. Nevertheless, they still can be applied for the frontwall superstrate devices, which will be discussed in section 7.2.

Table 5.4: Device properties of cells made on different back contacts. Valence band offsets (ΔE_V) at the back contact, determined by XPS analysis, are also presented for comparison.

Sample	Back contact	WO ₃ thickness	WO ₃ anneal (°C)	Eff. (%)	V _{OC} (mV)	J _{SC} (mA/cm ²)	FF (%)	ΔE_V (eV)
A	Mo	---	---	13.8	602	29.8	77.0	0.2
B	Mo+WO ₃	10 nm	none	10.8	606	26.3	69.1	0.9
C	Mo+WO ₃	30 nm	none	8.2	444	30.1	61.3	0.9
D	Mo+WO ₃	10 nm	400	4.3	451	24.2	39.1	0.7
E	Mo+WO ₃	30 nm	400	4.6	411	27.1	41.0	0.7
F	ITO	---	---	2.6	502	16.6	31.6	0.9
G	ITO+WO ₃	10 nm	none	3.1	584	17.4	30.3	0.7
H	ITO+WO ₃	10 nm	400	0.2	195	3.32	24.7	0.7

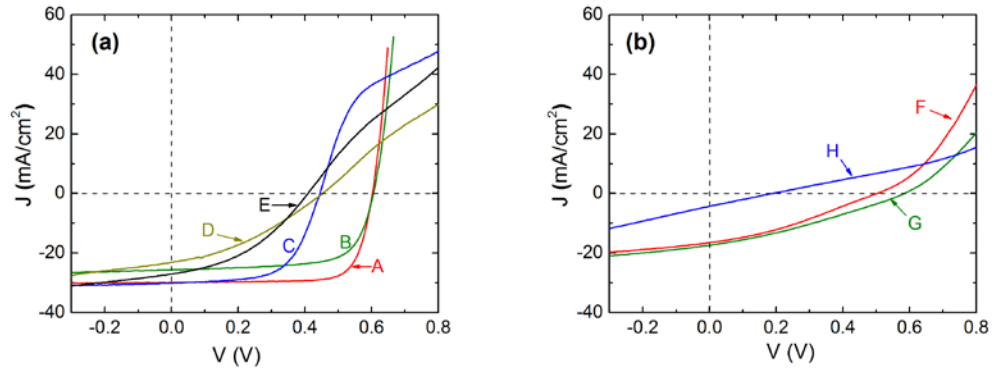


Figure 5.15: J-V curves of devices made on the WO₃ back layer with a) Mo, and b) ITO contact layers, as identified in Table 5.3.

5.3.3 Structural Properties

Figure 5.16 shows the XRD patterns of 2 μm thick Cu(In,Ga)Se₂ films deposited on the Mo, Mo-WO₃, ITO, and ITO-WO₃ back contact structures. In all cases, the chalcopyrite Cu(In,Ga)Se₂ phase was observed without any contribution

from binary or ternary phases. However, the presence of oxide layers altered the crystallographic orientation of the Cu(In,Ga)Se₂ absorber layer. As a result, the (112) to (220)/(204) peak ratios reduced from ~10 for the control sample on Mo to 0.6, 3.4, and 1.8 for the Cu(In,Ga)Se₂ films deposited on Mo/WO₃, ITO, and ITO/WO₃ layers, respectively.

SEM cross sections of the devices made on different back contacts are shown in Figure 5.17. The different layers of back contact/Cu(In,Ga)Se₂/CdS/ZnO:Al device structure are noted in the figure. It can be seen that the film deposited on the Mo back contact (Figure 5.17a) has a large grain size, on the order of 0.5 μm . Introducing the WO₃ interlayer reduced the Cu(In,Ga)Se₂ grain size (Figure 5.17b). The coverage of the WO₃ layer was uniform and no void was observed at the Cu(In,Ga)Se₂/WO₃ interface. Figs. 5.17c and 5.17d show that Cu(In,Ga)Se₂ films grown on ITO and ITO-WO₃ back layers have a much smaller grain size than films made on the Mo substrate. This may be caused by different nucleation and growth mechanisms for Cu(In,Ga)Se₂ deposited on the oxide layers (ITO or WO₃) [125]. In the case of ITO-WO₃ back contact, some adhesion issues were also observed during the CdS deposition by chemical bath deposition.

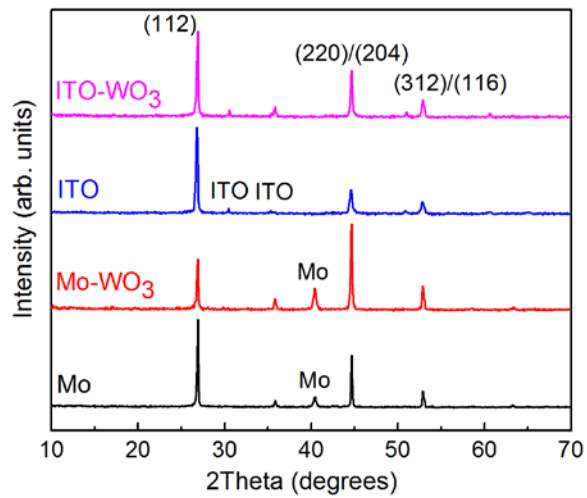


Figure 5.16: XRD pattern of the Cu(In,Ga)Se₂ deposited on Mo, Mo-WO₃ stacks, ITO, and ITO-WO₃ stacks.

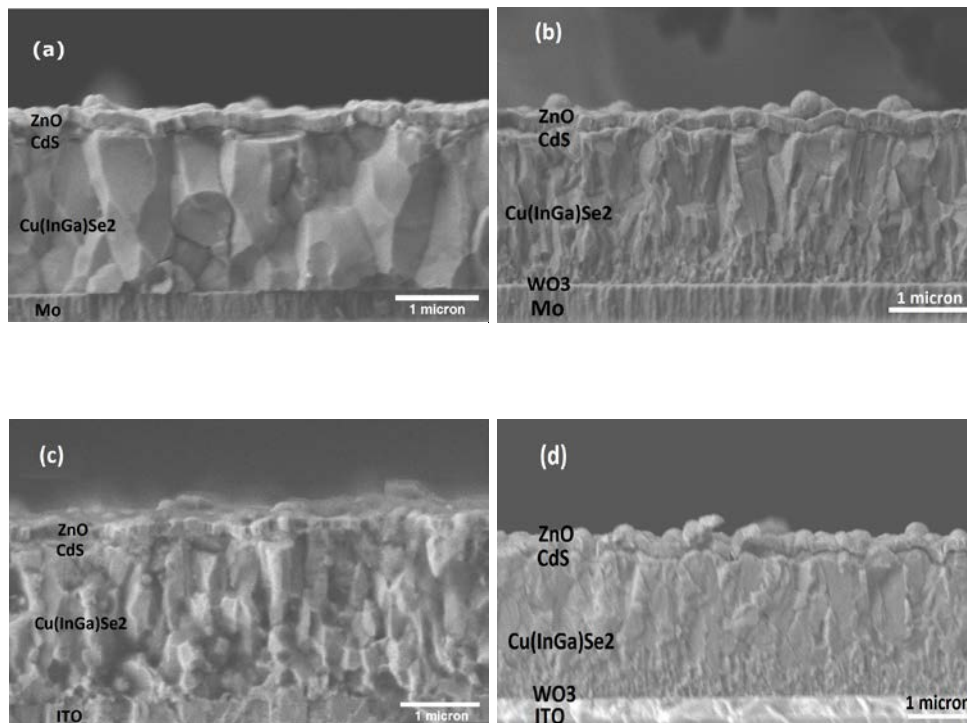


Figure 5.17: SEM cross-section of the cells made on the a) Mo, b) Mo-WO₃, c) ITO, and d) ITO-WO₃ back contacts.

Chapter 6

BACKWALL SUPERSTRATE DEVICES

6.1 Introduction

As discussed in the section 2.2.3, one approach to overcome the inter-diffusion of CdS and CuInSe₂, limiting performance of superstrate solar cells [37,38], would be implementing of a “backwall superstrate structure” that we have proposed recently [39] (see Fig. 6.1b).

In the backwall superstrate configuration, illumination is from the back surface and light is being absorbed primarily at the back of the absorber layer and not at the p-n junction. This dictates to use thin absorbers to ensure collection of the short wavelength generated carriers. However, when the absorber thickness is reduced below 1 μm , the performance of Cu(In,Ga)Se₂ devices begins to deteriorate due to incomplete optical absorption leading to lower J_{SC} [19]. This can be mitigated by adding a front reflector (i.e. Ag) after all other device processing.

In addition, backwall superstrate configuration necessitates application of a wide band gap transparent back contact in the structure. It was shown in chapters 4 and 5 that MoO₃ and WO₃ can be considered as the primary back contacts for the backwall superstrate cells. They are found to be thermodynamically stable under Cu(In,Ga)Se₂ growth conditions with Se vapor; however, band structure measurements revealed the valence band offsets of 0.1 eV (for MoO₃) and 0.9 eV (for WO₃) between contacts and Cu(In,Ga)Se₂. Therefore, only MoO₃ forms a ohmic contact with Cu(In,Ga)Se₂, and was considered for making backwall devices.

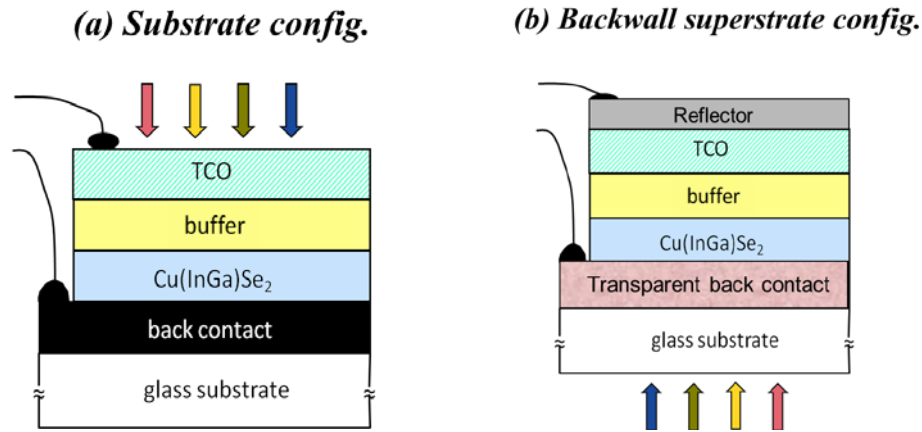


Figure 6.1: Schematic illustration of (a) substrate configuration and (b) backwall superstrate configuration.

6.2 Device Properties

Backwall devices had the structure of Glass/ITO/MoO₃/Cu(In,Ga)Se₂/CdS/i-ZnO/Ag. Control substrate devices were deposited in the same Cu(In,Ga)Se₂ runs as the backwall devices to allow for comparison of devices with the two different configurations produced under the same conditions. The control samples were of the structure Glass/Mo/Cu(In,Ga)Se₂/CdS/i-ZnO/ITO/Ni-Al grid. The absorber thickness was varied from 0.1 μm to 1 μm in order to find the optimum condition for the backwall cells.

Fig. 6.2 shows the device parameters open circuit voltage (V_{OC}), short circuit current (J_{SC}), fill factor (FF) and efficiency determined by JV measurement. The substrate control samples perform better than the backwall devices on all parameters for thick absorbers above 0.7 μm . The poor performance of the backwall devices with $d_{CIGS} > 0.7 \mu\text{m}$ can be explained by the fact that the majority of the light is absorbed at the back of the absorber outside the space charge region. The absence of a built-in field in this part of the absorber reduces the chance of separation and collection of the

generated charge carriers. As a result light-generated charge carriers are more likely to recombine leading to the poor performance observed for all device parameters. On the other hand, with $0.1 \leq d_{\text{CIGS}} \leq 0.5 \mu\text{m}$ the backwall devices are superior to the control samples. The advantage of the backwall configuration is especially reflected in J_{SC} with an improvement of 100% observed for the absorber with $d_{\text{CIGS}} \approx 0.11 \mu\text{m}$ and 35% enhancement for the $0.43 \mu\text{m}$ thick absorber. The V_{OC} is similarly higher for the backwall devices compared to the control samples. The improvement is, however, smaller with an increase of 12% for the $0.12 \mu\text{m}$ thick absorber and 8% for $d_{\text{CIGS}} \approx 0.43 \mu\text{m}$. A decrease in V_{OC} with reduced absorber thickness is observed for both control and backwall devices. This could be related to imperfect passivation of the interface between the back contact and the Cu(In,Ga)Se_2 absorber which is expected to play a larger role for thinner absorbers [21] or poorer electronic quality of the thinnest Cu(In,Ga)Se_2 films.

The overall benefit of the backwall structure for thin absorbers is reflected clearly in the efficiency of the devices. For the very thin absorber of $0.12 \mu\text{m}$ the control sample produced a device with an efficiency of only 1.6% whereas the backwall device had a significantly higher efficiency of 5.1%. At the absorber thickness of $0.43 \mu\text{m}$, the benefit of the backwall configuration remains clear since the control sample had an efficiency of 6.6% while the backwall device achieved an efficiency of 8.3%. These results clearly demonstrate the potential of this device structure.

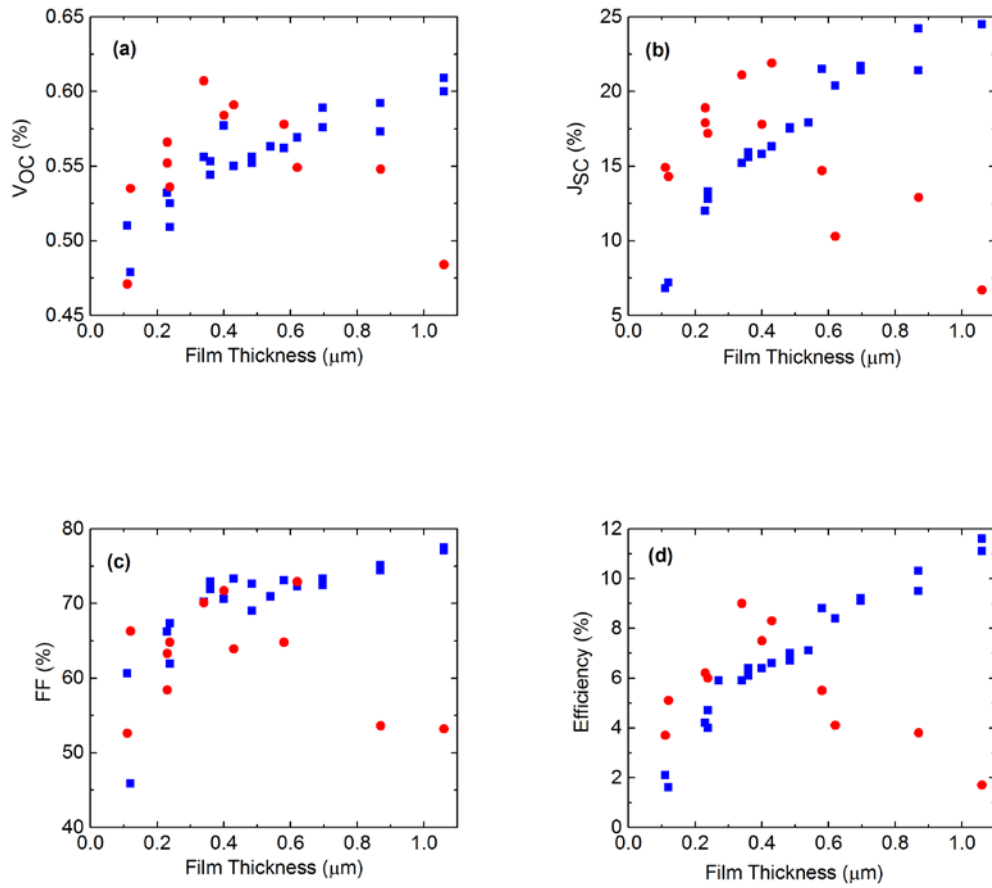


Figure 6.2: Device parameters as a function of absorber thickness. Results obtained with backwall devices are shown with circles (red) and control samples with substrate configuration are shown with square symbols (blue).

6.3 Structural Properties

Figure 6.3 shows the XRD analysis of $\text{Cu}(\text{In,Ga})\text{Se}_2$ films with varying thicknesses deposited on ITO- MoO_3 contact layer. In all cases, the chalcopyrite $\text{Cu}(\text{In,Ga})\text{Se}_2$ phase was formed without any contribution, detectable by XRD, from binary or ternary phases. However, the presence of oxide layers has affected the crystallographic orientation of the $\text{Cu}(\text{In,Ga})\text{Se}_2$ absorber layer. This was more noticeable for films with low thickness $d_{\text{CIGS}} \approx 0.2 \mu\text{m}$ were (220)/(204) preferential

orientation was observed. Increasing the film thicknesses to $d_{\text{CIGS}} > 0.5 \mu\text{m}$ resulted in a gradual change to (112) preferential orientation, though the (112) to (220)/(204) peak ratios are less than 2. No correlation between the film orientation and device properties was found in either cases.

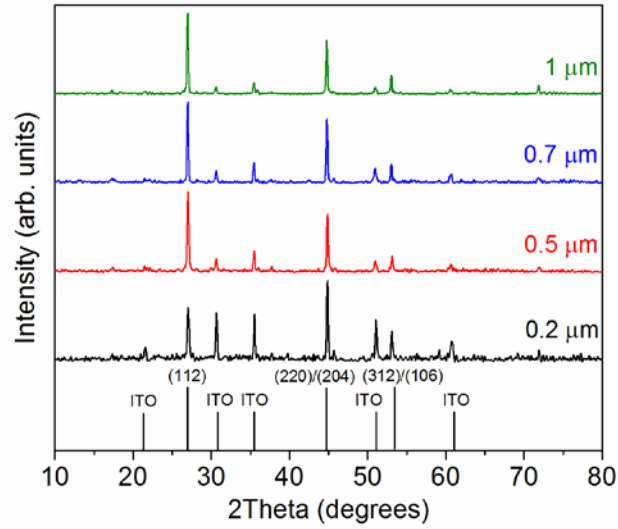


Figure 6.3: XRD profiles of Cu(In,Ga)Se₂ films with different thickness deposited on ITO-MoO₃.

6.4 Effect of Ag Alloying

To further enhance the performance of backwall devices, Ag-alloying of the absorber layer was considered. Substitution of Cu with Ag in Cu(In,Ga)Se₂ films offers specific advantages such as increasing the optical bandgap and decreasing the melting point of the alloy which may allow films to be deposited with lower defect density than other Cu(In,Ga)Se₂ alloys [207]. Evidence of this has been reported with improved device performance [208] and sharper band tails [209].

Ag alloyed absorber layers were made by multi-source elemental evaporation at a substrate temperature of 550°C. The ratios $\text{Ga}/(\text{Ga}+\text{In})=0.3$ and $\text{Ag}/(\text{Ag}+\text{Cu})=0.6$ resulting in an absorber layer with bandgap of 1.3 eV.

Figure 6.4 shows the device parameters of the backwall devices for the thickness range 0.1-1.1 μm . Best results are also summarized in Table 6.1. It was shown in section 6.2 that with $0.1 \leq d_{\text{CIGS}} \leq 0.5 \mu\text{m}$ the backwall devices are superior to the control samples [39]. An 8.3% efficient cell for a $d_{\text{CIGS}} \approx 0.4 \mu\text{m}$ was demonstrated, noted as CIGS-1 in Table 6.1.

The performance is improved further by increasing the deposition temperature of the absorber layer (570 °C) resulting in a 9% efficiency cell with $d_{\text{CIGS}} \approx 0.4 \mu\text{m}$ (CIGS-2 in Table 6.1). Adding Ag further enhanced the performance of the backwall cells and a 9.7% efficient device was achieved with $V_{\text{OC}} = 0.64 \text{ V}$ (Table 6.1).

Figure 6.4 shows improved V_{OC} , J_{SC} , and efficiency for ACIGS compared to CIGS, but a lower fill factor.

Table 6.1: Device parameters of best cells

	d μm	V_{OC} V	J_{SC} mA/cm^2	FF %	Eff. %
CIGS-1 Control	0.4	0.55	16.3	73.3	6.6
CIGS-1 Backwall	0.4	0.59	21.9	63.9	8.3
CIGS-2 Control	0.3	0.56	15.2	70.2	5.9
CIGS-2 Backwall	0.3	0.61	21.1	70.1	9.0
ACIGS Control	0.3	0.50	15.2	46.2	3.6
ACIGS Backwall	0.3	0.64	23.6	63.8	9.7

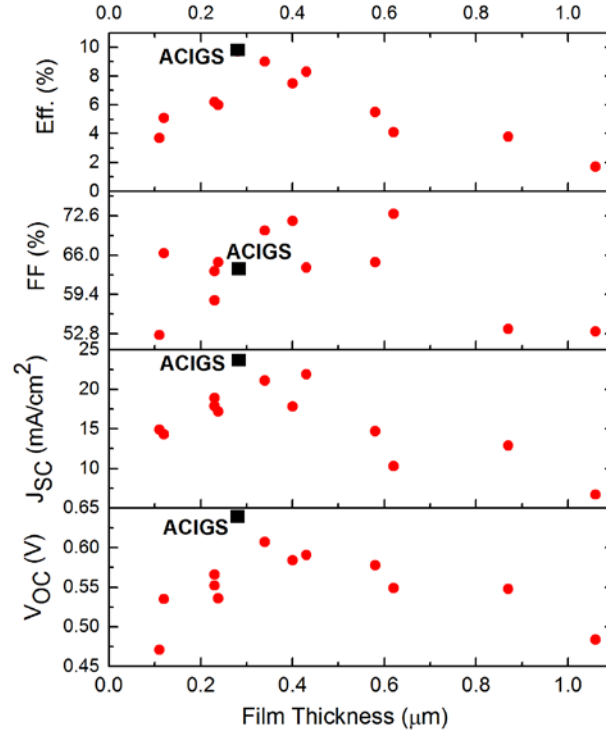


Figure 6.4: Device parameters of backwall cells as a function of absorber thickness. CIGS and ACIGS devices are shown with dots and squares, respectively. All films have the $\text{Ga}/(\text{Ga}+\text{In}) \approx 0.3$.

The J-V and QE profiles of the ACIGS backwall superstrate cell in comparison with the CIGS cell are shown in Fig. 6.5. QE profiles show that the ACIGS devices have a higher response over the whole spectral range. Lower fill factor of the ACIGS cells might be partly due to voltage dependent collection, as shown in the QE of backwall cells obtained at 0 and -0.5 V (Fig. 6.5b). There is a voltage dependent in the short wavelength range, as the negative applied potential improves collection of the blue part of the spectrum in the backwall devices. There are several possible mechanisms for a voltage dependent photo current including variations with voltage of

the space charge region width, interface recombination, photo current barrier and low diffusion length [5]. Our group has shown previously [207] that Ag-alloying reduces the voltage dependent collection of typical substrate devices, which is in contrast with our current results.

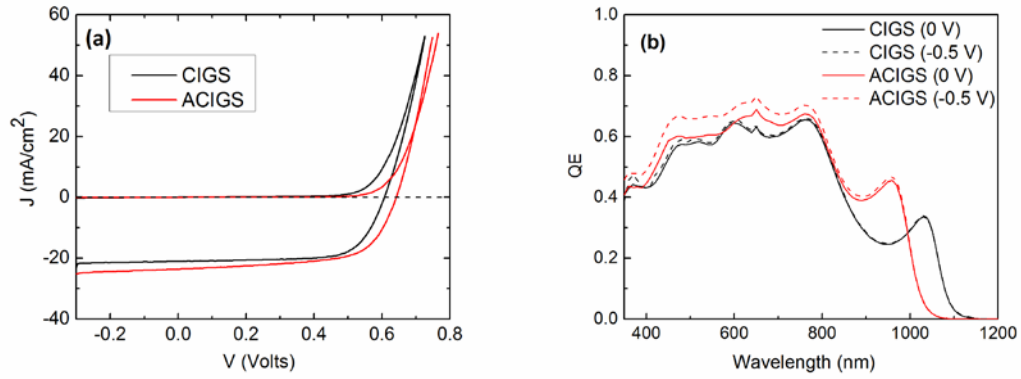


Figure 6.5: a) J-V profile and b) QE profile of backwall devices for the CIGS and ACIGS cells for $d \approx 0.3 \mu\text{m}$, $\text{Ag}/(\text{Ag}+\text{Cu})=0.67$, and $\text{Ga}/(\text{Ga}+\text{In})=0.30$. Solid lines and dashed lines show QE profiles obtained under dark condition at 0 V and -0.5 V, respectively.

SEM cross sections of the backwall devices made with CIGS and ACIGS absorber layer are shown in Figure 6.6. The different layers of ITO/MoO₃/absorber/CdS/ZnO:Al/Ag device structure are noted in the figure. It can be seen that the CIGS device (Figure 6.6a) has a very small grain size, much lower than typical CIGS devices (made on Mo substrate). This may be caused either because of very low thickness of the film or by different nucleation and growth mechanisms for Cu(In,Ga)Se₂ deposited on the oxide layers (ITO or MoO₃) [125]. Introducing the moderate amount of Ag increased the Cu(In,Ga)Se₂ grain size (Figure 6.6b).

Delamination of the Ag layer is likely to have happened during the sample preparation for the SEM analysis.

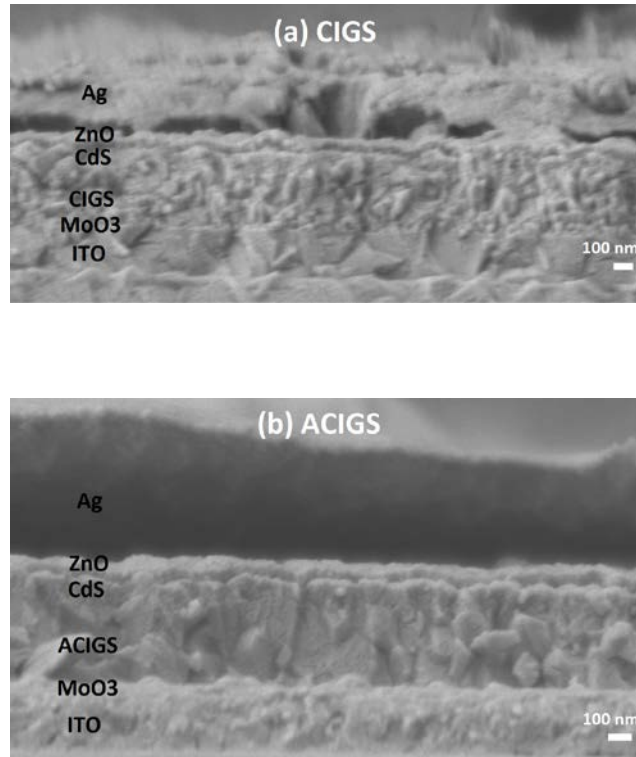


Figure 6.6: SEM images of backwall devices for the (a) CIGS and (b) ACIGS cells for $d \approx 0.4 \mu\text{m}$.

The interfaces between the absorber layer and the back contacts were characterized by XPS measurements. High resolution scans of the Ga 3d region (Figure 6.7a) show a shoulder at high energy with its highest intensity at the Cu(In,Ga)Se₂/MoO₃ interface. Peak deconvolution of the Ga 3d area suggests that the satellite peak is due to the Ga₂O₃ phase [180] (Figure 6.7a). Formation of Ga₂O₃ at the interface of Cu(In,Ga)Se₂-TCO's has been reported previously [38,68,69].

Fig. 6.7b shows the XPS scans of Ga3d region for (Ag,Cu)(In,Ga)Se₂/MoO₃ interface. It can be seen that the intensity of the satellite peak is significantly decreased, suggesting much lower amount of Ga₂O₃ phase at the interface. This can be explained by the fact that Ag-alloyed films are more stable than the Cu-alloyed counterparts (Table 6.2). Therefore, the reaction of Ga with the oxide phase at the back surface is diminished, resulting in reduced amount of Ga₂O₃ phase at the interface (Fig. 6.7b).

Table 6.2: Gibbs free energy (at 298 K) of ternary Chalcogenides [210].

Compound	Gibbs free energy (kJ/mol)
CuInSe ₂	-201
AgInSe ₂	-236
CuGaSe ₂	-313
AgGaSe ₂	-442

Parameters that might contribute to better overall performance of the ACIGS absorber include:

- Adding Ag decreases the melting point of the alloy which may allow films to be deposited with bigger grain size and lower defect density than other Cu(In,Ga)Se₂ alloys.
- Ag-alloying causes a down shift of the valence band edge of the absorber layer [211]. Therefore, a better band alignment, with lower barrier height, might have been achieved at the back surface.

Ag-alloyed absorber layers (AgGaSe₂ and AgInSe₂) have a more negative Gibbs free energy of formation and are therefore more stable than Cu-alloyed

counterparts (CuGaSe_2 and CuInSe_2) [113]. Therefore, the formation of Ga_2O_3 phase, with undesired band alignment, at the interface would be remarkably limited, as confirmed by XPS analysis.

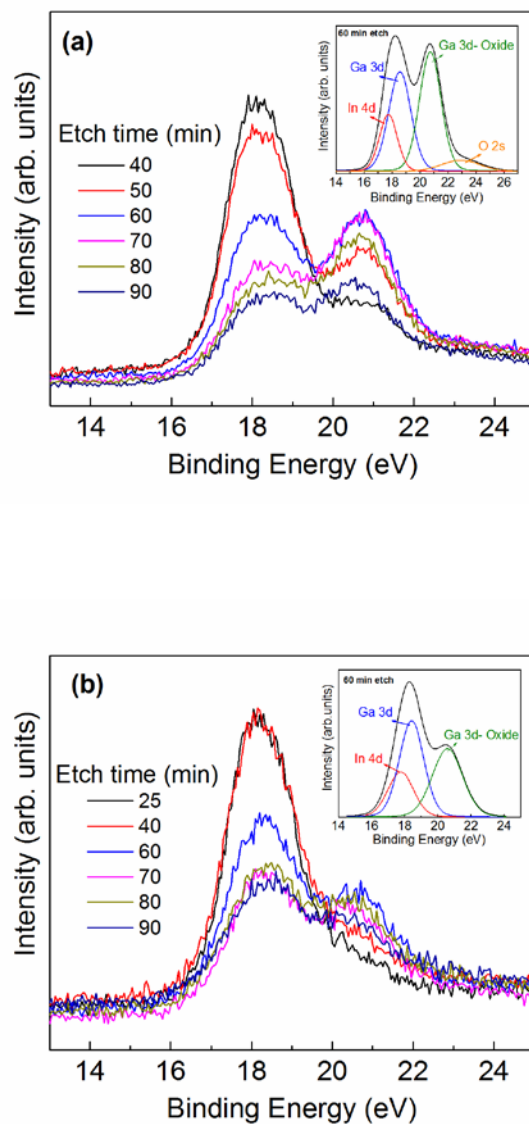


Figure 6.7: XPS analysis of Ga 3d peak at the interface of a) $\text{MoO}_3/\text{Cu}(\text{In,Ga})\text{Se}_2$, and b) $\text{MoO}_3/(\text{Ag,Cu})(\text{In,Ga})\text{Se}_2$.

Chapter 7

EFFECT OF Ag ALLOYING ON THE PROPERTIES OF Cu(In,Ga)Se₂ FILMS

7.1 Surface Characterization of (Ag,Cu)(In,Ga)Se₂ Films

7.1.1 Introduction

Substitution of Cu with Ag in Cu(In,Ga)Se₂ films offers specific advantages such as increasing the optical bandgap and decreasing the melting point of the alloy which may allow films to be deposited with lower defect density than other Cu(In,Ga)Se₂ alloys [207]. Evidence of this has been reported with improved device performance [208] and sharper band tails [209]. The improved performance of backwall devices made with (Ag,Cu)(In,Ga)Se₂ absorber layer supports this idea (see section 6.4).

Investigations on the surface properties of Ag-alloyed CuInSe₂-based films are limited. Since the surface of the absorber layer is where the junction forms in substrate and backwall superstrate solar cells, its characteristics may highly influence the electrical properties of the device and is of importance to study.

This chapter will present characterization of the surface properties of (Ag,Cu)(In,Ga)Se₂ films with a broad range of compositions using glancing incidence x-ray diffraction (GIXRD) and x-ray photoelectron spectroscopy (XPS) to elucidate the depth variation in composition and structure of films deposited by elemental co-evaporation. The surface measurements are used in conjunction with symmetric x-ray diffraction (XRD) and energy dispersive x-ray spectroscopy (EDS) that determine more bulk film properties.

7.1.2 Structural Properties

Figure 7.1 shows the symmetric XRD pattern of a (Ag,Cu)(In,Ga)Se₂ film with $x \equiv \text{Ga}/(\text{Ga}+\text{In}) = 0.75$ and $w \equiv \text{Ag}/(\text{Ag}+\text{Cu}) = 0.78$. The (Ag,Cu)(In,Ga)Se₂ is highly (112) oriented, and the peak positions are consistent with the bulk composition from EDS. This was typical for all (Ag,Cu)(In,Ga)Se₂ films, independent of composition.

However, there is a high-angle satellite reflection on the (112) peak which is marked with an arrow in the high resolution XRD pattern in Fig. 7.2. The peak at $2\theta = 27.6^\circ$ does not match any available diffraction cards of International Center for Diffraction Data (ICDD) for (Ag,Cu)(In,Ga)Se₂ or sub-set binary phases or elements. In particular, it cannot be attributed to the (Ag,Cu)(In,Ga)Se₂ (103) peak which is seen at $2\theta = 28.0^\circ$. Previously, the presence of a minor secondary phase was reported beside the (112) chalcopyrite phase in the bulk of an (Ag,Cu)(In,Ga)Se₂ film with the composition of $x = 0.5$ and $w = 0.76$, but it was not attributed to any pattern of chalcopyrite/ordered phases available in the literature [212].

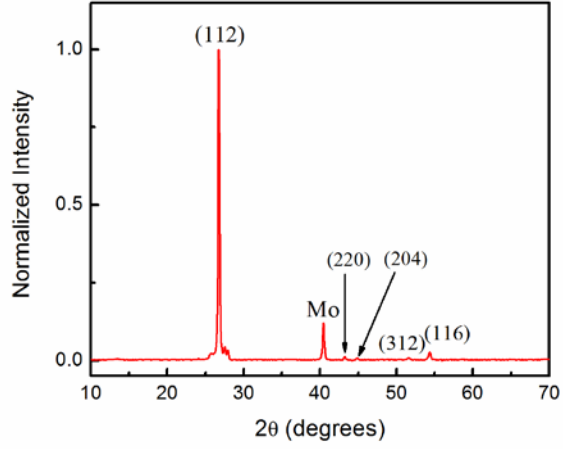


Figure 7.1: Symmetric XRD pattern of a $(\text{Ag,Cu})(\text{In,Ga})\text{Se}_2$ film with $x = 0.75$ and $w = 0.78$

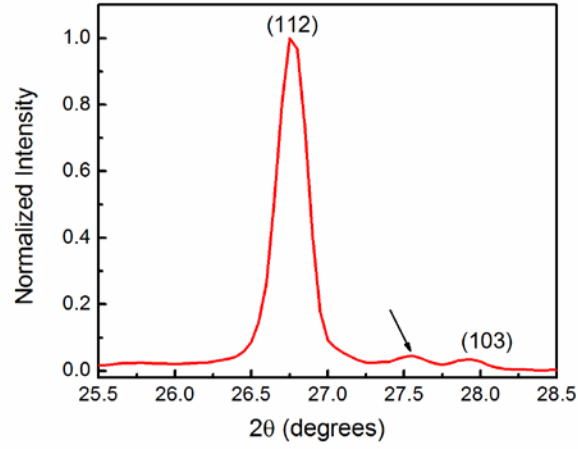


Figure 7.2: High resolution symmetric XRD pattern of a $(\text{Ag,Cu})(\text{In,Ga})\text{Se}_2$ film with $x = 0.75$ and $w = 0.78$

The satellite peak is seen more clearly in the GIXRD patterns at different incident angles shown in Figure 7.3 for the same film. The peak has stronger intensity

with a shallower incident angle indicating that its origin is closer to the surface. The position of the (112) chalcopyrite peak at $2\theta = 26.8^\circ$ is independent of sample depth and the peak broadens with incident angle due to x-ray refraction at small angles and surface roughness [213].

In addition to the peak in Figures 7.2 and 7.3, a similar set of satellite peaks were observed on the high 2θ side of other chalcopyrite peaks, which are shown by arrows in Figure 7.4.

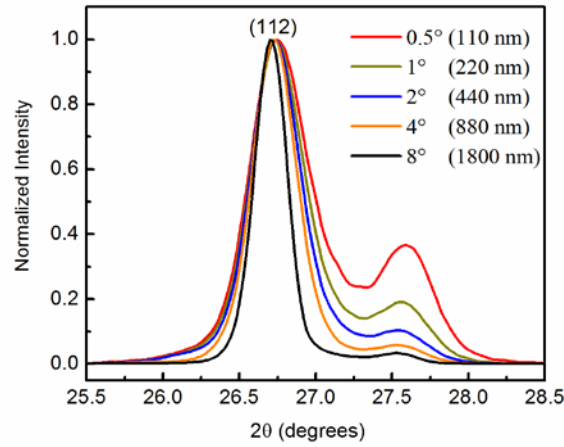


Figure 7.3: GIXRD pattern of the (112) peak (Ag,Cu)(In,Ga)Se₂ film with $x = 0.75$ and $w = 0.78$ at different incidence angles with calculated sampling depth

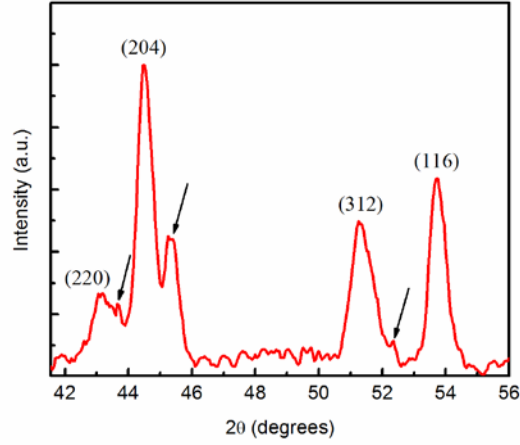


Figure 7.4: GIXRD pattern of an (Ag,Cu)(In,Ga)Se₂ film with $x = 0.75$ and $w = 0.78$. The incident angle was 0.5° corresponding to a penetration depth of 110 nm.

Figures 7.5a and 7.5b show the GIXRD patterns at 0.5° incident angle for films with different x and w ratios. In Figure 7.5a, the samples have $x = 0.64$ and w varied from 0 to 1. The secondary peak appears only at high Ag concentration ($w = 0.74$ and 1) and the position of the peak changes negligibly with the amount of Ag.

In Figure 7.5b, w is held constant at 0.74, at which the secondary phase has the strongest intensity, and x is varied from $0 \leq x \leq 1$. The secondary peak is observed with $w > 0.5$ but not in the Ag(In,Ga)Se₂ sample. The peak shifts to higher 2θ with increasing Ga. Therefore the following conditions cause the secondary peak to be observed:

- High Ag concentration: $w > 0.5$
- Ga concentrations: $0.5 < x < 1$

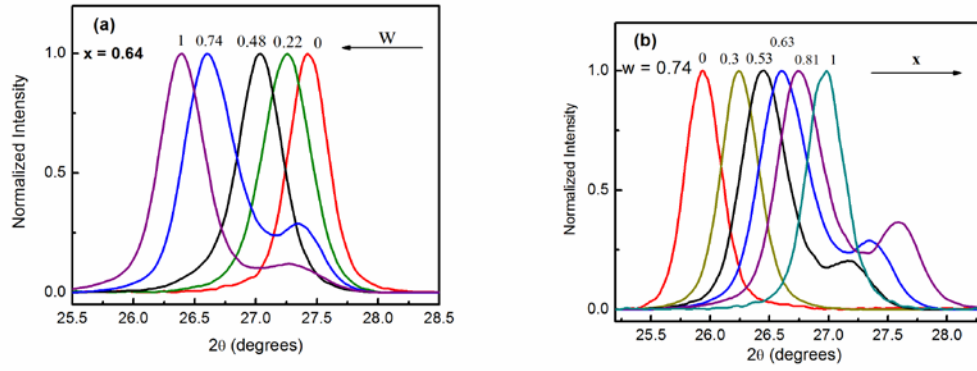


Figure 7.5: Effect of varying Ag with $x = 0.64$ (a) and varying Ga with $w = 0.74$ (b) content on the (112) and satellite peaks. The incident angle was 0.5° corresponding to a calculated penetration depth of 110 nm.

The consistent appearance of peaks at lower d-spacing than the chalcopyrite peaks suggests the presence of a phase having related crystal structure with a smaller lattice. Previous studies on CuInSe_2 film structure have shown the presence of different ordered defect compounds (ODC) phases which typically segregate near the surface [10,53–55]. These had chalcopyrite structure with a structurally ordered insertion of intrinsic defects [11].

In Table 7.1, the differences between the lattice parameter of peaks from available ICDD files of chalcopyrite and $\text{I}_1\text{III}_3\text{VI}_5$ or $\text{I}_1\text{III}_5\text{VI}_8$ ODCs are given. In each case, the inter-plane spacing (d) has been calculated using Bragg's equation ($n\lambda = 2d\sin\theta$) where the diffraction angle (θ) is either determined from the ICDD database [214] or measured. Afterwards, lattice parameters of the crystal were determined using the standard equation for the tetragonal lattice:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (1)$$

where hkl's are miller indices of the corresponding plane group, a and c are lattice parameters. For simplicity, the c/a ratio is assumed to be 2 for all samples and the displacement of Se in the unit cell is not considered here.

As shown in Figure 7.6, the difference between the chalcopyrite peaks and unknown satellite peaks lie in the range between the calculated values for CuGa_5Se_8 and AgIn_5Se_8 . Although there is no ICDD card available for the $\text{I}_1\text{III}_3\text{VI}_5$ phase of Ag compounds, the $\text{I}_1\text{III}_3\text{VI}_5$ phase would be expected to give much larger peak shifts from the chalcopyrite phase especially with higher x values. Therefore, it is proposed that the unknown reflections are consistent with the crystal structure of the $\text{I}_1\text{III}_5\text{VI}_8$ ODC phase.

Table 7.1: The calculated [214] or measured difference Δa between the lattice parameter of the chalcopyrite phase and the corresponding ODC phase.

Materials		Δa (Å)
<i>Calculated</i>		
$\text{CuInSe}_2 - \text{CuIn}_3\text{Se}_5$		0.037
$\text{CuGaSe}_2 - \text{CuGa}_3\text{Se}_5$		0.890
$\text{CuGaSe}_2 - \text{CuGa}_5\text{Se}_8$		0.102
$\text{AgInSe}_2 - \text{AgIn}_5\text{Se}_8$		0.218
<i>Measured</i>		
w = 0.74	x = 0.53	0.154
	x = 0.63	0.155
	x = 0.81	0.174
x = 0.64	w = 0.74	0.155
	w = 1	0.194

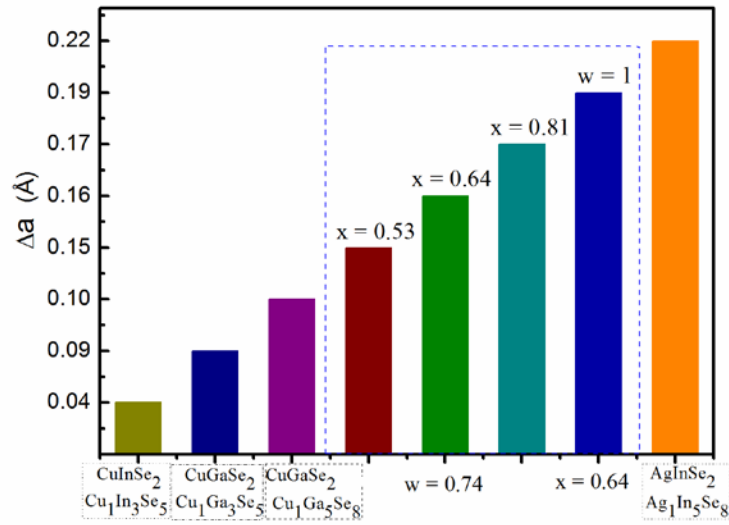


Figure 7.6: The difference between lattice parameter of the chalcopyrite peaks and unknown satellite peaks for films with different x and w values.

Further confirmation of the existence of the ODC phase on the surface was obtained from high resolution GIXRD scans. These scans indicated the presence of low structure factor reflections in the I-42d space group (chalcopyrite) but more intense reflections in ODC phases such as AgIn_5Se_8 in the P-42m space group.

Reflections such as (102), (202), (114), and (301) were detected at Bragg angles expected for the ODC phases having the composition measured for the primary chalcopyrite phase. Table 7.2 shows these diffraction planes of the studied sample with $x = 0.64$ and $w = 0.74$ along with the corresponding diffraction angles at which the peak would be expected. It can be seen that all of the measured peaks are present in the ICDD card of AgIn_5Se_8 , but are not present or have very low intensity in the card of AgInSe_2 .

Table 7.2: Comparing the GIXRD pattern of sample with $x = 0.64$ and $w = 0.74$ with available ICDD cards¹

Diffraction plane	Measured 2θ	Calculated 2θ	Position (2θ) & Intensity ²	
			AgIn_5Se_8	AgInSe_2
102	22.20	22.25	21.7, 54m	---
202	35.55	35.53	34.6, 59m	33.1, 1
211	36.30	36.44	35.5, 101	33.7, 1
114	39.3	39.06	37.9, 38m	---
301	49.05	48.84	47.7, 34	45.2, 1

¹ m $\equiv$ minor intensity on ICDD data cards.

² The (112) peak had the highest intensity of with intensity full scale of 1000.

7.1.3 Surface Properties

Figures 7.7 show XPS depth profiles on four samples with $x = 0.64$ and $w = 0$, 0.22, 0.74, and 1. The Ar ion etch rate was calibrated using a $\text{Ta}_2\text{O}_5/\text{Ta}$ foil sample and found to be about 1 nm/min. For the film samples of this study this rate was applied as a depth etch rate. Elemental XPS composition of the deepest data point was

normalized with respect to the EDS bulk composition [215]. The effect of potential preferential sputtering was corrected by modification of relative sensitivity factors [135] using the EDS normalization and was applied to all elements. Abou-Ras et al. [216] have applied similar conditions (2 kV ion energy with a 2 μ A beam current) for sputter depth profiling of Cu(In,Ga)Se₂ films and obtained good resolution depth profiles without noticeable surface roughening.

The variation of the (Ag+Cu)/Se ratio is shown in Figure 7.7. All samples show group I deficiency near the surface. The surfaces of the Cu(In,Ga)Se₂ and Ag(In,Ga)Se₂ samples ($w = 0$ and 1) have a (Ag+Cu)/Se ratio close to 0.3, while (Ag+Cu)/Se = 0.15 – 0.2 for the samples with $w = 0.22$ and $w = 0.74$.

In Figure 7.8, the (Ag+Cu)/(Ga+In) ratios are shown for the same four films. All samples are group I (Ag+Cu) deficient near the surface, and the deficiency of the samples with $w = 0$ and 1 is less than the samples with $w = 0.22$ and 0.74 which have (Ag+Cu)/(Ga+In) ratios in the range of 0.2 – 0.3, within the surface region characterized. Thus, XPS results confirm that, for all samples, low group I content occurs at the surface, which is consistent with the existence of an ODC surface phase and similar to what has been reported at the surface of Cu(In,Ga)Se₂ films [10].

The creation of such defect phases accommodates the (Ag+Cu) deficiency in (Ag,Cu)(In,Ga)Se₂ films through modification of crystallographic ordering, in a manner analogous to that in the CuInSe₂ system [10], in which various ODC phases such as Cu₂In₄Se₇, CuIn₃Se₅, and CuIn₅Se₈ were predicted.

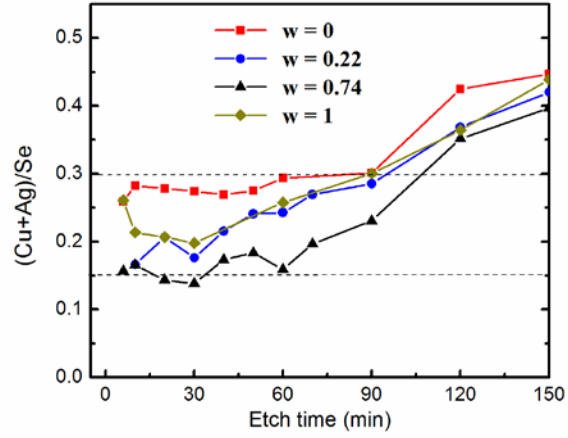


Figure 7.7: XPS depth profile of (Cu+Ag)/Se for alloys with $x = 0.64$ and various w .

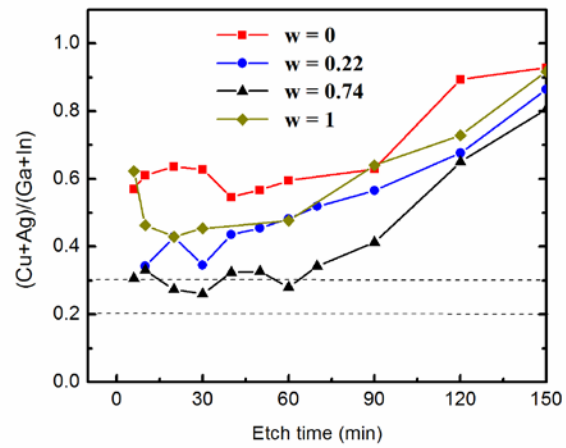


Figure 7.8: XPS depth profile of (Cu+Ag)/(In+Ga) for alloys with $x = 0.64$ and various w .

Figure 7.9 shows the variation of w values through the film for the samples with $w = 0.22$ and 0.74 . For both films, the surface region is relatively Ag-rich compared to the bulk.

Comparing the XRD and XPS results reveals that the $(\text{Ag,Cu})(\text{In,Ga})\text{Se}_2$ films with $0.5 < w < 1$ and $0.5 < x < 1$ have the secondary phase with highly group I deficiency near the surface. In particular, the sample with $w = 0.74$ is found to have $(\text{Ag}+\text{Cu})/\text{Se} \approx 0.15$ and $(\text{Cu}+\text{Ag})/(\text{Ga}+\text{In}) \approx 0.2$ consistent with the composition of $(\text{Ag,Cu})(\text{In,Ga})_5\text{Se}_8$ compound. Therefore, it is proposed that a surface phase of $(\text{Ag,Cu})(\text{In,Ga})_5\text{Se}_8$ is formed because it is kinetically favorable. On the other hand, films with no Ag ($w = 0$) and no Cu ($w = 1$) have $(\text{Ag}+\text{Cu})/\text{Se} \approx 0.25$ and $(\text{Ag}+\text{Cu})/(\text{Ga}+\text{In}) \approx 0.6$ at the surface and they also match with the composition of 1:3:5 ODC phases. However, those phases apparently have not crystallized well and therefore are not seen in the XRD patterns.

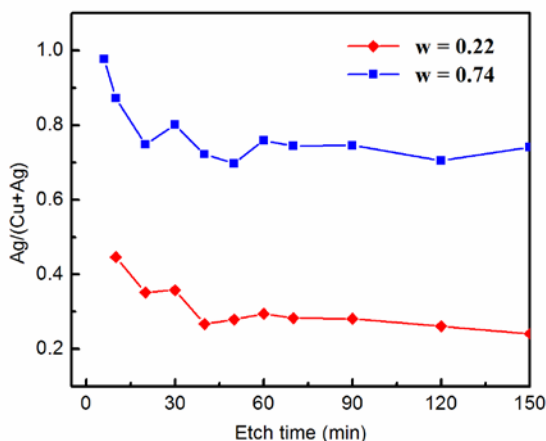


Figure 7.9: XPS depth profile of w for alloys with bulk composition of $x = 0.64$ and $w = 0.22$ and 0.74 .

Although the surface of all (Ag,Cu)(In,Ga)Se₂ films was found to be group I deficient, similar to the Cu(In,Ga)Se₂ alloys, the following results are important to notice:

- A secondary phase with lower d-spacing than the chalcopyrite phase was observed at the surface of films with $w > 0.5$ and $0.5 \leq x < 1$ by GIXRD measurements.
- The reflections in near-surface layers are in good agreement with the available ICDD cards of the AgIn₅Se₈ ODC phase, with changes in the position due to the difference in layer composition.
- XPS results revealed that all samples have low (Ag+Cu)/Se and (Ag+Cu)/(Ga+In) ratios near the surface, consistent with the formation of an ordered defect compound. The ratios are close to (Ag,Cu)(In,Ga)₅Se₈ for the samples with $0 < w < 1$.
- The near-surface regions of (Ag,Cu)(In,Ga)Se₂ contain a higher Ag/(Ag+Cu) ratio than the bulk and Ag(In,Ga)Se₂ film contains excess Ag near the surface.

7.2 Application of MoO₃ and WO₃ Transparent Contacts for Frontwall Superstrate (Ag,Cu)(In,Ga)Se₂ Solar Cells

7.2.1 Introduction

Frontwall superstrate solar cells can potentially be used as the top cell of tandem devices thereby lowering manufacturing costs with increased efficiency. This requires a top cell with wide bandgap [64]. One way, would be Ag alloying of the absorber layer to make wide band gap (Ag,Cu)(In,Ga)Se₂ alloy. Alloying the absorber with Ag not only increases the bandgap, but also decreases the melting point of the alloy [217] which may allow films to be deposited with lower defect density than

other Cu(In,Ga)Se₂ alloys [207]. Still, an ohmic transparent back contact is required enabling the low energy portion of the spectrum to be reach the bottom cell.

It was shown in chapters 4 and 5 that MoO₃ and WO₃ can be viable candidates for the primary back contact of CuInSe₂-based thin film solar cells [3,4]. In this section, the interface properties of ACIGS films with MoO₃ and WO₃ contacts were studied using X-ray photoelectron spectroscopy. Effects of Ag-alloying on the valence band discontinuities are addressed since the valence band offset (ΔE_V) is equivalent to the barrier height for the back contact in devices. Mo, widely used for the back contact in CuInSe₂-based thin film solar cells, is also characterized for comparison.

For this purpose, 30 nm MoO₃ and WO₃ films were deposited on the ACIGS layers by reactive rf sputtering of Mo and W targets. For comparison, Mo films were also deposited using electron-beam evaporation. Figure 7.10 shows the cell structure used for the XPS analysis of ACIGS/back contact interface, in which the back contact is deposited after the absorber layer.

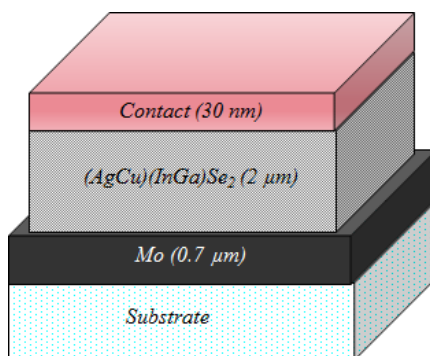


Figure 7.10: The cell structure used for the XPS analysis.

7.2.2 Valence Band Alignment

Our previous studies on the effects of sputtering conditions on the structural, optical, and surface properties of MoO₃ (chapter 4) and WO₃ (chapter 5) films [116,117] shows that their compositions are nearly stoichiometric and have high transparency in the thickness range of interest. Figure 7.11 shows high resolution XPS analysis of the Mo 3d and W 4f doublets on the surfaces of MoO₃ and WO₃, respectively. In both cases, the 6+ oxidation state dominated with a small contribution of 5+ due to slight oxygen deficiency.

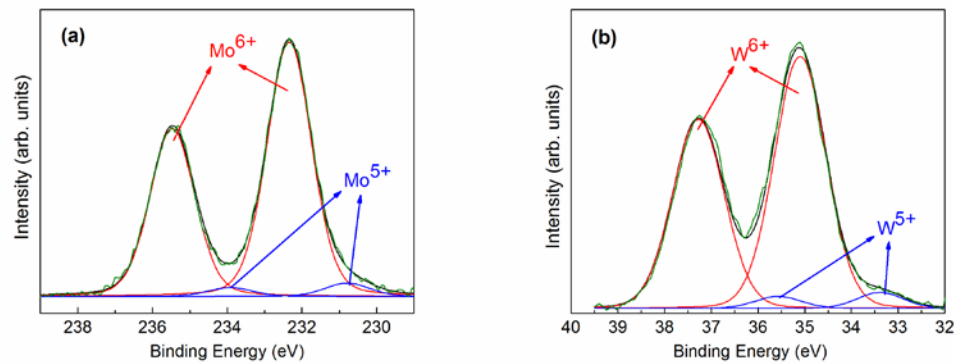


Figure 7.11: XPS analysis of a) Mo 3d and b) W 4f doublets at the surface of MoO₃ and WO₃ films, respectively.

Valence band edge energies were obtained by analysis of the XPS spectra and used to characterize the interface band offsets, ΔE_V . Specifically, the valence band maximum, E_V , was measured by linear extrapolation of the leading edge of the valence band spectrum to the energy axis and defining the slope intercept as E_V . For example, Fig. 7.12 shows data for the MoO₃/Cu(In,Ga)Se₂ sample after sputter etching for 120 min; corresponding to the valence band edge of Cu(In,Ga)Se₂ layer.

The effect of possible preferential sputtering (reducing the oxygen content) has not been taken into account here so only relative differences are significant. The valence band offsets were determined using the following equation [141]:

$$\Delta E_V = (E_{CL1} - E_{V1}) - (E_{CL2} - E_{V2}) - \Delta E_{CL} \quad (7.1)$$

where E_{CLi} is the core level binding energy in the bulk, E_{Vi} is the valence band edge in the bulk, and ΔE_{CL} is the energy difference between the core levels at the interface. The Cu 2p/In 3d, Mo 3d, and W 4f peaks were considered as the core peaks of the ACIGS, MoO₃, and WO₃ layers, respectively. In this work, positive values of ΔE_V indicate that the valence band edge of the ACIGS layer is located below the contact layer (cliff) while negative ΔE_V indicates a spike in the valence band, as shown schematically in Fig. 7.13. Device models have shown that the cell performance is not impeded if the barrier height at the back contact doesn't exceed 0.3 eV [218].

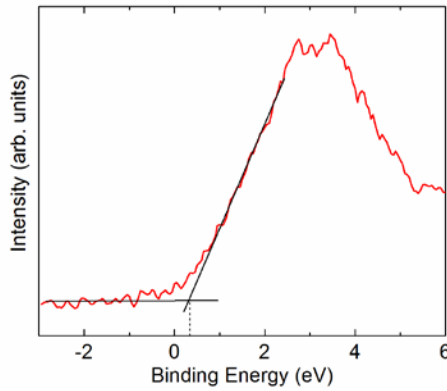


Figure 7.12: The valence band edge of MoO₃/Cu(In,Ga)Se₂ sample sputter etched for 120 min.

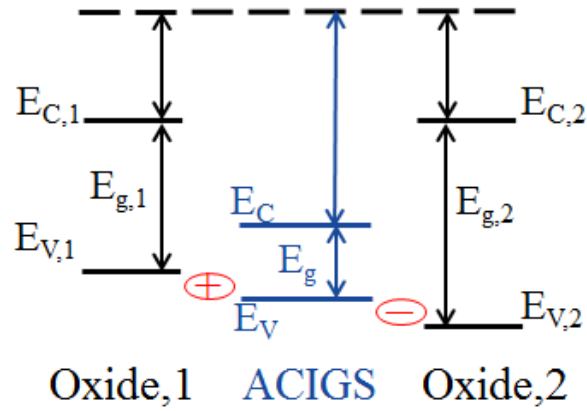


Figure 7.13: The Schematic band alignment between ACIGS and oxide layers, showing positive (cliff) and negative (spike) valence band offsets.

Figure 7.14 shows ΔE_V between MoO_3 and WO_3 films with ACIGS layers containing different Ga and Ag ratios. For all cases, MoO_3 has a better band alignment with ACIGS compared to the WO_3 contact layer. Increasing Ag content lowers the valence band edge of the ACIGS layer, changing the alignment of the absorber layer-back contact interface. With $\text{Ga}/(\text{Ga}+\text{In}) = 0.3$, increasing the Ag ratio from 0 to 0.6 caused a 0.5 eV down shift of the valence band, affecting the back contact-absorber layer band structure. This was more pronounced for the MoO_3 in contact with $(\text{AgCu})(\text{In}_{0.7}\text{Ga}_{0.3})\text{Se}_2$, in which ΔE_V changed from a cliff-type to a spike-type diagram by adding Ag (Figure 7.15). For the WO_3 , a flat band structure was found in films with $\text{Ag}/(\text{Ag}+\text{Cu}) = 0.6$.

Variation of the valence band edge with Ag content is in general agreement with the theory by Chen et al. who calculated a 0.5 eV down shift from CuGaSe_2 to AgGaSe_2 [219]. On the other hand, our results revealed that the effect of Ag-alloying was less distinct in films with $\text{Ga}/(\text{In}+\text{Ga}) = 0.8$. Figure 7.14 shows that while adding

Ag (for MoO₃ contact) has lowered the valence band edge of the films with Ga/(In+Ga) = 0.3 by about 0.4-0.5 eV, this value changed only by 0.2 eV for the films with Ga/(In+Ga) = 0.8. The same story is true for the WO₃ contact, though the difference is smaller.

The difference observed for the samples with high Ga and Ag content could be related to presence of the (Ag,Cu)(In,Ga)₅Se₈ phase near the surface of these films. As discussed in section 7.1, films with $0.5 \leq \text{Ga}/(\text{Ga}+\text{In}) < 1$ and $\text{Ag}/(\text{Ag}+\text{Cu}) > 0.5$ have near-surface phases consistent with an ordered defect compound identified as (Ag,Cu)(In,Ga)₅Se₈ [220].

Current XPS results also showed that the valence band offset is higher for the films with higher Ga content, in contrast with previous studies showing that the Ga content has a minor effect on the valence band position of the CuInSe₂-based alloys [221]. This contradiction might come from the different properties of surface and bulk of the films, or formation of surface phases which are kinetically more favorable, especially in the presence of Ag atoms.

Finally, the valence band offsets with Mo contact were also examined for the same range of Ag/(Ag+Cu) ratios. CuInSe₂ and AgGaSe₂ films were studied for comparison. $\Delta E_v = 0.85$ eV was found for the CuInSe₂ films, in agreement with previous studies where a barrier height of 0.8 eV relative to the CuInSe₂ was found in the absence of a MoSe₂ layer [49]. However, Figure 7.16 shows that the valence band offset between the Mo and ACIGS films is 1 eV, independent of the film composition, and no valence band shift due to Ag-alloying of absorber layer was observed.

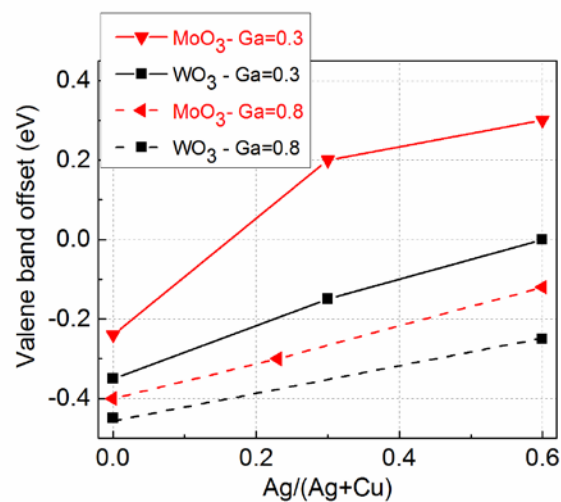


Figure 7.14: Valence band offset between ACIGS films and MoO₃ and WO₃ contacts, determined by XPS analysis. Error bars are about 0.1 eV.

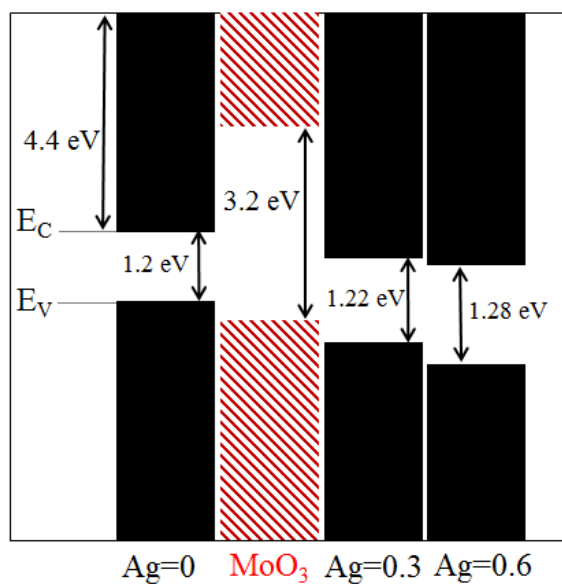


Figure 7.15: Effect of Ag alloying on the band offset between MoO₃ and ACIGS films, with Ga/(Ga+In)=0.3, determined by XPS analysis.

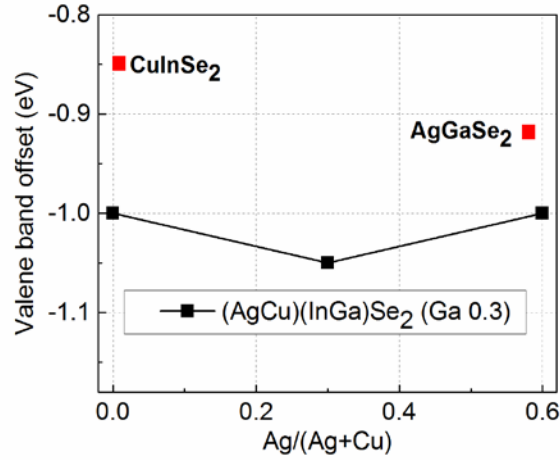


Figure 7.16: Valence band offset between ACIGS films (with Ga/Ga+In) = 0.3) and Mo, determined by XPS analysis. CuInSe₂ and AgGaSe₂ films are also shown.

Bardeen [43] and Rhoderick [45] models have shown that the barrier height may not follow the simple Schottky model and can even be independent of the metal work function, in part due to interface reactivity. The dependence of barrier height on choice of metal depends on the semiconductor, the nature of its surface before contact formation, and the interfacial chemistry, highlighting the role of other factors such as crystal quality and density of surface states. This study confirms that Mo should not be a good back contact candidate for the superstrate ACIGS solar cells. Therefore, it would be necessary to develop either an opaque or transparent back contact via surface modification or introduction of buffer layers to have an ohmic contact in the back surface.

Chapter 8

CONCLUSION AND FUTURE WORK

8.1 Conclusion

The main goal of this research is to develop a technology to reduce the manufacturing cost of the Cu(In,Ga)Se₂ thin film solar cells by lowering the absorber thickness. This leads to lower material usage and higher manufacturing throughput. On the other hand, the performance of Cu(In,Ga)Se₂ devices begins to deteriorate due to incomplete optical absorption leading to lower J_{SC}, and increased back surface recombination which may reduce the V_{OC}.

Therefore, it is important to develop a new method to improve the current collection, and to understand the characteristics of the Cu(In,Ga)Se₂-back contact interface in order to design ohmic back contacts for Cu(In,Ga)Se₂-based solar cells with a range of band gaps and device configurations.

In this project, candidate back contact materials were identified based on the chemical stability under Cu(In,Ga)Se₂ growth condition at temperatures > 500 °C, modeling of band alignments and surface chemical properties of the absorber layer and back contact. For the first time, MoO₃ and WO₃ transparent back contacts were developed for Cu(In,Ga)Se₂ solar cells. The structural, optical, and surface properties of MoO₃ and WO₃ were studied using XRD, SEM, XPS, and UV/Vis/NIR spectrophotometry, and optimized by controlling the oxygen partial pressure during reactive sputtering and post-deposition annealing.

This enabled the illumination of the device from the back, resulting in a recently developed “backwall superstrate” device structure that outperforms conventional substrate Cu(In,Ga)Se₂ devices with submicron thick absorbers. Devices with the backwall configuration outperform substrate devices in the absorber thickness range 0.1-0.5 μm . The “backwall superstrate” device has a higher J_{SC} with an improvement of 100% observed for the absorber with $d_{\text{CIGS}} = 0.11 \mu\text{m}$ and 35% enhancement for the 0.43 μm thick absorber. The V_{OC} was also higher for the backwall devices compared to the control samples, with an increase of 12% for the 0.12 μm thick absorber and 8% for $d_{\text{CIGS}} = 0.43 \mu\text{m}$.

Further enhancements were achieved by introducing moderate amounts of Ag into the Cu(In,Ga)Se₂ lattice during the co-evaporation method resulting in an improved open circuit voltage, and diminished defect concentration of the absorber layer due to the lower melting point of the alloy. In fact, this 9.7% cell (with 0.3 μm thickness) has the highest efficiency reported for ultrathin CIGS solar cells to date.

In addition, sulfized back contacts including ITO-S and MoS₂ with different thicknesses were also examined with the aim of reducing recombination at the back surface and increasing the voltage. XPS analysis and thermodynamics of reactions suggest that sulfization of the back contacts has highly restricted the formation of Ga₂O₃ phase at the interface. Still, backwall devices with MoO₃ back contact have a better V_{OC} and overall performance compared to devices with sulfized back contacts.

8.2 Future Work

The above-mentioned results clearly exhibit the potential of the backwall structure for utilization of ultrathin absorber layers. Still, there are several

opportunities to further improve the performance of the backwall devices. This could include the following:

- Composition grading in the absorber to improve current collection. Another approach could be deposition of a thin layer at the back contact with high Ga concentration in order to reduce recombination.

- Incorporating controlled amounts of K & Na atoms in the Cu(In,Ga)Se_2 absorber layer to enhance the junction quality and surface passivation.

- Optical enhancement by e.g. texturing of the TCO layers and optimizing the thicknesses of different layer to increase absorption in the Cu(In,Ga)Se_2 layer.

- Design and fabrication of tandem cells incorporating MoO_3 and WO_3 transparent contacts with $(\text{Ag,Cu})(\text{In,Ga})\text{Se}_2$ absorber layer.

In addition, the following experiments can be done in order to have a better understanding of the device properties:

- Capacitance-voltage spectroscopy in order to find the depletion width of different alloys.

- Temperature dependent current-voltage analysis (J-V-T) to investigate the main loss mechanism and measure the back contact barrier height.

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Appendix A

AFM ANALYSIS

A.1 Surface roughness

AFM images of ITO, ITO-MoO₃, and ITO-WO₃ films are shown in Fig. A.1, and also summarized in Table A.1. It can be seen that both as-deposited and annealed ITO films have a very smooth surface morphology, with the height variation $\Delta z \approx 6$ nm. These results suggests that there would be a uniform coverage of MoO₃ and WO₃ layers over the ITO layer, and these oxides can be considered as the primary contact layers.

Deposition of 10 nm MoO₃ or WO₃ films changed the surface morphology, resulting in a rod-like morphology. Still, the surface roughness is ≈ 9 nm, showing the presence of very smooth contact layer.

Table A.1: AFM results of different transparent back contact layers

	ITO As-dep	ITO Ar ann	ITO-MoO ₃	ITO-WO ₃
Z range (nm)	5.7	6.3	9.1	8.6
Root mean square	0.53	0.56	1.26	1.02
Surface area difference* (%)	0.30	0.45	1.89	1.42

* The surface area difference represents the percentage increase of the three-dimensional surface area over the two-dimensional surface area.

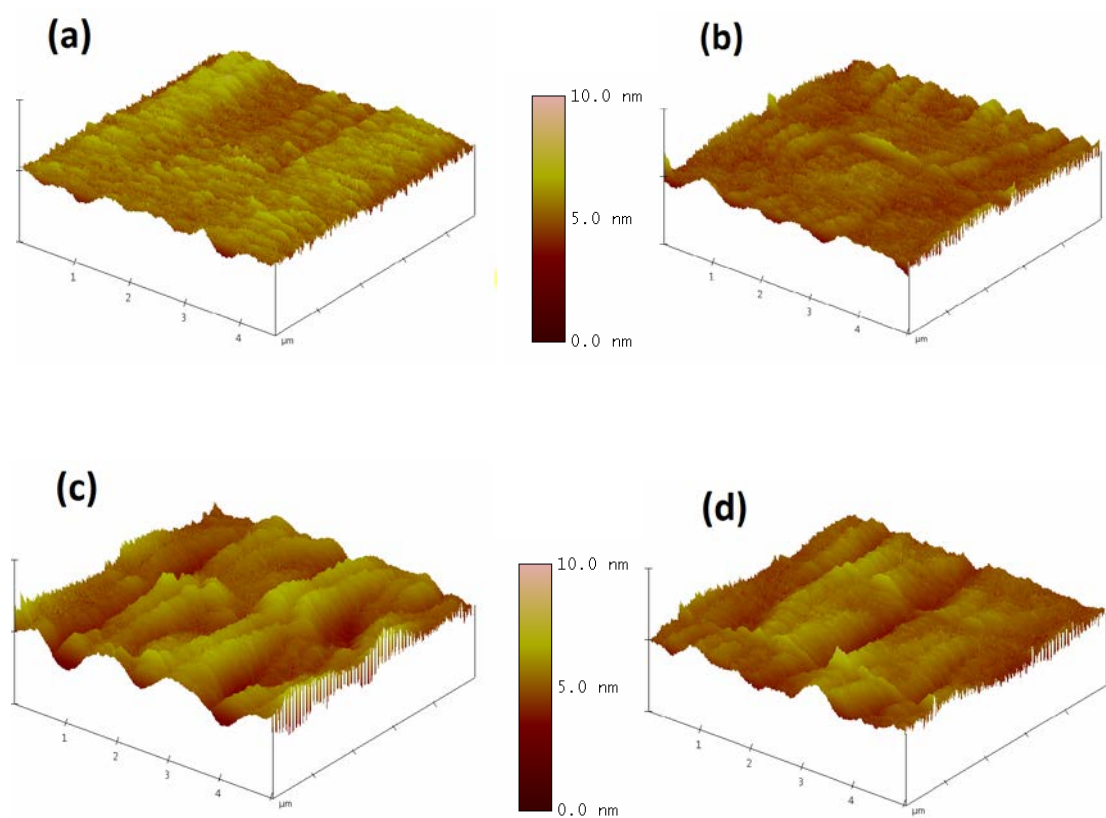


Figure A.1: AFM micrographs of a) as-deposited ITO, b) Ar-annealed ITO, c) ITO-MoO₃, and d) ITO-WO₃.

Appendix B

HIGH TEMPERATURE DEPOSITION OF MoO₃ FILMS

B.1 Introduction

In chapter 4, effect of oxygen partial pressure and post deposition annealing on the structural, optical, and surface properties of the MoO₃ films deposited at room temperature were presented. Here, characteristics of MoO₃ films sputtered at different substrate temperatures are being studied.

Molybdenum oxide (MoO₃) thin films were prepared via rf sputtering at fixed ambient oxygen concentration $O_2/(O_2+Ar) = 35\%$. The effects of substrate temperatures in the range of 25-400 °C, and post-deposition annealing, in Air at 300-500 °C, on the structural, optical, and surface properties of the deposited films were investigated. The films were analyzed using glancing incidence x-ray diffraction, UV/Vis/NIR spectrophotometry, and x-ray photoelectron spectroscopy. Evaluation of the MoO₃ electronic properties and back contact role in Cu(In,Ga)Se₂ thin film solar cells is in progress and not reported here.

B.2 Structural Properties

Fig. B.1 shows the GIXRD patterns, with an incidence angle of $\Omega = 0.5^\circ$, of reactive-sputtered MoO₃ films deposited at different substrate temperatures, and annealed in the temperature range of 300-500 °C. Films deposited at room temperature show a broad peak centered at $\sim 26^\circ$ (Fig. B.1a) indicating an amorphous structure with a short range order of the atoms in the crystal lattice. Thus, low temperature

deposition didn't provide sufficient energy for nucleation and growth of MoO₃ crystallites, in good agreement with Nirupama et al. [114]. Increasing the deposition temperatures to 200 °C (Fig. B.1a) resulted in crystallization of the molybdenum oxide films to the β -MoO₃ phase, which is the meta-stable form of the MoO₃ structure with a monoclinic lattice structure. Diffraction peaks at 200 °C show reflections at $2\theta = 23.14^\circ, 25.01^\circ, 27.36^\circ, 35.05^\circ$, and 49.19° identified as (10-1), (002), (011), (012), and (020), of the β -MoO₃ phase, respectively [97]. The peak positions and d-spacing are listed in Table B.1 along with standard values from the ICDD database.

Table B.1: The peak positions and d-spacing of MoO₃ film, deposited at 200 °C in comparison with ICDD card 047-1320 [222].

Peak position (2 θ)	d-spacing calculated	Peak position ICDD	d-spacing ICDD	Phase
12.61	7.02	12.84	6.89	β
23.14	3.84	23.67	3.76	β
25.10	3.55	25.84	3.44	β
27.36	3.26	27.41	3.25	β
35.05	2.56	35.63	2.52	β
49.19	1.85	49.40	1.84	β

Samples deposited at 300 °C (Fig. B.1a, and Table B.2) showed reflection at $12.89^\circ, 23.40^\circ, 25.71^\circ, 27.36^\circ, 39.20^\circ, 45.90^\circ$ and 49.35° which were identified as the (001), (10-1), (002), (011), (11-2), (20-1), and (020) reflections of the β -MoO₃ phase. Other reflections at $22.65^\circ, 24.35^\circ$, and 33.79° were recognized as the (211), (60-1), and (41-2) reflections of the Mo₄O₁₁ phase. Therefore, films deposited at 300 °C were a mixture of β -MoO₃ and Mo₄O₁₁ phases.

Higher deposition temperature of 400 °C (Fig. B.1a, and Table B.3) resulted in phase transformation to α -MoO₃ phase with reflections at $2\theta = 12.80^\circ$, 23.36° , 25.75° , 27.47° , 39.14° , and 58.84° corresponding to (020), (110), (040), (021), (060), and (081) planes, respectively.

Table B.2: The peak positions and d-spacing of MoO₃ film, deposited at 300 °C in comparison with corresponding ICDD cards. (ICDD (β) 047-1320 and (Mo₄O₁₁) 013-0142) [222,223].

Peak position (2θ)	d-spacing calculated	Peak position ICDD	d-spacing ICDD	Phase
12.89	6.86	12.84	6.89	β
22.65	3.92	22.58	3.93	Mo ₄ O ₁₁
23.40	3.80	23.67	3.76	β
24.35	3.73	24.67	3.60	Mo ₄ O ₁₁
25.71	3.46	25.84	3.44	β
27.36	3.26	27.41	3.25	β
33.79	2.65	33.82	2.65	Mo ₄ O ₁₁
39.20	2.30	39.20	2.30	β
45.90	1.98	45.90	1.98	β
49.35	1.85	49.40	1.84	β

Table B.3: The peak positions and d-spacing of MoO₃ film, deposited at 400 °C in comparison with corresponding ICDD card of 00-005-0508 [224].

Peak position (2θ)	d-spacing calculated	Peak position ICDD	d-spacing ICDD	Phase
12.80	6.91	12.76	6.93	α
23.36	3.80	23.32	3.81	α
25.75	3.46	25.70	3.46	α
27.47	3.24	27.33	3.26	α
39.14	2.30	38.97	2.31	α
58.84	1.57	58.80	1.57	α

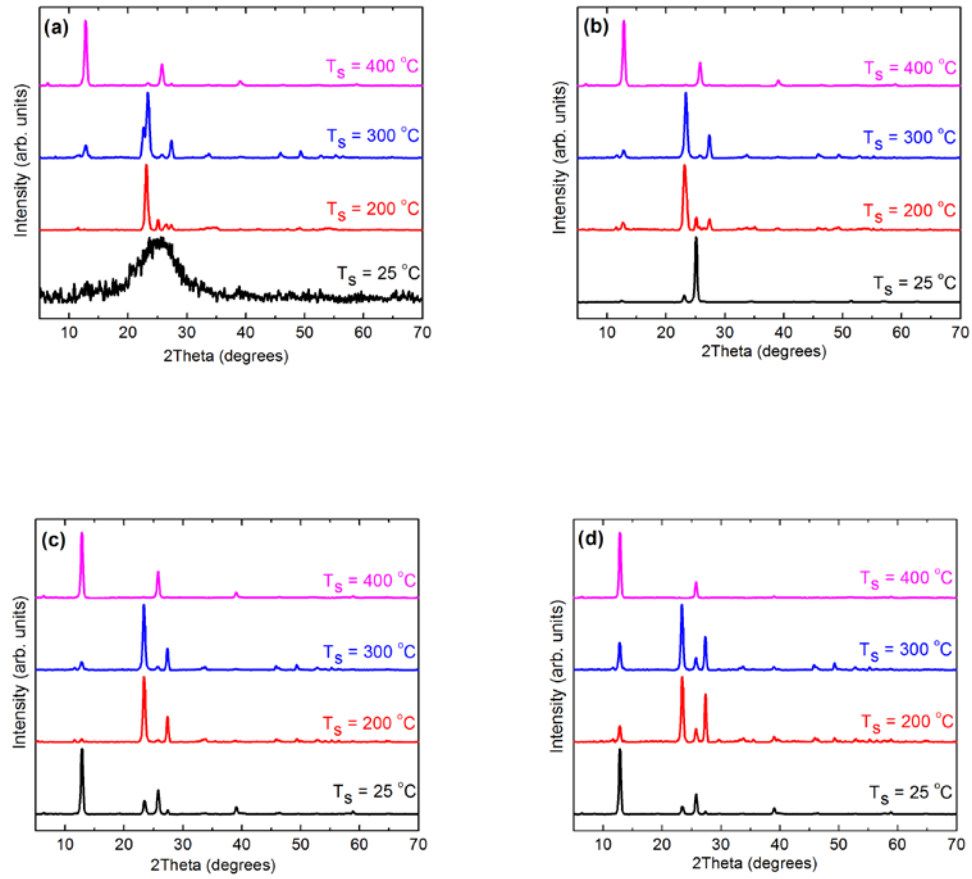


Figure B.1: Effect of deposition and annealing temperature on the x-ray diffraction patterns of reactive-sputtered MoO₃ films; a) as-deposited, b) annealed at 300 °C, c) 400 °C, and d) 500 °C.

Table B.4: Effect of deposition and annealing temperature on the structural properties of reactive-sputtered MoO₃ films.

Substrate Temp. (°C)	As-deposited	300 °C	400 °C	500 °C
RT	Amorphous	β	α	α
200	β	β	α	α
300	β , Mo ₄ O ₁₁	β	α	α
400	α	α	α	α

The effects of substrate temperature during deposition and post-deposition annealing are summarized in Table B.4. It can be seen MoO₃ films deposited at room temperature were amorphous, while increasing the deposition temperature resulted in crystallization of the films to a β , $\beta + \text{Mo}_4\text{O}_{11}$, and α phases, respectively.

Annealing at 300 °C resulted in crystallization of the molybdenum oxide films to the β -MoO₃ phase, which is the metastable form of the MoO₃ structure. Samples annealed at high temperatures of 400-500 °C are identified as the orthorhombic α -MoO₃ phase. These results are in good agreement with Fan et al. [115] who have reported the crystallization of initially amorphous MoO₃ films to a monoclinic and then orthorhombic structure at substrate temperatures of 300 °C and 400 °C, respectively.

B.3 Surface Properties

Fig. B.2 shows the XPS survey scan of a MoO₃ film deposited at room temperature with O₂/(O₂+Ar) = 35%. The correlated elements of major core level binding energies are mentioned in the graph. This was typical for all MoO₃ films, independent of deposition temperature. The carbon peak (C 1s) observed at ~284 eV is due to the surface contamination of the film since they were exposed to atmosphere. Further small peaks related to other core energy levels were also identified and recorded in Table B.5.

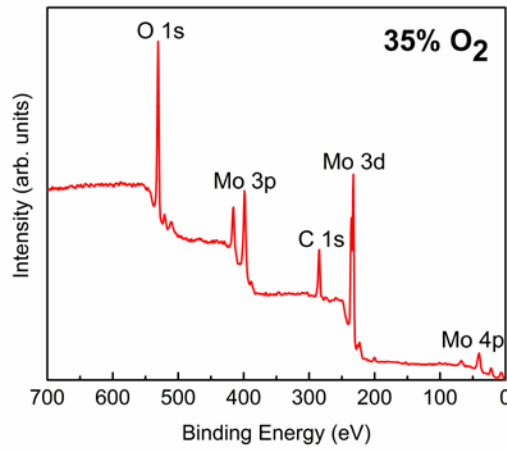


Figure B.2: XPS survey spectrum of MoO_{3-x} film deposited at $\text{O}_2/(\text{O}_2+\text{Ar}) = 35\%$.

Table B.5: Core level binding energies of MoO_{3-x} film, deposited at room temperature with $\text{O}_2/(\text{O}_2+\text{Ar}) = 35\%$.

Core level	Binding energy (eV)	Core level	Binding energy (eV)
O 1s	530.81	Mo 3d _{3/2}	236.01
Mo 3p _{3/2}	398.02	Mo 3d _{5/2}	232.88
Mo 3p _{1/2}	416.09	Mo 4p	40.83
C 1s	284.83	O 2s	22.76

High resolution scans of Mo 3d doublet core levels of MoO_3 films formed at different substrate temperatures are shown in Fig. B.3, and summarized in Table B.6. All patterns show a slight asymmetric line shape, indicating the presence of mixed oxidation states of Mo. The peaks were fitted by Gaussian-Lorentzian curves satisfying the following constraints: a) the 3d_{5/2} to 3d_{3/2} ratio is 3:2; b) each doublet has equal FWHM; and c) the spin orbit splitting of Mo 3d doublets are 3.13 eV [136,137,152].

The peak fitting resolved that all of the as-deposited films contain two oxidation states of Mo^{6+} and Mo^{5+} . Increasing the deposition temperature to 200 °C resulted in the slight shift of both Mo $3d_{5/2}$ and Mo $3d_{3/2}$ core levels to lower energy levels. This might be from the loss of oxygen resulting in an increase in the Mo^{5+} phase. Consequently, the amount of Mo^{6+} phase decreases as shown in B.4.

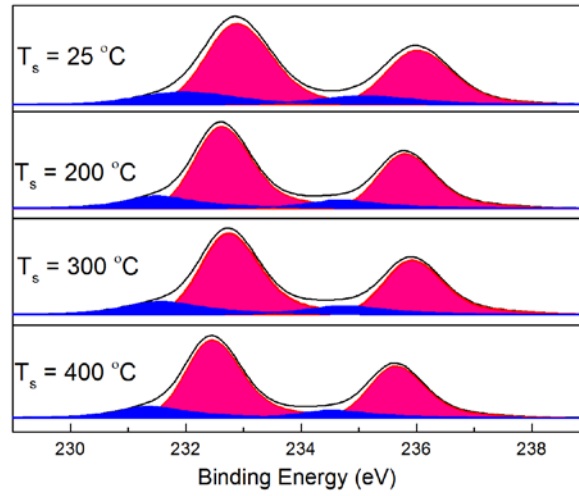


Figure B.3: XPS core level binding energy of Mo 3d doublets of MoO_3 films deposited at different substrate temperatures.

Table B.6: Core level binding energies of Molybdenum in as-deposited MoO_3 films.

Substrate Temp. (°C)	Binding energy (eV)			
	Mo^{+6}		Mo^{+5}	
	Mo $3d_{5/2}$	Mo $3d_{3/2}$	Mo $3d_{5/2}$	Mo $3d_{3/2}$
RT	232.88	236.01	231.96	235.09
200	232.43	235.56	231.49	234.62
300	232.71	235.84	231.73	234.86
400	232.59	235.72	231.62	234.76

Similar analysis was completed for samples deposited at different temperatures and annealed at 300-500°C, for 1 h in air and the results are also shown in Fig B.4. It can be seen that increasing the deposition temperature to 200-300 °C caused oxygen loss at the surface of the films. It was shown in the previous section (Table B.4) that these films have the β -MoO₃ and Mo₄O₁₁ phases. On the other hand, films deposited at 400 °C, which were identified as the α -MoO₃ phase, absorbed more oxygen at the surface and have higher Mo⁶⁺ to Mo⁵⁺ ratios.

Samples deposited at room temperature and annealed at 400-500 °C have a stoichiometric surface composition. This was not the true for the sample deposited at high temperature. In this case, high temperature annealing couldn't compensate the oxygen deficiency at the surface and all films have $0.6 < \text{Mo}^{6+} / (\text{Mo}^{6+} + \text{Mo}^{5+}) < 0.75$.

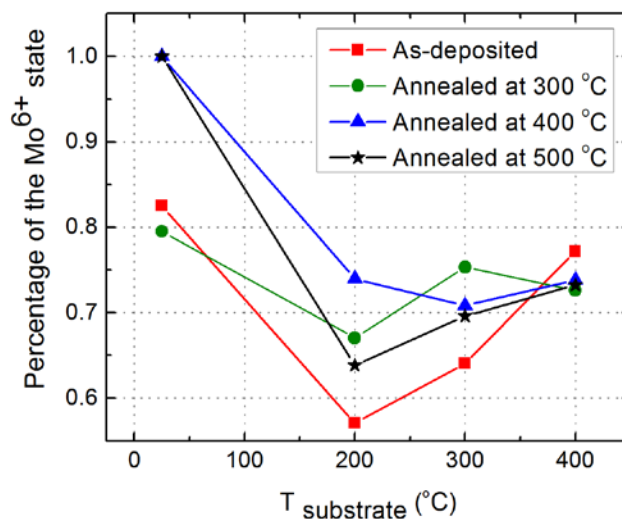


Figure B.4: The percentage of the Mo⁶⁺ state present in the MoO_{3-x} films sputtered at different oxygen partial pressures, and different annealing temperatures.

B.4 Optical Properties

Figure B.5 shows the normalized transmittance curves of the MoO_3 films deposited at different $\text{O}_2/(\text{O}_2+\text{Ar})$ ratios. The film thickness were 500 nm.

All films show high regular transmittance ($> 80\%$) in the visible range, indicating less oxygen ion vacancies [177]. The transmittance values drop steeply at $\lambda \approx 400$ nm indicating a strong absorption due to band-to-band absorption. Increasing the deposition temperature didn't significantly affect the total transmittance of films, but it did correspond to a shift in the absorption edges to higher energy ranges, thus increasing in higher bandgaps.

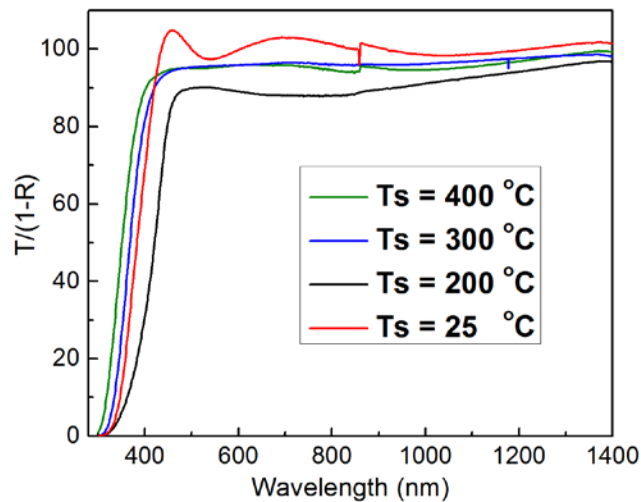


Figure B.5: Normalized transmittance of the MoO_3 films deposited at different temperatures.

Figure B.6 shows the variation of optical bandgap for samples deposited at various deposition temperatures and annealed at different temperatures of 300-500 °C.

This assumes the indirect bandgap as the primary transition, as discussed in section 4.2.4.

The optical bandgap for the films deposited at room temperature is 2.9 eV. Increasing the deposition temperature to 200 °C reduced the optical bandgap to 2.5 eV. The 200 °C annealed films were β phase, as shown in section 4.2.2. Lower bandgap values of β -MoO₃ compared to the α -MoO₃ phase had been reported previously [118,179].

Samples deposited at 300 °C had wider bandgap of 3.1 eV compared to low temperature deposited samples. These films have a β -MoO₃ and Mo₄O₁₁ mixture phase. Higher deposition temperature of 400 °C increased the bandgap further to 3.2 eV. These films have the α -MoO₃ phase, which is the stable form of the MoO₃ structure.

Annealing at 300 °C had a small effect on the optical properties of the MoO₃ films, and they behave similarly to the as-deposited films (Fig. B.6).

Samples annealed at 400 and 500°C had wider bandgaps, in the range of 3.0 to 3.4 eV, compared to the as-deposited samples (Fig. B.6). These films have the α -MoO₃ phase, which is the stable form of the MoO₃ structure. This has a lower density of impurity states induced primarily by oxygen deficiency, and hence a wider bandgap [168]. MoO₃ films deposited at room temperature and 400 °C have the highest bandgap values in the studied range.

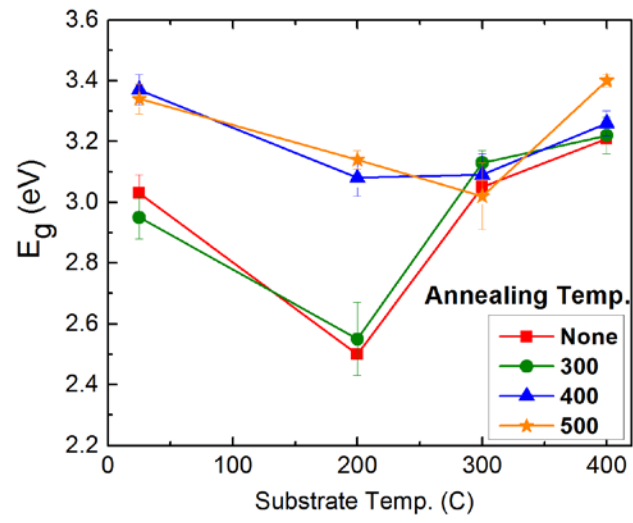


Figure B.6: Variation of optical bandgap as a function of substrate and annealing temperature

Appendix C

SULFIZED BACK CONTACTS

Low V_{OC} of devices with thin absorbers may be caused by recombination at the interface between the back contact and the Cu(In,Ga)Se₂ absorber, which is expected to play a larger role for thinner absorbers [21] or poorer electronic quality of the thinnest Cu(In,Ga)Se₂ films. The backwall cells discussed in chapter 6 use a MoO₃ transparent back contact. MoO₃ has a bandgap in the range 3.1 to 3.4 eV when annealed at 500°C [116], and forms an ohmic contact with Cu(In,Ga)Se₂ [184,225] making it well suited for backwall devices.

ITO-S and MoS₂ films with different thicknesses were also examined with the aim of reducing recombination at the back surface and increasing the voltage. They were prepared by sulfization reaction of ITO or Mo films in a hot zone reactor with flowing H₂S(0.35%) / O₂(0.0035%) / Ar(balance) at 550 °C.

C.1 Device Properties

Table C.1 shows that all devices have V_{OC} close to 0.6 V. The best overall performance was achieved from sulfized-ITO back contact. Still, backwall devices with MoO₃ back contact (see chapter 6) have a better V_{OC} and overall performance compared to devices with sulfurized back contacts.

For the MoS₂ back contacts, increasing the film thickness caused a drop in J_{SC} , probably due to incomplete sulfization of the Mo films, reducing the transparency of the back contact. This can be clearly seen in the QE profile of the CIGS backwall

superstrate cell in which lower spectral response is observed for devices with 3 and 5 nm MoS₂ contacts (Fig. C.1).

Table C.1: Device parameters of backwall Cu(In,Ga)Se₂ cells made on sulfized back contacts

Back contact	d _{CIGS} μm	V _{OC} V	J _{SC} mA/cm ²	FF %	Eff. %
ITO	0.4	0.33	13.4	41.5	1.8
ITO-S	0.3	0.55	22.9	62.8	7.9
ITO-MoS ₂ (2nm)	0.3	0.59	20.6	61.5	7.6
ITO-MoS ₂ (3nm)	0.4	0.58	19.3	55.0	7.4
ITO-MoS ₂ (5nm)	0.4	0.57	18	65.9	6.8

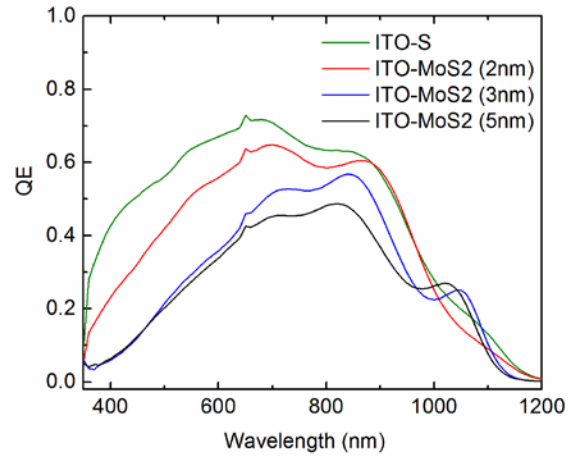


Figure C.1: QE profile of backwall devices for the CIGS cells for sulfized back contacts.

C.2 XPS Analysis

The interface between the Cu(In,Ga)Se₂ and sulfized-ITO or ITO back contact was characterized by XPS measurements (Fig. C.2). We previously showed that performance of devices with ITO back contacts was limited due to undesired band alignment and formation of Ga₂O₃ phase at the interface [38,184]. This is confirmed by analysis of the Ga 3d peak at the interface in Figure C.2a.

Interpretation of the XPS results was facilitated by considering the thermodynamics of potential reactions using bulk enthalpy and entropy for reactant and product phases at 550 °C. The Gibbs free energies for potential reactions of different species are listed in Table C.2.

Table C.2 suggests that sulfization of ITO films will result in formation of In₂S₃ and SnS₂ phases. On the other hand, reaction of ITO with Se vapor is not likely since Gibbs free energies of selenide phases are very small or positive. Besides, during the Cu(InGa)Se₂ deposition, Ga atoms react with In₂S₃ and SnS₂ phases, or remaining S atoms on the surface, creating Ga₂S₃ phase at the interface. Therefore, reaction of Ga with oxygen atoms and subsequent formation of Ga₂O₃ phase would be highly restricted.

High resolution XPS analysis of the Ga 3d region for the sulfized-ITO/CIGS stack (Fig. C.2b) indicates that there is only a small amount of Ga₂O₃ phase at the interface. Instead, the Ga₂S₃ phase is formed at the interface which is thermodynamically favorable (Table C.2).

This was further confirmed by high resolution scans of the S 2p region (Fig. 7c). The peaks were fit by Gaussian-Lorentzian curves satisfying the following constraints: a) the 2p_{3/2} to 2p_{1/2} ratio is 2:1; b) each doublet has equal full width at half

maximum (FWHM); and c) the spin orbit splitting of the S 2p doublets is 1.2 eV [136,180].

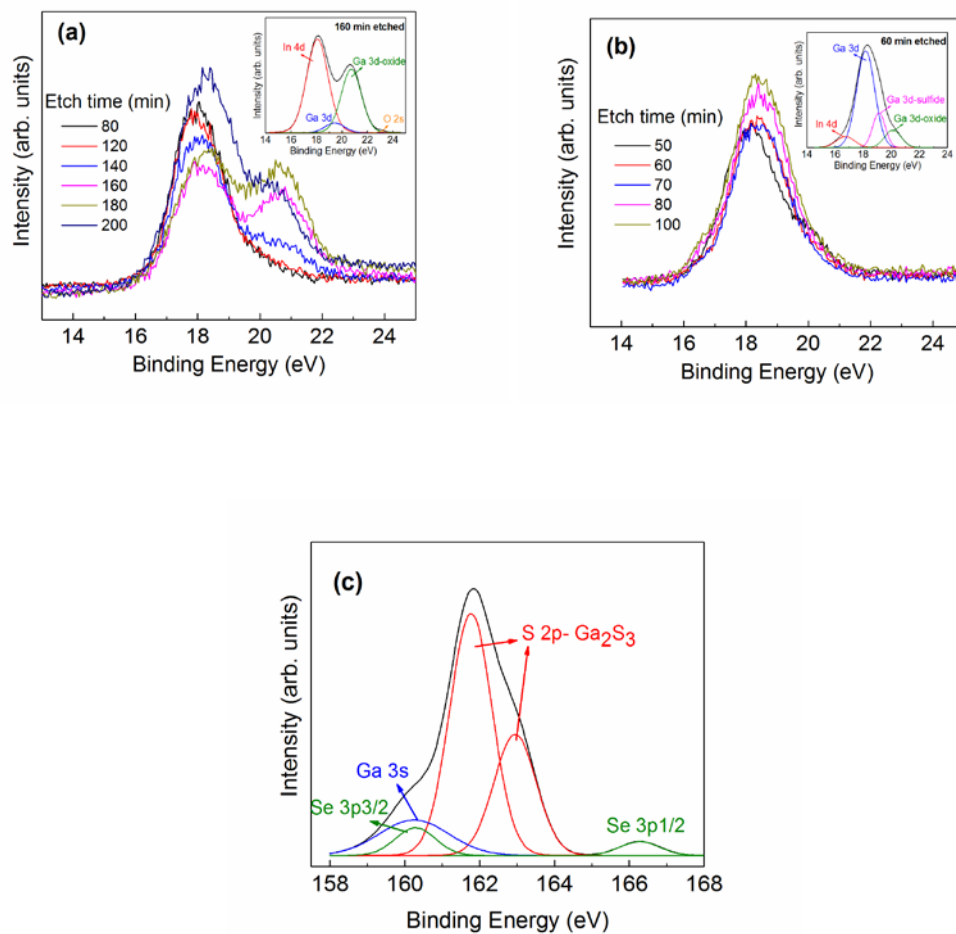


Figure C.2: XPS analysis of Ga 3d peak at the interface of a) ITO/Cu(In,Ga)Se₂, and b) ITO-Sulfized/Cu(In,Ga)Se₂. C) XPS analysis of S 2p after 60 min etch.

Table C.2: Gibbs free energy of potential reactions at the Cu(In,Ga)Se₂ / back contact interface at 550 °C [113]. S and Se are in the liquid phase.

Reaction	Gibbs free energy (kcal/mol)
$\text{In}_2\text{O}_3 + 3\text{Se} \rightarrow \beta\text{-In}_2\text{Se}_3 + 3/2 \text{O}_2$	-3.3
$\text{SnO}_2 + 2\text{Se} \rightarrow \text{SnSe}_2 + \text{O}_2$	14.6
$\text{In}_2\text{O}_3 + 3\text{S} \rightarrow \beta\text{-In}_2\text{S}_3 + 3/2 \text{O}_2$	-34.7
$\text{SnO}_2 + 2\text{S} \rightarrow \text{SnS}_2 + \text{O}_2$	-11.1
$\text{Ga} + \text{In}_2\text{O}_3 \rightarrow \text{Ga}_2\text{O}_3 + \text{In}$	-36.4
$\text{Ga} + \text{In}_2\text{Se}_3 \rightarrow \text{Ga}_2\text{Se}_3 + \text{In}$	-13.9
$\text{Ga} + \text{In}_2\text{S}_3 \rightarrow \text{Ga}_2\text{S}_3 + \text{In}$	-34.8
$2\text{Ga} + 2\text{In}_2\text{Se}_3 \rightarrow \text{Ga}_2\text{Se}_3 + 3\text{InSe} + \text{In}$	-38.5
$2\text{Ga} + 2\text{In}_2\text{S}_3 \rightarrow \text{Ga}_2\text{S}_3 + 3\text{InS} + \text{In}$	-44.0
$2\text{Ga} + 2\text{In}_2\text{Se}_3 \rightarrow \text{Ga}_2\text{Se}_3 + 2\text{In}_2\text{Se} + \text{Se}$	-2.8
$2\text{Ga} + 2\text{In}_2\text{S}_3 \rightarrow \text{Ga}_2\text{S}_3 + 2\text{In}_2\text{S} + \text{S}$	81.8
$2\text{MoS}_2 + 2\text{Ga} \rightarrow \text{Ga}_2\text{S}_3 + \text{S} + 2\text{Mo}$	+48.3
$2\text{Ga} + 3\text{Se} \rightarrow \text{Ga}_2\text{Se}_3$	-177.1
$2\text{Ga} + 3\text{S} \rightarrow \text{Ga}_2\text{S}_3$	-229.4
$\text{Ga}_2\text{Se}_3 + 3/2 \text{O}_2 \rightarrow \text{Ga}_2\text{O}_3 + 3\text{Se}$	-19.2
$\text{Ga}_2\text{S}_3 + 3/2 \text{O}_2 \rightarrow \text{Ga}_2\text{O}_3 + 3\text{S}$	+33.1

Therefore, results of XPS analysis and thermodynamics calculations indicates that the interface of sulfized contacts/Cu(In,Ga)Se₂ contains a combination of In₂S₃, SnS₂, Ga₂O₃, and Ga₂S₃ phases making the precise interpretation very difficult. Better performance of devices with sulfized-ITO back contact compared to ITO can be attributed to reduced amount of Ga₂O₃ at the interface.

Appendix D

EFFECT OF RAPID THERMAL PROCESSING ON THE PROPERTIES OF (Ag,Cu)(In,Ga)Se₂ DEVICES

D.1 Introduction

Adding Ag not only increases the optical bandgap, but also decreases the melting point of the alloy which may allow films to be deposited with lower defect density than other Cu(In,Ga)Se₂ alloys [217]. We have previously reported improved device performance [208] and sharper band tails [209]. These results suggest that Ag incorporation may be an effective means of increasing V_{OC} without the detrimental effect on the other device parameters that is typically observed at bandgaps > 1.3 eV [207,226].

Rapid Thermal Processing (RTP) can be used to activate doping impurities and improve electrical and optical properties of various photovoltaic materials such as InGaAsN [227], CdTe/CdS [228], and Cu(In,Ga)Se₂ [229,230]. The advantages of RTP include short processing time and reduced thermal budget. RTP has been shown to decrease the number of undesirable thermally driven physical and chemical effects of longer high temperature processes, reduce the density of near-surface defects and therefore diminish the losses due to recombination via defect centers, and improve cell properties [231]. For Cu(In,Ga)Se₂ solar cells, Wang et al. [230] showed that RTP treatments under optimal annealing conditions improved the electrical properties of Cu(In,Ga)Se₂ films and cell performance with no change in the overall film composition and surface morphology. Miyazaki et al. [232,233] showed that RTP can

improve the V_{OC} and efficiency of cells with $Cu(In,Ga)Se_2$ absorber layers that contain an additional $Cu_{2-x}Se$ phase.

D.2 Experimental

$(Ag_wCu_{1-w})(In_{1-x}Ga_x)Se_2$ films were deposited on Mo-coated soda lime glass substrates using multi-source elemental evaporation. Films were deposited with constant fluxes over time so that they have no intentional through-film composition gradients. The ratios $x \approx 0.78$ and $w \approx 0.80$ were considered for this study. All films have bulk compositions with group I/III ratio, $(Ag+Cu)/(In+Ga) \approx 0.8-0.9$ and are 2 μm thick.

The RTP system developed at the Institute of Energy Conversion (IEC) allows isothermal annealing of the 2.5 x 2.5 cm samples. Treatments were carried out using a 700 W halogen lamp for the duration of 30 sec for different temperatures ranging from 450 to 575 °C, under Ar atmosphere (Fig. D.1a). Samples were cooled down to less than 300 °C in about 10 sec and reached room temperature in 3 min. In order to compensate for potential Se loss in the absorber layer, a 200 nm layer of selenium was deposited on some samples after the absorber layer deposition, and the Se was confined by a quartz cap (Fig. D.1b).

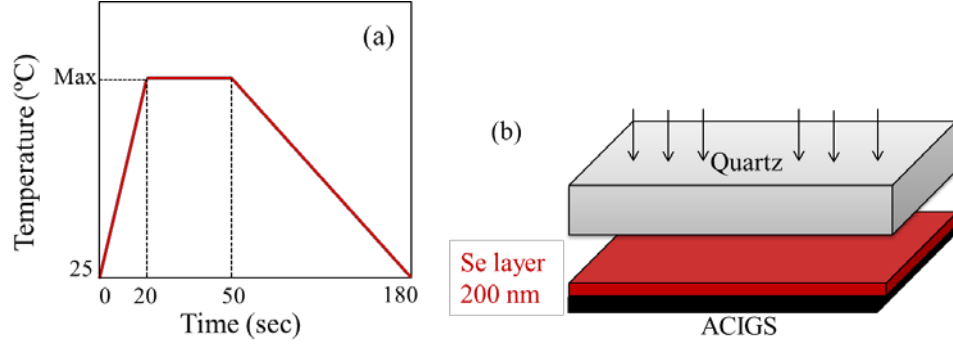


Figure D.1: Schematic picture of the (a) RTP process temperature profile and (b) configuration of the RTP with extra Se supply.

D.3 Device Properties

The effect of RTP temperature on the efficiency and V_{OC} of an $(Ag_wCu_{1-w})(In_{1-x}Ga_x)Se_2$ device with $w = 0.80$ and $x = 0.78$ is shown in Figure D.2. The optical bandgap with this composition is about 1.65 eV. The highest improvement was achieved at an annealing temperature of 500°C for which V_{OC} and efficiency of device were enhanced by 112 mV and 1.3%, respectively. Figure D.2 also shows the results with films which received RTP treatment with the 200 nm Se cap. As with un-capped samples, the best cell results were obtained at annealing temperature of 500°C and the current-voltage parameters are listed in Table D.1. RTP in the presence of excess Se improved all cell parameters, and V_{OC} , short circuit current (J_{SC}), fill factor (FF) and efficiency (Eff.) were increased by 127 mV, 3.8 mA/cm², 7.9% and 2.8%, respectively. These are comparable to our best previously reported cell [207], with wide bandgap (1.66 eV) $(Ag_wCu_{1-w})(In_{1-x}Ga_x)Se_2$ via single stage uniform deposition.

Table D.1: Effect of RTP (+ extra Se supply) on V_{OC} , J_{SC} , FF and Eff. of $(Ag_wCu_{1-w})(In_{1-x}Ga_x)Se_2$ sample with $w \approx 0.8$ and $x \approx 0.78$. The reported values are maximum values of each device.

Sample	w	x	RTP Temp. (°C)	Voc (mV)	Jsc (mA)	FF (%)	Eff. (%)
ACIGS	0.80	0.78	Ref.	743	17.9	57.7	7.3
ACIGS	0.83	0.79	500	855	17.6	58.4	8.6
ACIGS + Se cap	0.83	0.78	500	870	21.7	65.6	10.1

The same trend as in Figure D.2 was also observed for other samples with various x and w ratios. So annealing at 500°C was taken as the optimum RTP temperature for our experimental conditions, including the fixed 30 sec time, and further investigations of cell properties were carried out.

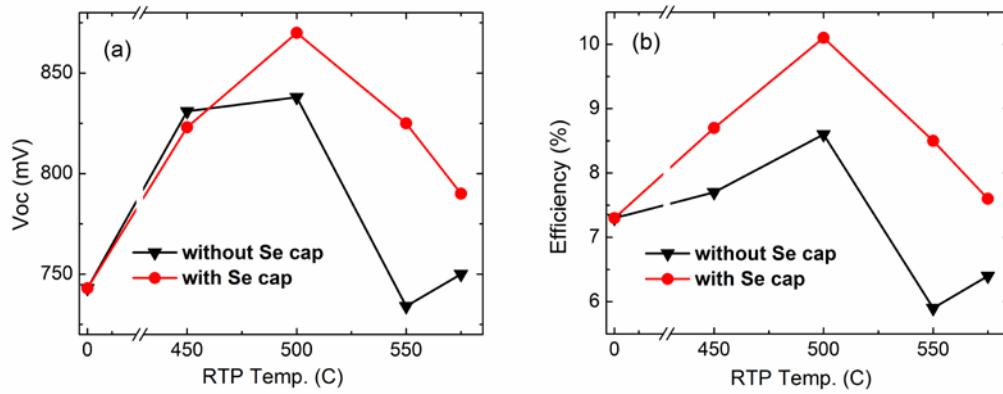


Figure D.2: Effect of RTP temperature and Se capping layer on the (a) V_{OC} and (b) efficiency, for a sample with $w=0.80$ and $x=0.78$. The reported values are maximum values of each device.

D.4 Structural Properties

Scanning electron microscopic images before and after RTP show that the surface structure of the sample has not been influenced much by the RTP (Fig. D.3). EDX analysis also didn't reveal any significant change in the composition of samples after RTP with/without Se cap.

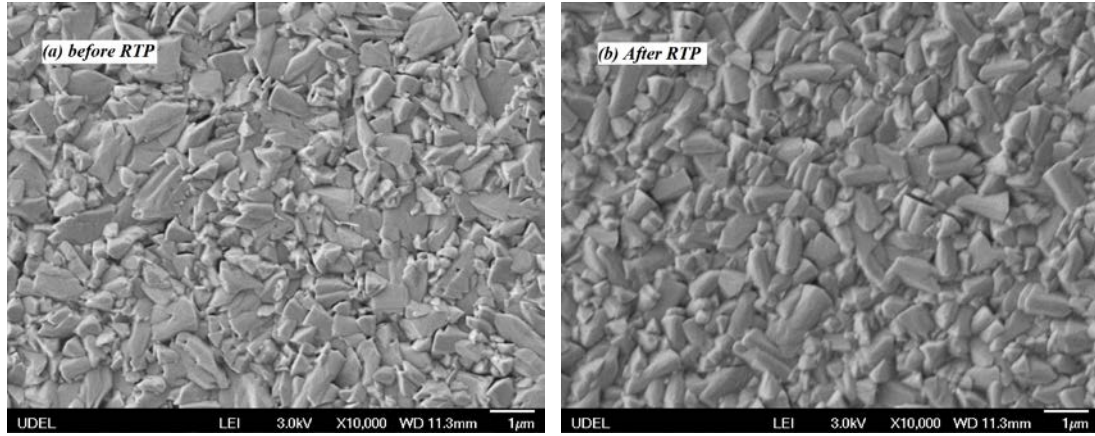


Figure D.3: Effect of RTP (without Se cap) on the structure of $(\text{Ag}_w\text{Cu}_{1-w})(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ sample with $w = 0.80$ and $x = 0.78$.

Recently, we reported [234] that $(\text{Ag}_w\text{Cu}_{1-w})(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ films with high Ga, $0.5 \leq x < 1$ and high Ag, $w > 0.5$ have additional x-ray diffraction peaks originating from the near-surface region of the film. Specifically, high resolution GIXRD patterns at different incident angles (Fig. D.4) showed a high-angle ($2\theta = 27.6^\circ$) satellite peak on the (112) reflection with higher intensity closer to the surface. This peak does not match any available ICDD diffraction cards for tetragonal or cubic quaternary, ternary, or sub-set binary phases or elements. In particular, it cannot be attributed to the $(\text{Ag}_w\text{Cu}_{1-w})(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ (103) peak which would be expected at $2\theta \approx 28.0^\circ$.

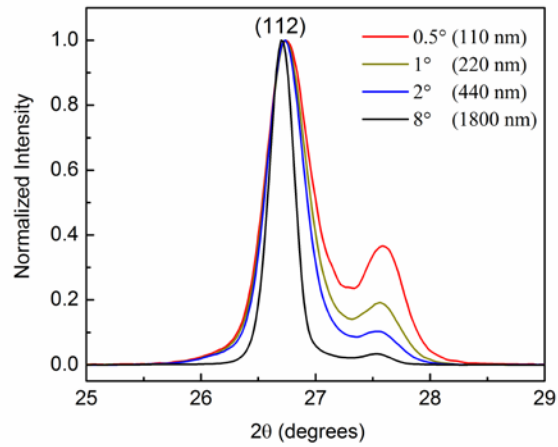


Figure D.4: GIXRD patterns at different incidence angles of the (112) peak of chalcopyrite phase, for an as-deposited sample with $x = 0.76$ and $w = 0.78$, with estimated sampling depth.

Detailed examination of broad-range diffraction patterns showed the consistent appearance of additional peaks at lower d-spacing than all chalcopyrite peaks, which tracked in d-spacing with alloy compositions w and x . This suggested the presence of a related phase having similar crystal structure and smaller lattice. Further, crystallographic analysis revealed that the unknown reflections were consistent with the crystal structure of the $I_1III_5VI_8$ ordered defect compound (ODC) phase. XPS analysis of the terminating surface also confirmed that $(Ag_wCu_{1-w})(In_{1-x}Ga_x)Se_2$ films with $0.5 \leq x < 1$ and $w > 0.5$, have compositions near the surface consistent with an ordered defect compound. All samples containing Ag with $0 < w < 1$ had surface composition consistent with $(Ag,Cu)(In,Ga)_5Se_8$.

Overall, RTP was found to decrease the intensity of satellite peaks in the near-surface region. Figure D.5 shows the effect of RTP at the $T = 500$ °C on an un-capped film with $x = 0.78$ and $w = 0.76$. RTP has decreased the intensity of the satellite peak

(ODC phase) as seen in the surface sensitive 0.5° GIXRD scan. For the bulk measurement at 8° there is negligible difference between the intensity of the ODC peak before and after the RTP.

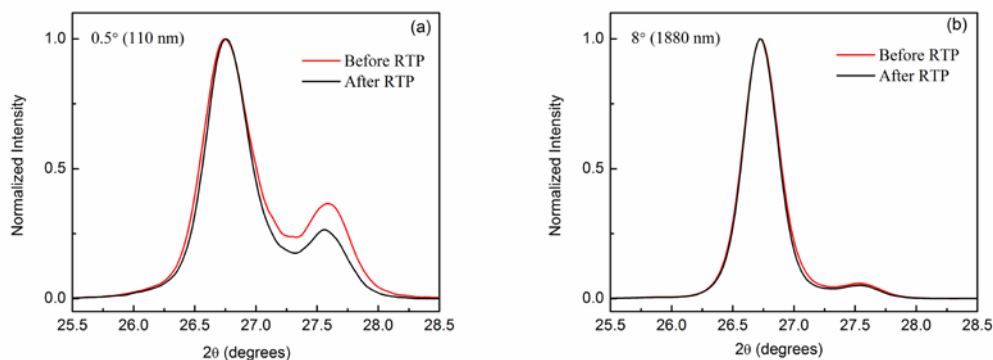


Figure D.5: XRD pattern of ACIGS sample with $x = 0.78$ and $w = 0.76$ before (red line) and after RTP (black line) for an incident angle of (a) 0.5° and (b) 8° .

On the other hand, RTP with the Se capping layer (Figure D.6) completely removed the secondary phase. Figure D.7 illustrates that the satellite ODC peaks beside other chalcopyrite peaks have been removed by the RTP as well. Each pattern was normalized to the (112) peak.

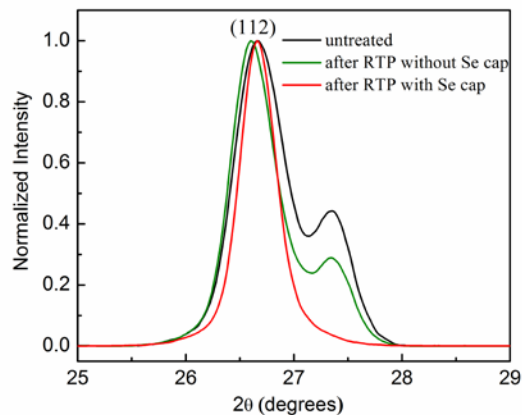


Figure D.6: GIXRD pattern of an ACIGS sample with $x = 0.78$ and $w = 0.76$; untreated (black), after RTP at 500°C without Se cap (green) and after RTP at 500°C with Se cap (red). The incident angle was 0.5° corresponding to a calculated penetration depth of 110 nm.

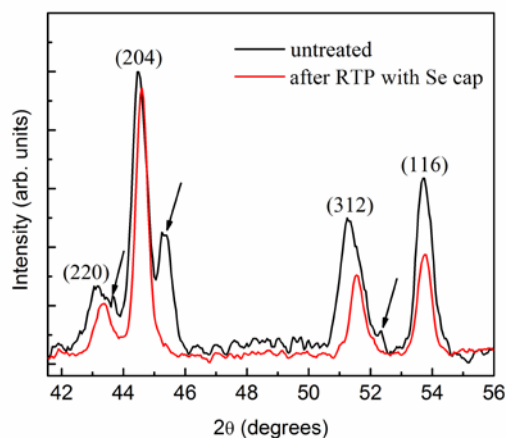


Figure D.7: GIXRD pattern of high-angle chalcopyrite peaks; representing the effect of RTP + Se cap. Arrows are showing the satellite peaks, corresponding to ODC phase. The incident angle was 0.5° corresponding to a calculated penetration depth of 110 nm.

D.5 Surface Properties

Figures D.8-10 show XPS depth profile results for three $(\text{Ag}_w\text{Cu}_{1-w})(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ films with $x = 0.78$ and $w = 0.8$, prior to RTP, after RTP with no Se cap, and after RTP with a Se cap. For depth profiling, the Ar^+ etch rate was about 1 nm/min and the data was normalized with respect to the EDX bulk composition at the deepest measured data point [215]. The effect of potential preferential sputtering was corrected by modification of relative sensitivity factors using the EDX normalization and was applied to all elements [135]. Abou-Ras et al. [216] have applied similar condition (2 kV ion energy with a 2 μA beam current) for sputter depth profiling of $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$ films and obtained good resolution depth profiles without noticeable surface artifacts.

The variation of the $(\text{Cu}+\text{Ag})/\text{Se}$ ratio is shown in Figure D.8. All samples show group I deficiency near the surface. However, the surface of the film treated by RTP with the Se cap has $(\text{Ag}+\text{Cu})/\text{Se} \approx 0.2$, while $(\text{Ag}+\text{Cu})/\text{Se} \approx 0.15$ for the raw and uncapped RTP samples. In Figure D.9, the $(\text{Ag}+\text{Cu})/(\text{Ga}+\text{In})$ ratio is shown for the same three films. In the near surface region, ~ 50 nm, this ratio appears slightly higher with the Se cap than on the as-deposited and uncapped films.

Thus, XPS results show that all samples have low group I content at the surface, consistent with the existence of an ODC surface phase, similar to what has been reported at the surface of $\text{Cu}(\text{In},\text{Ga})\text{Se}_2$ films [10]. However, RTP with excess Se has altered the elemental distribution producing films with less group I deficiency after processing consistent with a change from the composition of $\text{I}_1\text{III}_5\text{VI}_8$ compound to the composition close to that of $\text{I}_1\text{III}_3\text{VI}_5$ ODC phase. The creation of such defect phases accommodates the $(\text{Ag}+\text{Cu})$ deficiency in $(\text{Ag}_w\text{Cu}_{1-w})(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ films through modification of crystallographic ordering, in a manner analogous to that in the

CuInSe₂ system, in which various ODC phases such as Cu₂In₄Se₇, CuIn₃Se₅, and CuIn₅Se₈ were predicted [10,11].

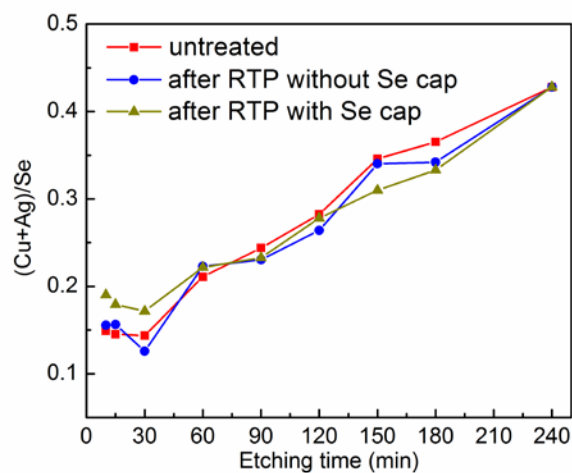


Figure D.8: XPS depth profiles of (Cu+Ag)/Se for alloy with $x = 0.78$ and $w = 0.8$.

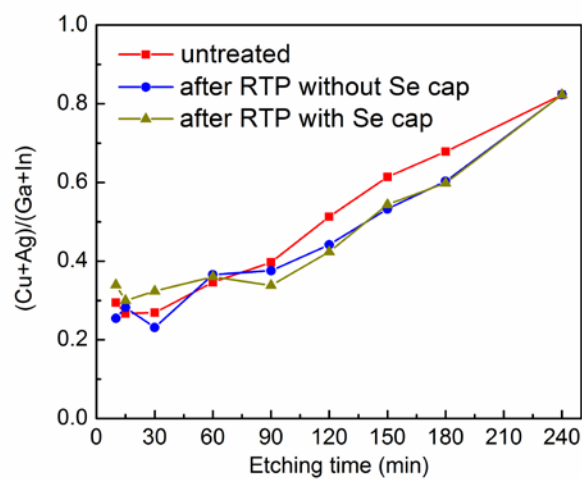


Figure D.9: XPS depth profile of (Cu+Ag)/(In+Ga) for alloy with $x = 0.78$ and $w = 0.8$.

Figure D.10 shows the variation of $\text{Ag}/(\text{Ag}+\text{Cu})$ through the films. For all films, the surface region is relatively Ag-rich compared to the bulk. Again, the $\text{Ag}/(\text{Ag}+\text{Cu})$ ratio is higher for the film treated with the Se cap compared to the other samples. The theoretical calculations by Maeda et al. [235] showed that the formation energy of V_{Ag} and $(2V_{\text{Ag}} + M_{\text{Ag}})$, where M represents the group III metals, are lower under Ag-poor condition compared to Ag-rich AgMSe_2 alloys. This is also true for CuMSe_2 alloys. Since the RTP + Se process was found to increase the group I concentration near the front surface (Figures D.8 and D.9), the formation of V_{Ag} and V_{Cu} is likely to be suppressed in those layers.

As the RTP has the potential of improving electrical properties of absorber layer by decreasing the amount of near surface defects, doing RTP with extra Se supply may have a beneficial effect on achieving desirable properties of $(\text{Ag}_w\text{Cu}_{1-w})(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ thin film solar cells. It is believed that RTP with extra Se supply changes the characteristics (ordering and composition) of defect phases resulting in enhancement of cell properties (specifically V_{OC} and Efficiency) and has the potential to improve the performance of wide bandgap chalcopyrite devices.

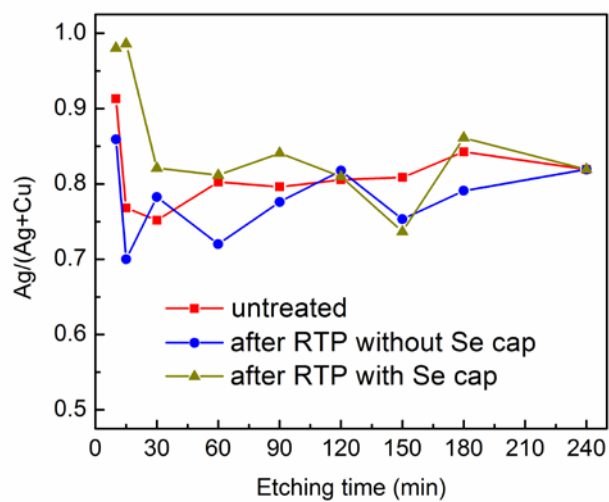


Figure D.10: XPS depth profile of Ag/(Ag+Cu) for alloy with $x = 0.78$ and $w = 0.8$.

Appendix E

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COMPLETE LIST OF AUTHORS: **Hamed Simchi, Kihwan Kim, Brian McCandless, William Shafarman, Robert Birkmire**

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