SINGLE-STAGE CO-EVAPORATION AND SURFACE

CHARACTERIZATION OF (AG,CU)(IN,GA)SE2 SEMICONDUCTORS FOR

SOLAR CELL APPLICATION

by

Kevin Jones

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ABSTRACT

Substituting Ag for some of the Cu in (Ag,Cu)(Ga,In)Se₂ solar cells may improve their performance. We have used photoelectron spectroscopy to study how this substitution changes the surface electronic structure of these compounds. The research is motivated by two factors: 1) decreasing the amount of Cu leads to less Se p- metal d hybridization, thereby lowering the valence band maximum (VBM), and 2) since the Ag4d level is deeper than the Cu3d level, the hybridization of Ag4d-Se4p results in a different VBM, further below the Fermi level than that in Cu-In-Ga-Se systems.

The VBM of CuInSe₂, Cu(In,Ga)Se₂, and AgInSe₂ single crystals were verified by angle-resolved photoemission spectroscopy. We show that AgInSe₂ has a VBM roughly 0.72eV below the VBM of Cu(In,Ga)Se₂ film and 0.66eV below CuInSe₂, with a total shift of 1.25eV below the Fermi level. Polycrystalline films of (Ag,Cu)(In,Ga)Se₂ were then fabricated by co-evaporation, and the valence band measurements confirmed the shift in the VBM of Ag polycrystalline alloys. X-ray photoemission spectroscopy and energy dispersive spectroscopy successfully identified the phase segregation between (Ag,Cu)(In,Ga)₃Se₅ (ordered vacancy compound - OVC) and (Ag,Cu)(In,Ga)Se. The phase segregation, as determined by composition, is apparent at all ratios Ag/(Ag+Cu) (AAC). Concomitant changes in electronic structure were verified by soft x-ray photoemission spectroscopy. Furthermore, increasing the Ga content, while keeping the Ag and Cu content constant in these alloys, also causes a decrease in the apparent presence of OVCs. In addition, we have evidence to support that these new surface (bulk-like) valence bands are most likely CuGaSe₂ and not CuInSe₂ related compounds.

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Chapter 1

INTRODUCTION

1.1 Solar Cells

Solar photovoltaic (PV) energy conversion is a simple process that generates electrical energy from light energy [1,2]. The main idea is based off the photoelectric effect, where normally, when light is absorbed by matter, electrons are displaced to higher energies and quickly relax back to their ground state [1-3]. For PV devices however, there is an integral device that pulls electrons away before they relax [1-4]. These excited electrons generate a potential difference, which is the force that drives the electrons through the external circuit [1-4]. High performing device is determined by the number of mobile electrons, where success of high performing devices is governed by the light absorbing material and the method of how such device is connected [1-3].

1.1.1 Thin-Film Solar Cells

Thin-film materials based on polycrystalline or amorphous semiconductors have been extensively studied for lower cost photovoltaics [2-3]. Many advantages include strong potential of deposition over large areas on cheap substrates (i.e. glass, plastic, or foil), and the potential of monolithic integration, which has major advantages in terms of robustness, ease and speed of fabrication, and the relatively small area required for the interconnects [1-3]. The main disadvantage is lower power

1

conversion efficiency, mainly from poor charge transport properties. To compensate for the disadvantage, suitable materials must have high optical absorption, in which for amorphous thin-films, amorphous silicon (a-Si) is the leading material, and for polycrystalline thin-films, cadmium telluride (CdTe) and copper indium gallium diselenide (CIGS) are the leading materials [1-4].

For chalcopyrite-based cells, a high efficient cell of Cu(In,Ga)Se₂ normally have a band gap between 1.0-1.2, with Ga/(Ga+In) (GGI) ratio between 0.1 - 0.3 (best efficiency 22.6% ± 0.5). To increase the band gap, Ga can be added which can tune the energy band gap from 1.04-1.68eV [1-5]. Unfortunately, wider band gaps of CIGS have poor device performance, therefore, the aim of this study is to investigate ways to improve wider band gap absorbers based on CIGS system.

1.2 Cu(In,Ga)Se₂ Solar Cells

Cu(In,Ga)Se₂ (CIGS) remains one of the most promising semiconductors for thin film photovoltaics [5-7]. Its solar cells and modules have shown great long-term stability in outdoor settings and have shown to have potential terrestrial applications [8-10]. CIGS also can be made lightweight and flexible, which has been suggested to be used on mobile homes and commercial buildings [9,10].

The base material CuInSe₂ was first synthesized in the 1950s, along with other ternary chalcopyrite materials [11,12]. Many years of researching lead to the first high-efficient 9.4% thin-film solar cell based off CIGS technology in the year 1981 [13]. Such device used a coevaporation method to fabricate the CIGS absorber, which is a technique to fabricate high efficient solar devices, along with other depositions methods (reactive sputtering, hybrid sputtering, closed-space sublimation, chemical bath deposition, laser evaporation, and spray pyrolysis) [14-20].

Figure 1 displays a typical heterostructure solar cell based on polycrystalline thin-films that consist of the following structure: glass-substrate/back contact/absorber/window/transparent conducting oxide/metal grid, with the materials: soda-lime glass/Mo/CIGS/CdS/ZnO-ITO/Ni-Al Grid.



Figure 1 Schematic outline of a Cu(In,Ga)Se₂ substrate-type solar cell

The film thickness of the absorber layer is typically around 1.5-2µm, which is enough to absorb most of the photons incident from the sun. CIGS is deposited on a sodalime glass, coated with a sputtered Mo layer as a back contact. A p-n junction is formed by chemical bath deposition of CdS with a thickness of 50nm, followed by a radio frequency (RF) sputter of a high-resistant ZnO layer and a doped high-conductivity ZnO layer.

In the CIGS solar cell, high energy ($E_g > 2.4 eV$) photons are absorbed by the CdS window (buffer layer) and low energy photons are transmitted and absorbed by the absorber, which creates photoelectrons [1-4]. The excited electrons can either

dissipate the energy as heat, emit light, or travel through the cell until it reaches an electrode, and participate in the solar circuit [1-4].

1.2.1 Material Properties

The base material CuInSe₂ has the chalcopyrite lattice structure. The chalcopyrite structure is a diamond-like structure with ordered Cu, In and Se elements. This ordering gives a tetragonal unit cell, shown in Figure 2.



Figure 2 Chalcopyrite crystal structure of CuInSe₂. Reprinted with permission [5].

In Figure 3, a phase triangle of Cu, In, and Se elements in a ternary compound is shown. The possible phases lie along the Cu₂Se-In₂Se₃ tie line, which is near the chalcopyrite CuInSe₂ [5,21]. Ordered vacancy compounds of CuInSe₂ are also close to this tie line, which the stable compounds have been found to be CuIn₃Se₅, CuIn₅Se₈ and Cu₃In₅Se₉ [5,21]. The chalcopyrite phase in Figure 4 is denoted as α , and other phases are CuIn₃Se₅ (β), CuIn₅Se₈ (χ), and a high temperature phase that modification of both CuInSe₂ and CuIn₃Se₅ [22]. The existence range of the β -phase extends from a Cu content of 10.5 – 16.0 at%, and the α -phase has a smaller but measurable existence range of 24 – 24.5 at%. Materials with a Cu content \geq 25 at% (the nominal composition of CuInSe₂) are not single phase but includes binary phases of Cu-Se (Cu₂Se) [22]. Typical samples are usually fabricated with a Cu content less than 24 at%, which contains a mix of α + β phases [5,22].



Figure 3 Phase triangle of Cu, In, and Se atoms. The tie line of Cu₂Se-In₂Se₃ connect phases CuInSe₂. Reprinted with permission [5].



Figure 4 Pseudobinary equilibrium phase diagram of In_2Se_3 -Cu₂Se. The following are represented phases: α -phase is the CuInSe₂ chalcopyrite phase, β is the ordered defect phase, and δ -phase is the high-temperature sphalerite phase. Cu₂Se(HT) and Cu₂Se(RT), high-temperature (HT) and room temperature (RT), exist at higher amounts of Cu at%. Reprinted with permission [5].

The α -phase in Figure 4 can be increased by CuInSe₂ alloying with Ga [5,23,24]. This is mostly due to the high formation energy of the defect complex $(2V_{Cu} + Ga_{Cu})$ when compared to $(2V_{Cu}^- + In_{Cu}^{2+})$ [1-4,5,24]. In CuInSe₂, preferential formation of electrical neutral defect complexes: $(2Cu_i^+ + Cu_{In}^{2-})$, $(Cu_{In}^{2-} + In_{Cu}^{2+})$, $(2V_{Cu}^- + In_{Cu}^{2+})$ give rise to ordered vacancy compounds (OVCs) [25]. Amongst these complexes, $(2V_{Cu}^- + In_{Cu}^{2+})$ has the lowest formation energy, in which a periodic repetition of this complex gives rise to a secondary phase (Figure 5) [25]. OVCs in CuGaSe₂, however, do not form as easily as they do in CuInSe₂ [24]. The reduced tendency to form OVCs in CuGaSe₂ is due to the high defect formation energy of Ga_{Cu}

antisite defect. In comparison, the Ga_{Cu} to In_{Cu} has a 17:1 defect formation energy measured in (eV). Less formation of OVCs of CuGaSe₂ have been suggested why CIGS solar cells are not as efficient at higher Ga content, however little is still known [26], therefore, more needs to be understood with the OVCs on the surfaces of Cuchalcopyrite.



Figure 5 1D view of OVC layer surface forming on bulk CIGS by periodic repetition of $(2V_{Cu} + In_{Cu})$ defect complex. V_{Cu} = vacancy copper and In_{Cu} = In on Cu antisite defect



Figure 6 1D view of OVC layer surface forming on bulk CuGaSe₂ by periodic repetition of $(2V_{Cu} + Ga_{Cu})$ defect complex. V_{Cu} = vacancy copper and Ga_{Cu} = Ga on Cu

1.3 CuInSe₂ Valence Band

In CuInSe₂, the valence bands (VBs) are dominated by Cu3*d*-Se4*p* interactions, leading to antibonding, nonbonding and bonding regions [24,25]. The upper VB is profoundly influenced by the proximity of noble metal d-levels, which hybridizes with the p-levels of Se. This hybridization has been observed to reduce the band gaps of the chalcopyrites relative to their binary analogues [25]. For CuInSe₂, this p-d hybridization (repulsion) is considered strong and pushes the VBM closer to the Fermi level as opposed to its OVCs (CuIn₃Se₅ and CuIn₅Se₈) [25,40]. In OVCs, for example CuIn₅Se₈, three Cu atoms in each unit cell are replaced by two V_{Cu} and one In_{Cu}, thus the p-d hybridization (repulsion) is weaker, and lowers the VBM, shown in Figure 10 [25]. The strength of the repulsion can be shown by the Cu/(Cu+Se) ratio, in which for CuInSe₂ is obviously greater than both OVCs, therefore the VBM is closer to the Fermi level at higher ratios of Cu/(Cu+Se) (Figure 7) [25].



Figure 7 A comparison of measured valence band maxima of OVCs to the parent CuInSe₂. VBM positions from reference [25]

The main idea in Figure 7 is to show that the decrease in Cu content lowers the VBM. By alloying CuInSe₂ with AgInSe₂, some Cu atoms will exchange with Ag, therefore forcing a reduction of Cu content. The p-d hybridization of Ag4d-Se4p is believed to be much lower than the Cu3d-Se4p hybridization, which is based off the atomic subshell of Ag4d being much lower than Cu3d (Hartree-Fock-Slater binding energy Ag4d - 12.6eV, Cu3d - 10.1eV) [41]. Therefore, the VBM should be lower for Ag fractions of CuInSe₂, CuIn₃Se₅ and CuIn₅Se₈ in two ways. First, a reduction of copper content would lead to a reduced Se *p*-Cu *d* hybridization (weaker repulsion), and second, the VBM formed with the Ag-Se hybridization is further away than CuInSe₂, CuIn₃Se₅ and CuIn₅Se₈. A comparison of the Cu-Se and Ag-Se bonding is depicted in Figure 8.



Figure 8 A schematic of the molecular interaction diagram of Cu-Se and Ag-Se from CuInSe₂ and AgInSe₂ compounds

In this work, we primarily focus on the changes in the valence region via photoemission spectroscopy of different Ag and Ga fractions in Cu-In-Se materials. The following is expected: Ag replacing Cu lowers the position of VBM; AgInSe₂ and CuInSe₂ both should have distinctive valence spectra, therefore, the corresponding OVCs (i.e. CuIn₃Se₅ and AgIn₃Se₅) should both show less *d*-like character; Ga replacing In should show no changes in VBM position and no changes to the upper valence spectra.

1.4 Proposed (Ag,Cu)(In,Ga)Se₂ for Wide Band Gap Absorber

Improved performance of wide bandgap cells using $(Ag,Cu)(In,Ga)Se_2$ have been studied recently, and has shown great promise as a candidate for Cu-chalcopyrite wide band gap absorber [42,43]. Institute of Energy Conversion (IEC) has demonstrated that Ag alloying can reach cell efficiencies of 19.9% with a V_{OC} of 730mV, with this absorber having a measured band gap of 1.2eV [44].

This work pertains to the relative Ga and Ag alloying fraction in the ACIGS absorber to produce wider band gap absorbers of single-stage co-evaporated (Ag,Cu)(In,Ga)Se₂ films, which are addressed by fundamental characterization: x-ray photoelectron spectroscopy (XPS), soft x-ray photoelectron spectroscopy, ultra-violet photoelectron spectroscopy (UPS), angle-resolve photoemission spectroscopy (ARPES), energy dispersive spectroscopy (EDS) and x-ray diffraction (XRD). The subsequent chapters/sections will discuss the following:

- Brief introduction to Ag alloys of CIGS
- Relevant photoemission spectroscopy work on Cu-chalcopyrite and background
- Materials, deposition and characterization methods

- Single crystal study of CuInSe₂, AgInSe₂ and Cu(In,Ga)Se₂
- Evidence of OVCs in ACIGS
- Surface contribution of *d*-orbital (Ag4*d* and Cu3*d*)
- Discussion
- Conclusion and future work

Chapter 2

BACKGROUND

2.1 Review on Ag Alloys of Cu(In,Ga)Se₂

An apparent method to further improve device efficiencies of solar cells is to increase the band gap (E_g) to better match the AM1.5 solar spectrum (optimal E_g approximately 1.40eV) [45]. The E_g of group I-III-VI₂ can easily be tuned to the optimal E_g , specifically Cu(In_{1-x}, Ga_x)Se₂, where x = 0.6 (corresponding to a E_g of 1.40eV). One of the drawbacks however, is that single junction solar cells based on wide-band gaps of group I-III-VI₂ tend to show lower device performance as compared to those based on low-band gap group I-III-VI₂ [46].

Recent studies of Ag alloys of CIGS have been sought after for potential wide band gap absorbers, though Ag-alloying does not increase E_g much [42,43]. Considerations in device performance, film morphology, grain size, structural and optical properties from varies studies all have indicated the promise ACIGS have for wide band gap solar cells [42,43,47]. CIGS solar device with Ga content 0.3 < GGI < 0.5 can tolerate Ag incorporation up to Ag/(Ag+Cu) (AAC) = 0.5 without appreciable performance loss [47]; tetragonal distortion induced by substitution of Ag onto Cu sites causes the crystal field splitting to change from slightly positive to negative [42]; and Ag alloying induces significant recrystallization in the bulk as compared to its CIGS counterpart, with comparable improvement in device performance [43,48]. The best efficiency of ACIGS is 19.9% at Institute of Energy Conversion at University of Delaware [44], and 21.1% at Uppsala University, both used the established 3-stage coevaporation method [69].

2.2 Surfaces of Cu-Chalcopyrite

XPS work on CuInSe₂ has shown that the surfaces contain Cu-poor composition, closely in the form of CuIn₃Se₅ [31,40]]. It is now apparent that the surface composition is noticeably different than the bulk in CuInSe₂. The reduced Cu content on the surface is attributed to the low defect formation energy of V_{Cu} [25]. Other OVCs, such as CuIn₅Se₈ has not been observed on the surface yet, therefore it has been suggested that the surface composition stops at CuIn₃Se₅ [51]. When Ga is added to CuInSe₂, OVCs still appear on the surface, however, its appearance tends to fade out at higher Ga content [26]. It is most likely due to the surplus of CuGaSe₂ compound formation due to the high defect formation energy of Ga_{Cu} [24].

A recent work on $(Ag,Cu)(In,Ga)Se_2$ films with 0.5 < Ag/(Ag+Cu) < 1 and 0.5 < Ga/(Ga+In) < 1 revealed that a secondary phase with high group I deficiency forms near the surface, mostly in the form of $(Ag,Cu)(In,Ga)_5Se_8$ [70]. A combination of XRD and XPS depth profiling were used to characterize samples. We used a similar method of defining the $(Ag,Cu)(In,Ga)_5Se_8$ composition, in which we found the $(Ag,Cu)(In,Ga)_5Se_8$ composition mostly for AAC = 0.3 - 0.5 and GGI = 0.3-0.8 ratios, and $(Ag,Cu)(In,Ga)_3Se_5$ for AAC = 0.0 and 0.8 and GGI = 0.3-0.8 ratios. The valence band of $(Ag,Cu)(In,Ga)Se_2$ and $(Ag,Cu)(In,Ga)_5Se_8$ should also be dramatically different, as in the case of CuInSe₂ and CuIn₅Se₈ calculated density of states [25]. In Chapter 5, we show that Ag-d measured valence bands are unchanged at varying AAC and GGI ratios. The overall shape shows strong resemblance of AgInSe₂ calculated density of states [63], however does not agree with the surface composition we measured. Further verification in the valence band shape of AgIn₃Se₅ or AgIn₅Se₈ calculated density states is needed.

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When CIGS is exposed to the atmosphere for a long time, the surface oxidizes in the form of In_2O_3 , Ga_2O_3 and SeO_x , and small traces of Na atoms [53]. This long exposure causes the natural forming CuIn₃Se₅ (OVC) compound to "experimentally" disappear. Typically, for full devices, the composition of CIGS samples is measured immediately after absorber deposition, followed by a chemical bath deposition of CdS, which overall eliminates the possibility of a thick oxide layer forming. For surface studies of polycrystalline and single crystals however (for this work), the internal surfaces were exposed by fracturing the material in a nitrogen-filled atmosphere (fractured at the ACIGS/Mo interface, looking at the ACIGS side of the fracture) or a chemical etch of the capping layer, and immediately transferred into vacuum system. This lead to minimum exposure to air.

2.3 Photoionization Cross Section

Understanding the contributions of the *d*-orbitals from Cu3*d* in the valence band is difficult to interpret in the presence of Ag4*d* while using Al or Mg K α X-rays. This could be understood by the atomic subshell photoionization cross sections. Photoabsorption cross sections have been studied extensively by J.J. Yeh and I. Lindau [41]. It was found in their work that the photoionization cross section of atomic subshells is vastly energy dependent. Knowledge of the energy dependence of subshell photoionization cross section is of great value and necessity for many spectroscopic experiments on materials.

In Figure 9, it shows the complete cross section for Ag4*d*, Cu3*d*, Ga4*s*, In5*s* and Se4*p* from discrete line sources and some intermediate photon energies from synchrotron radiation: 8047.8 (CuK α) – not included, 1486.6 (Al K α), 1253.6 (Mg K α), 1041.0 (Na K α), 151.4 (Zr M ζ), 132.3 (Y M ζ), 40.8 (He_{II}), 26.8 (Ne_{II}), 21.2

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(He_I), 16.7 (Ne_I) and 10.2 (H) eV [41]. The cross sections are visually unnoticeable at higher energies in Figure 9. Figure 10 enlarges the cross sections at the higher photon energies and shows the dominance of Ag4*d* cross section. This Ag4*d* cross section of photon energy 1253.6eV (Mg K α) explains the overall appearance of the valence spectra's have more Ag-like characteristics, than Cu-like characteristics.

In Figure 9, it was noticed that the cross section of Cu3*d* increases at lower photon energies. To investigate the contributions of Cu3*d* in the valence region more clearly, other competing orbital's cross section need to be much lower than Cu3*d* cross section. The point where Cu3*d* is most dominant appears around the dip of Ag4d's cross section around hv = 120eV (Figure 11). The ratio of Cu3*d* to Ag4d cross section is 25.95 at hv = 120eV, which has the largest proportion amongst any other photon energy. At this energy, the d-orbitals of Cu3*d* is isolated more clearly, therefore the valence band would have more Cu-like rather than Ag-like characteristics. We investigated the valence region of polycrystalline (Ag,Cu)(In,Ga)Se₂ materials using hv = 120eV.



Figure 9 Complete photoionization cross section of Ag4*d*, Cu3*d*, Ga4*s*, In5*s*, and Se4*p* at photon energies of 1486.6 (Al K α), 1253.6 (Mg K α), 1041.0 (Na K α), 151.4 (Zr M ζ), 132.3 (Y M ζ), 40.8 (He_{II}), 26.8 (Ne_{II}), 21.2 (He_I), 16.7 (Ne_I), 10.2 (H) eV, and synchrotron-based radiation for selected photon energies [41].



Figure 10 Photoionization cross section of Ag4*d*, Cu3*d*, Ga4*s*, In5*s*, and Se4*p* between 1100 to 1500 photon energies [41].



Figure 11 Photoionization cross section of Ag4*d*, Cu3*d*, Ga4*s*, In5*s*, and Se4*p* between 50 to 850 photon energies [41].

Chapter 3

MATERIALS AND METHODS

3.1 Evaporation Methods

3.1.1 Single-stage Co-evaporation for Polycrystalline Films

All polycrystalline thin-film materials were supplied at IEC. Films were deposited by thermal coevaporation from elemental sources. A typical setup is illustrated in Figure 12. The thermal technique uses line-of-sight delivery of Ag, Cu, In, Ga and Se from Knudsen-type effusion cells to the heated substrate. Typical ranges of melts are $1300 - 1400^{\circ}$ C for Cu, $1000 - 1100^{\circ}$ C for Ag, $900 - 1100^{\circ}$ C for In, $1100 - 1250^{\circ}$ C for Ga and $300 - 350^{\circ}$ C for Se (with the substrate temperature (T_{SS}) $500 - 580^{\circ}$ C). The main advantage of elemental coevaporation for depositing films is the flexibility to choose the process specifics and to control film composition. For this project, the aim was to investigate the manifestation of natural grown surface phases at different Ga and Ag fractions.



Figure 12 Schematic of thermal evaporation source. Reprinted with permission [5].

3.1.2 Hybrid Sputter Deposition

Single crystal films were grown and supplied by Rockett Research Group, Thin-film Photovoltaics, University of Illinois, at Urbana-Champaign [55,56]. Samples were prepared by hybrid sputter deposition on GaAs(111)_b and p-GaAs(100). On the GaAs(100) substrate, CuInSe₂ grows preferentially with a c-axis orientation parallel to the surface normal, which has been shown by reflection high-energy electron diffraction, resulting in a (001) orientation of film growth [57]. For the GaAs(111), (112) planes grow preferentially [57].

3.2 Analysis Tools

3.2.1 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was mainly used to study the surfaces of cleaved films, in which the primary XPS used for this project is the PHI 5600 XPS. Table 1 list the surface concentration of each polycrystalline sample studied.

XPS generates X-rays by bombarding a metallic anode with energetic electrons [58]. The anode material is usually Al or Mg, however other possible anodes for XPS are listed in Table 1 [58]. The choice of anode material for XPS determines the energy of the X-ray transition generated. The photon must be high enough to excite an intense photoelectron peak from all elements and possess a natural X-ray line width that will not broaden the resultant spectrum too much. The most used anodes are the Mg and Al. A typical setup of a twin anode configuration is shown in Appendix, where the single X-ray gun provides AlK α and MgK α photons of energy 1486.6eV and 1253.6eV respectively. One major benefit of both Al and Mg sources is the ability to differentiate between Auger and photoelectron transitions when the two overlaps in one radiation. XPS peaks will shift to a position 233eV higher on a kinetic

energy scale switching from AlK α and MgK α , whereas the energy of Auger transition remains constant. On a binding energy scale, the reverse happens.

			Full-width half
Element	Line	Energy (eV)	maximum (eV)
Y	Μζ	132.3	0.47
Zr	Μζ	151.4	0.77
Mg	Κα _{1,2}	1253.6	0.7
Al	Κα _{1,2}	1486.6	0.9
Si	Κα	1739.6	1.0
Zr	Lα	2042.4	1.7
Ag	Lα	2984.4	2.6
Ti	Κα	4510.9	2.0
Cr	Κα	5417.0	2.1

Table 1Alternative anode materials for XPS [58]

The PHI 5600 is also equipped with a monochromator (Appendix). The purpose of an X-ray monochromator is to produce a narrow X-ray line by using diffraction in a crystal lattice. Most commercially available X-ray monochromators, including the PHI 5600, uses a quartz crystal ($10\overline{1}0$) as the diffraction lattice [58]. Radiation which can be produced using a quartz crystal is capable with select materials, provided in Table 2. The advantage for using X-ray monochromator is the reduction in X-ray line width, for example, from 0.9eV to nearly 0.25eV for AlK α . Narrower line widths allow for better chemical state information. Three other advantages of monochromatic source are listed below

- Satellite peaks and bremsstrahlung continuum are removed
- Thermally induced damage is avoided due to the heat created by the monochromator being remote as compared to the twin source, usually

positioned close to the sample. This means the sample is therefore exposed to the radiant heat.

• Small are XPS can be conducted with high sensitivity

Table 2Radiation produced by quartz crystal monochromator [58].

Diffraction Order	X-ray Line	Energy (eV)
1	AlKa	1486.6
2	AgLα	2984.3
3	ΤίΚα	4510.0
4	CrKβ	5946.7

3.2.1.1 Photoemission Spectroscopy Continued

According to commonly used models, three different energy regions for the exciting radiation can be distinguished [59]:

- hv < 20eV is the ultraviolet photoemission spectroscopy (UPS) regime
- 20eV < hv < 200eV is the soft XPS regime
- hv > 200eV is the XPS regime

UPS has the same principles as XPS, with the only difference is the ionizing radiation energies. To induce the photoelectric effect, XPS typically uses photons of energy greater than 200eV, while UPS has photons of energy less than 20eV. In a lab setting, ultraviolet photons are created by a gas discharge lamp filled with helium, where the emitted photons have energies of 21.2eV (He I) and 40.8eV (He II). At these low photon energies, core level photoemission is not accessible, making UPS acquisition limited to the valence band region.

Many of the molecular orbitals from which valence band photoelectron signal originates possess a high degree of hybridization, therefore the shifts in peak binding

energy are far more varied and subtle than those observed for core level photoemission peaks. This very reason predominately makes valence band spectra used for material identification through spectral fingerprinting, and individual peak assignments is either performed on surfaces with well-known electronic structure or agrees with related computational studies. Assignments of valence band peaks can be ambiguous however, therefore is never used for quantification purposes.

UPS is more surface sensitive than XPS. The inherent surface sensitivity of XPS is due to the short inelastic mean free path (IMFP, λ) of free electrons within a solid, with the so-called information depth from which > 99% of a photoemission signal originates conventionally being defined at 3λ , which in XPS is usually ~ 10nm [58]. The lower incident photon energies used in UPS emit photoelectrons of much lower kinetic energies, therefore an approximated information depth is usually ~ 2 – 3nm.

Soft X-rays and Ultraviolet radiation experiments were both performed at Stanford Synchrotron Radiation Laboratory (SSRL). Beamline 8-1 was for soft Xrays, which this beamline is equipped with a 6m toroidal grating monochromator, with a provided energy range 15 – 185eV (120eV excitation for reported work). Calibration of the Fermi energy (E_F) was performed periodically with a clean Au film. Ultraviolet radiation experiment was performed on beamline 5-4. This beamline produced a spot size $\geq 0.1 \times 0.1 \text{mm}^2$ with a resolution $\geq 5 \times 10^{-5} (\Delta \text{E/E})$. The energy range is 16-40eV (17-40eV excitation for reported work).

3.2.2 Energy Dispersive Spectroscopy

Energy Dispersive Spectroscopy (EDS) is analytical technique we used for bulk elemental analysis, where the Amray 1810T Digital Scanning Electron

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Microscope (15X to 100,000X) with EDS and Electron Back-Scatter Imaging capabilities, with a sampling depth 0.5µm at 20kV. One of the main differences between EDS and XPS is that EDS measures X-rays emitted from a sample, while XPS measures photoelectrons. The technique of EDS involves a high-energy beam of electrons is irradiated onto a sample. The process then relies on the uniqueness of characteristic X-rays of each element. Table 3 list the surface and bulk concentration of polycrystalline samples studied.

	Concentrations (%)									
Samples	Ag%		Cu%		In%		Ga%		Se%	
	Bulk	Surf.	Bulk	Surf.	Bulk	Surf.	Bulk	Surf.	Bulk	Surf.
GGI(0.0)AAC(0.0)	0	0	23.3	13.5	26.1	29.3	0	0	50.7	57.2
GGI(0.0)AAC(0.3)	6	8.2	16.3	6.7	25.7	30.3	0	0	52	54.9
GGI(0.0)AAC(1.0)	23.3	9.7	0	0	25.7	31.9	0	0	51	58.4
GGI(0.3)AAC(0.0)	0	0	23.6	13.2	17.5	24.7	7.7	2.9	51.3	59.2
GGI(0.5)AAC(0.0)	0	0	22.9	11	13.3	17.1	12.4	6.6	51.3	65.4
GGI(0.8)AAC(0.0)	0	0	21.9	6.2	4.9	10.3	20.5	9.9	52.7	73.6
GGI(0.3)AAC(0.3)	6.2	7.5	15.5	1.6	18.2	17.3	7.7	5.4	52.4	68.2
GGI(0.5)AAC(0.3)	5.9	7.8	16.3	1.4	12.8	13.9	12.8	8	52.2	68.9
GGI(0.8)AAC(0.3)	5.7	8	15.2	6.1	4.9	6.1	21.6	13.3	52.6	66.5
GGI(0.3)AAC(0.5)	12	10.4	10.6	2.4	18.3	23.4	8.9	4.8	50.2	58.9
GGI(0.5)AAC(0.5)	9.1	9	10.7	1.7	13.6	12.2	13.4	9.3	53.3	67.7
GGI(0.8)AAC(0.5)	10.8	9.6	10.8	2	4.4	7.9	21.3	11.2	52.6	69.3
GGI(0.3)AAC(0.8)	15.3	12.5	4.7	1.5	18.4	21.4	8.1	5.9	53.5	58.7
GGI(0.5)AAC(0.8)	16.3	12.7	5.1	1.2	12.5	12.9	13.9	12.2	52.2	60.9
GGI(0.8)AAC(0.8)	16.8	12.2	5.3	1.6	4.9	6.7	20.6	10.7	52.4	68.8

Table 3Surface and bulk concentration of polycrystalline samples. Measured by
XPS and EDS.

3.2.3 X-ray Diffraction

X-ray diffraction (XRD) served as a source of data primarily for phase identification of crystalline material. The fundamental principles of XRD is based on constructive interference of monochromatic x-rays and a crystalline sample. These Xrays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy **Bragg's Law** ($n\lambda=2d \sin \theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted.

3.2.4 Angle-Resolved Photoemission Spectroscopy

Angle-resolved photoemission spectroscopy (ARPES) has become one of the leading tools for photoemission on solid systems. Today, ARPES experiments have resolutions well below 2meV and 0.2° angular, which is a major improvement from two decades ago. ARPES plays a major role in superconducting, conducting, semiconducting and insulating materials, because it is the most direct method of studying the electronic structure of solids. One major drawback of ARPES is the extreme surface sensitivity. The mean free path for unscattered photoelectrons is characterized by a minimum of approximately 5Å at 20-100eV kinetic energies, which are typical value in ARPES experiments. Therefore, to derive information about the bulk electronic structure, ARPES experiments must be performed on atomically clean and well-ordered systems in ultra-high vacuum conditions (pressures lower than 5 x 10^{-11} torr).

ARPES works by a beam of monochromatized radiation supplied by either a gas-discharge lamp or by synchrotron beamline is incident on a sample, which the sample must be a properly aligned single crystal (the only way to perform momentum resolved measurements). Collecting the photoelectrons with an electron energy analyzer characterized by a finite acceptance angle allows one to measure the kinetic

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energy (E_{kin}) of the photoelectrons for a given emission angle. Thus, the photoelectron momentum (p) can be determined by

$$p = \sqrt{2mE_{kin}} \tag{1}$$

and the components parallel and perpendicular to the sample surface can be obtained from the polar (ϑ) and azimuthal (ϕ) emission angles. The E_{kin} of the photoelectrons can be related to the binding energy (E_b):

$$E_{kin} = h\nu - \phi - |E_B| \tag{2}$$

The momentum component parallel to the surface is conserved, therefore can directly be calculated:

$$k_{\parallel} = \frac{2\pi}{\hbar} \sqrt{E_{kin}} \sin \vartheta \tag{3}$$

The perpendicular component however is not conserved across sample surface (mostly due to lack of translational symmetry along the surface normal). This effect is accounted for by the inner potential V_0 , and with the approximation of free-electron-like final states, the k_{\perp} value can be calculated:

$$k_{\perp} = \frac{\sqrt{2\pi}}{\hbar} \sqrt{E_{kin} \left(\cos\vartheta\right)^2 + V_0} \tag{4}$$

Therefore, the k-resolved band structure perpendicular to the surface of the sample can directly be obtained by variation of the photon energy. For k-resolved band structure parallel to the surface of the sample, the photoemission paths are accessed by a variation of the emission angle.

In the ARPES chapter, the paths of k_{\perp} scans performed in normal emission on (112) AgInSe₂, and (001) CuInSe₂ and (001) Cu(In_{0.5}Ga_{0.5})Se₂ surfaces by variation of the photon energy (hv = 17 – 40 eV). Each sample was capped with a thin CdS layer (15-20nm), with AgInSe₂ sample thickness in between 800-900nm and both CuInSe₂ and Cu(In_{0.5}Ga_{0.5})Se₂ with a sample thickness of 700nm. For direct comparisons with

other measured and calculated band structures, we used the inner potential value ($V_0 = 1.0eV$) from Andreas Hofmann et al [57]. Crystallinity of samples were checked by X-ray diffraction, depicted in Figure 32. At the time of experiment, the low-energy diffraction (LEED) tool was not operational, therefore reconstruction images could not be obtained. However, it should be noted that a (4x2) reconstruction is preferred for (001) Cu-chalcopyrite and a hexagonal-like pattern reconstruction is preferred for (112) Cu-chalcopyrite materials. Both reconstructions permit distinctive energy dispersions, which we measured and compared to previous Cu-chalcopyrite ARPES studies, in which all spectral features are in great agreement with other works [57].



CasaXPS (K. Jones)

Figure 13 XRD survey of AgInSe₂ (112) (black), Cu(In_{0.5}Ga_{0.5})Se₂ (001)(red), and CuInSe₂ (001) (blue) single crystals.

To prepare the single crystal samples for photoemission studies, two methods were attempted. The first method we capped each single crystal sample with a thin layer of Se, which was flashed off by annealing, and the second method we capped each single crystal with a CdS layer and etched this layer off with a diluted HCl solution. For CdS-capped, this method required an extra-large glove bag to fit around the intro chamber, in which we purged nitrogen into bag and performed the etch. Additional heating was used to get rid of extraneous contamination.

Figure 14 and 15 shows the photoemission interface snapshot of the Se-capped and CdS-capped layers. Figure 14c and 15c shows the photoemission spectra of CdScapped and Se-capped. The y-axis is the kinetic energy, in which subsequent photoemission spectra in this work will use equation 5 to convert the kinetic energy to binding energy – also we reverse the axis

$$E_{B,E} = E_P - (E_{K,E} + \phi) \tag{5}$$

where $E_{B,E}$ is the binding energy (BE) of the electron, E_P is the energy of the X-ray photons being used, $E_{K,E}$ is the kinetic energy of the electron as measured by the instrument and ϕ is the work function dependent on both the spectrometer and the material, which the $\phi = 4.355$ eV.

Unfortunately, the Se-capped was unsuccessful. The main issue we believe was with the beamline's heater. It was malfunctioning on the first day. We used the first day to fix the heater, because all samples needed it, including the CdS etched samples (for cleaning purposes). The heater was fixed in the early afternoon of the second day, which we were limited to study the CdS etched samples and a collaborative sample with a University of Delaware research group. We should note that this is our second proposal at this beamline (SSRL 5-4). The first proposal verified that the CdS etch lead to clean unperturbed surfaces and showed nice dispersions. Removing the Se-capped was believed to result into better crystal quality based off previous CuInSe₂ ARPES studies [57,68]. Therefore, we attempted this technique, but showed poor results. All APRES figures in Chapter 4 were derived from CdS etched samples.



Figure 14 a-e)Theta map with at photon excitation of 25eV. Left is the AgInSe₂ (HCl etched) and right AgInSe₂ Se-cap.



Figure 15 Theta map with at photon excitation of 25eV. Left is the Cu(In,Ga)Se₂ (HCl etched) and right Cu(In,Ga)Se₂ Se-cap.

Chapter 4

VALENCE BAND MAXIMA OF AGINSE2, CUINSE2, AND CU(IN,GA)SE2 SINGLE CRYSTALS

4.1 Photoemission Study of AgInSe₂, CuInSe₂ and Cu(In_{0.5}Ga_{0.5})Se₂ Single Crystals (hv = 17 - 40 eV, Synchrotron-based Radiation)

Our study begins with electronic bandstructure of CuInSe₂, Cu(In,Ga)Se₂, and AgInSe₂ single crystals by way of APRES. The main idea for this part of the work was to locate the Γ -point in the band structure for each sample and determine its valence band maxima value. The band structures were obtained by taken the k_{\perp} scan in normal emission, which we followed the photoemission paths in Figure 16a.



Figure 16 Photoemission paths in reciprocal space for materials with tetragonal (chalcopyrite unit cell, black) and fcc symmetry (zinc blende, blue). Reprinted with permission [57].

According to Figure 16a, the Γ -points in the [001] path are located at photon energy's hv = 15eV, 36eV and 68eV and for Γ -points in the [112] are slightly below hv = 15eV, slightly above 25eV and 50eV for CuInSe₂ [57]. At the time of experiment, energies available at beamline 5-4 (section 3.2.1) were between hv = 16 - 40eV. For our experiment, not only was the Γ -point of interest, but also the peak positions of the antibonding, nonbonding and bonding of Cu-Se and Ag-Se bonds, therefore we chose hv = 17 - 40eV to ensure all peak positions were visible.

The photon dependence from hv = 17-40eV for CuInSe₂ and Cu(In,Ga)Se₂ (001) is depicted in Figure 17. The dispersion in the upper valence region is nicely produced for both samples (Figure 17b) [57]. A trough in the energy maps (Figure 17c) confirms the Γ -T- Γ path and validates that clean well oriented single crystals were formed. The antibonding, nonbonding, and bonding of Cu-Se are clearly noticed, and were recorded at hv = 17eV, depicted in Figure 20. The valence band maxima position was measured by linear extrapolation, which Cu(In,Ga)Se₂ VBM = 0.52eV, and CuInSe₂ VBM = 0.58eV (Figure 19a-b). The subtle difference of 0.06eV confirms the insignificance Ga content has on the changes in the valence band maxima in Cu-chalcopyrite materials



Figure 17 Photon dependence of CuInSe₂ (001) and Cu(In,Ga)Se₂ (001) in the Γ -T- Γ direction, recorded in normal emission for hv = 17 – 40eV a) 3rd to 4th Brillouin zone [57], b) Waterfall plot for CuInSe₂ (001) and Cu(In,Ga)Se₂ (001), c) k-energy map of CuInSe₂ (001) and Cu(In,Ga)Se₂ (001)

The photon dependence from hv = 17-40eV for AgInSe₂ (112) is depicted in Figure 18. The dispersion in the upper valence region is nicely produced, however developed a weak Γ -point (Figure 18b). The upper valence band is slightly flatter than previously recorded photon dependence on CuInSe₂ (112) (hv= 11-28eV) [57]. These less delocalized states could be due to the orientation studied. It was shown in the [57,61] that the growth chalcopyrite (112) planes on GaAs(111) substrate exhibit a twofold symmetry. This means, depending on the alignment of the *c* axis with respect to the substrate, other orientations of the CuInSe₂ (112) epilayer are possible. Therefore, the surface normal and two other orientations can be obtained of the CuInSe₂ (112) epilayer, which is obtainable when sample is rotated 120° around the surface normal (confirmed by low energy diffraction patterns (LEED)). At the time of this experiment however, the LEED was inactive, therefore only one direction could be obtained, the surface normal. Crystal quality could also be considered; however, no unwanted planes were noticed in the XRD scans (Figure 13).



Figure 18 Photon dependence of AgInSe₂ (112) in the C- Γ -C direction, recorded in normal emission for hv = 17 – 40eV a) 2nd to 3rd Brillouin zone [57], b) Waterfall plot for AgInSe₂ (112) c) k-energy map of AgInSe₂ (112)

Nevertheless, the VBM for each sample was obtained, and recorded in Figure 19. The valence band maxima were measured by linear extrapolating the leading valence edge for each sample. For CuInSe₂ and Cu(In,Ga)Se₂, the VBM were recorded from hv = 17eV, and hv = 28eV for AgInSe₂. AgInSe₂ had a measured VBM around 1.24eV, an additional 0.72eV from Cu(In,Ga)Se₂. The antibonding, nonbonding, and bonding of Ag-Se were also recorded, and showed a dramatic difference in binding energy positions as compared to Cu-Se binding energies (Figure 20). The most notable difference is the position of the Ag-Se antibonding to the Cu-

Se antibonding peak. Ag-Se antibonding peak is around 2.2eV while Cu-Se antibonding peak around 1.3eV. The lowering of the antibonding peak of Ag-Se is most likely the reason the VBM is further from the Fermi level than Cu-Se. If some Cu atoms in the Cu(In,Ga)Se₂ film were substituted by Ag atoms, the VBM would shift further below the Fermi level for two reasons: 1) the Cu/(Cu+Se) ratio is reduced, thereby reducing the amount of p-d hybridization, 2) the overall system of Ag-Cu-In-Ga-Se would have a VBM further below the Fermi level.



Figure 19 Valence band edge of Cu(In,Ga)Se₂, CuInSe₂, and AgInSe₂ single crystals. The VBM was measured from the Γ point for each sample (hv = 17eV for CuInSe₂ and Cu(In,Ga)Se₂, and hv = 28eV for AgInSe₂



Figure 20 Band diagram of CuInSe₂, Cu(In,Ga)Se₂ and AgInSe₂ with energy positions of the antibonding, nonbonding and bonding positions of Cu-Se and Ag-Se. The VBM was measured from the Γ point for each sample (hv = 17eV for CuInSe₂ and Cu(In,Ga)Se₂, and hv = 28eV for AgInSe₂ [57])

This information serves as a proof of concept, and is important for polycrystalline materials because we know substituting Ag for Cu atoms and Ga for In atoms in a Ag-Cu-In-Ga-Se system, the VBM should shift for Ag to Cu and not for Ga to In. In the subsequent chapters, we will investigate this change in VBM shift at different Ag and Ga fractions for polycrystalline samples, but first we will discuss and confirm the existence of ordered vacancy compounds on the surface of (Ag,Cu)(In,Ga)Se₂ compounds.

Chapter 5

X-RAY PHOTOEMISSION SURFACE STUDY OF (AG,CU)(IN,GA)SE2 SEMICONDUCTOR

5.1 Evidence of Surface Ordered Vacancy Compounds on (Ag,Cu)(In,Ga)Se₂ Semiconductor

 $(Ag,Cu)(In,Ga)Se_2$ films were prepared by single-stage coevaporation and cleaved prior to surface study (as described in section 3.1.1). Samples studied had varied Ag and Ga content, which will be mostly presented in the form of Ag/(Ag+Cu) and Ga/(Ga+In) (AAC and GGI). High-resolution scans were performed on Cu2*p*, Ag3*d*, In3d, Ga2*p* and Se3*d* regions by Mg K α x-rays, which the atomic concentration (both surface and bulk) recorded in Table 2. The calibration of binding energy scale was performed with the C1s line (284.6eV).

In Figure 21a, we show a comparison of the surface concentration to the bulk concentration, split into five groups. The first group is Ga/(Ga+In) = 0.0 with three samples: Ag/(Ag+Cu) (AAC) = 1.0, 0.3 and 0.0. This group shows a nice distinction between the surface and the bulk composition, with the surface showing more OVC-like composition than the bulk. In this group, AAC = 1.0 represents the AgInSe₂ polycrystalline sample, and shows to be more group I poor than AAC = 0.3 and 0.0. The VBM of AAC = 1.0 (Figure 21b) shows to have a value (VBM = 0.81eV) further below AAC = 0.3 and 0.0 (VBM = 0.22 and 0.35eV). These results agree with our single crystal study in Chapter 4. In chapter 4, we showed that the VBM for AgInSe₂ (001) sample is further below the Fermi level than CuInSe₂, and suggested that if Cu atoms replace Ag atoms, the VBM of the system should shift further below the Fermi level. However, this is not always the case. Sample AAC = 0.3 VBM is clearly closer to the Fermi level than AAC = 0.0. However, AAC = 0.3 is slightly more group I rich

than AAC = 0.0, which could be the reason why the VBM is closer to the Fermi level for AAC = 0.3 than AAC = 0.0.

Adding Ga to the Ag-Cu-In-Se system changes the composition and the position of the VBM. Four more groups were studied, where each group had the same Ga/(Ga+In) (GGI) ratio of 0.3, 0.5, and 0.8. The second group (AAC = 0.0, no Ag) showed a liner trend in the surface and the bulk composition (Figure 21a). Again, the surface resembled an OVC-like composition, and the bulk a (Ag,Cu)(In,Ga)Se₂ composition. As GGI increased, we noticed the surface becoming more group I poor, in which the shift in the VBM (Figure 21b) agreed with the changes in surface composition. It is apparent that Ga does change the composition and electronic properties of the surface, even more so with the addition of Ag.

The third, fourth and fifth group in Figure 21a has a AAC = 0.3, 0.5 and 0.8 ratio. First, we noticed the bulk composition becoming more group I poor as AAC ratio increases. The opposite, however, is shown for the surface, where the surface shows a slight increase in group I as AAC ratio increases. The phase segregation is still noticeable between the surface and bulk however, where the surface shows more OVC-like composition and the bulk (Ag,Cu)(In,Ga)Se₂ composition. As AAC increases, the VBM seems to follow a trend, accept for one sample (AAC = 0.3 and GGI = 0.8), which we consider this sample having a bad cleave. The trend we see is that when GGI = 0.3 ratio, the VBM stays around ~0.3eV, and when GGI > 0.3 ratio, the VBM shifts to values around ~0.9eV (Figure 21b). To see this distinction more clearly, we graphed the results in a different order (Figure 22a-b), having the x-axis AAC, and four groups of GGI. The one group missing in Figure 22 from Figure 21 is

group 1 is GGI = 0.0. The main idea was to show the distinction of GGI = 0.3 and GGI > 0.3.

In Figure 22b, we clearly see that the VBM is in a completely different position when GGI = 0.3 than it is when GGI > 0.3. The surface for GGI = 0.3 is slightly more group I rich than GGI > 0.3, in most cases. These results agree with the theory from reference 25, that if Cu-chalcopyrite materials are group 1 poor, the VBM would shift further below the Fermi level from its parent compound. It is apparent that the surface contains more OVC-like composition at higher GGI ratios, mostly in the form of Ag-like OVCs is suggested. To verify the existence of Ag-like OVCs, we investigated the valence band features by Mg K α x-rays.



Figure 21 a) XPS (surface) and EDS (bulk) composition of (Ag+Cu)/Se for varied AAC and GGI ratios. X-axis is Ga/(Ga+In) b) VBM measured positions for varied AAC and GGI ratios. Blue circles represent samples that were studied at the synchrotron. (Composition error $\pm 6.0\%$, VBM $\pm 0.1eV$)



Figure 22 a) XPS (surface) and EDS (bulk) composition of (Ag+Cu)/Se for varied AAC and GGI ratios. X-axis is Ag/(Ag+Cu) b) VBM measured positions for varied AAC and GGI ratios. Blue circles represent samples that were studied at the synchrotron. (Composition error \pm 6.0%, VBM \pm 0.1eV)

Figure 23 depicts the valence band of each sample studied in Figure 21 (except for group 1 GGI = 0.0). The valence band spectra show a strong photoemitted peak around 6eV, in which this peak represents the nonbonding Ag4d band (based off our single crystal study). The antibonding and bonding of Ag-Se are also observed but are sufficiently suppressed – most likely due to the low cross section of Ag4d at this photon energy (Chapter 2). While using Mg Ka x-rays, Cu-Se bonds in the presence of Ag can be omitted because Cu3d cross section is much lower than Ag4d (Chapter 2), but of course can be seen for AAC = 0.0 (Figure 23a). It is interesting to note that the valence band of each sample resembles the calculated density of states of AgInSe₂ and CuInSe₂ (Figure 24 and 27a). Based off our surface composition, we believed to have more Ag and Cu-like OVCs on the surface, especially at lower AAC ratios (Figure 21a). The VB, however, shows stronger resemblance of Ag and Cu-rich like compositions. To have stronger evidence of Ag-like OVCs on the surface, a lower photon excitation with high Ag4d cross section is suggested – best suggestion is hy =

40.8eV, He II lamp or synchrotron radiation (Figure 9). We were able, however, to locate the trend of Cu-like OVCs by using hv = 120eV (best cross section for Cu3d orbitals, amongst the competing orbitals Ag4d, Ga4s, In5s and Se4p – Figure 11).



Figure 23 Mg K α x-ray derived valence bands of varied AAC and GGI ratios, with recorded valence band maxima. a) AAC = 0.0, b) AAC = 0.3, c) AAC = 0.5 and d) AAC = 0.8. All have the same GGI = 0.3, 0.5 and 0.8



Figure 24 Calculated density of states of AgInSe₂. Reprinted with permission [63].

Chapter 6

SOFT X-RAY PHOTOEMISSION SURFACE STUDY OF (AG,CU)(IN,GA)SE2 SEMICONDUCTOR

6.1 Valence Band Contribution of Cu-d Orbitals in (Ag,Cu)(In,Ga)Se₂, a Photoemission Study (hv = 120eV, Synchrotron-based Radiation)

(Ag,Cu)(In,Ga)Se₂ films were prepared by single-stage coevaporation and cleaved prior to surface study. This surface study was held at beamline 8-1 at Stanford Synchrotron Radiation Lightsource (SSRL), with beam parameters located in Chapter 3. From our previous surface study, we showed that the surface composition seems to change for differing GGI ratios and shows a similar composition at different AAC ratios (Figures 21 and 22). Therefore, we selected samples from group 3 in Figure 21 (AAC = 0.3, with varying GGI ratios from 0.3 to 0.8 – circled in blue). For comparison, we also selected a sample with GGI = 0.0 and AAC = 0.3 (Figure 21a group 1 – circled in blue). The idea for this part of the work was to investigate the Cu-d orbital contributions to the valence band of ACIGS films and verify the existence of OVC-like valence band at varying GGI ratios. Figure 25 shows the valence band of the four samples. It should be noted that we shift the VB of each region to 0.0eV (Fermi level), due to lack of calibration of binding energy. Nevertheless, the intent of this work was to verify the features of the VB.

Peak labels are shown in Figure 25a, which depicts the Cu-Se bonding, nonbonding and antibonding peaks. The peak of interest is the nonbonding Cu3d (around 2.0 eV binding energy). This peak is the most verifiable peak when comparing a Cu-poor to a Cu-rich valence band, as determined in calculated density [25]. The nonbonding Cu3d peak is identified by the asterisk symbol (*) in each sample (Figures 25a-d). As GGI increases from 0.0 to 0.8, the nonbonding Cu3d peak

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increases in terms of intensity. We should emphasize that the Ag and Cu content are held constant for each sample, therefore the increase in the peak intensity of nonbonding Cu3d is only due to rich Cu-phases appearing at increased GGI ratios. We argue that the Cu-rich phases appearing at these higher GGI ratios favor the form CuGaSe₂ and not CuInSe₂. If CuInSe₂ were noticed, then values less than 0.5 of GGI ratio would resemble a CuInSe₂ valence band and not OVC like valence band [25]. This is confirmed by comparing the valence bands in Figure 25 to the calculated density of states Figure 27 [25,62]. The Cu3d peak can serve as an identifier, and is remarkably lower in intensity for OVC related DOS. Our data shows a similar reduction in the nonbonding Cu3d peak for GGI less than 0.5. We conclude that Culike OVCs of (Ag,Cu)(In,Ga)Se₂ are more likely to appear when GGI is less than 0.5, and slowly disappears at higher GGI.



Figure 25 Soft x-ray (hv = 120eV) derived valence bands of four samples: a) AAC = 0.3 and GGI = 0.0, b) AAC = 0.3 and GGI = 0.3, c) AAC = 0.3 and GGI = 0.5, and d) AAC = 0.3 and GGI = 0.8. Black (*) represent the position of the nonbonding Cu3d peak.

We were able to study two more samples at AAC = 0.5, one with GGI = 0.3 and the other GGI = 0.5 (Figure 26 – samples circled in blue from Figure 22). From Figure 22b, the VBM of these two samples are completely different, therefore the VB features should likely be different as well. Based off the VBM position in Figure 22b, we expect the VB to show stronger Cu-rich like features for sample AAC = 0.5/GGI = 0.3 than AAC = 0.5/GGI = 0.5. This is exactly the case, as shown in Figure 26. The decrease in nonbonding Cu3d peak from Figure 26a to 26b agrees with the corresponding changes of the surface composition and the VBM position in Figure 22. This helps confirms the two cases we suggested in Chapter 5, when GGI = 0.3 and GGI > 0.3. When GGI = 0.3, the surface seems to contain group I rich compounds, even more so at higher AAC ratios (Figure 22a). The position of the VBM for group GGI = 0.3 also resembles the case when AAC = 0.0 (Figure 22b). This suggest that when GGI = 0.3, the surface electronic properties are strongly affected by CuInSe₂/CuGaSe₂ and related OVCs. When GGI > 0.3, the VBM shifts further below the Fermi level, which we relate the electronic changes on the surface to the increase in AgInSe₂/AgGaSe₂ and related OVCs, however photoemitted VBs of Ag-like OVCs has yet to be determined – along with calculated density of states.



Figure 26 Soft x-ray (hv = 120eV) derived valence bands of four samples: a) AAC = 0.5 and GGI = 0.3 and b) AAC = 0.5 and GGI = 0.5. Black (*) represent the position of the nonbonding Cu3d peak.



Figure 27 Calculated density of states of a) CuInSe₂ [25] b) CuGaSe₂ [62] and c) OVC of CuInSe₂ [25]. All Reprinted with permission.

Chapter 7

PHOTOEMISSION STUDY OF POLYCRYSTALLINE CUINSE₂, AGINSE₂, AND CUGASE₂ (hv = 1486.6eV, MONO SOURCE AIK α)

In this chapter, we will discuss the pros and cons of additional photoemission studies on polycrystalline-cleaved samples of CuInSe₂ (CIS), CuGaSe₂ (CGS) and AgInSe₂ (AIS) materials by Al Ka XPS mono source. Suitable lines from known conducting specimens (foils of Cu, Ag and Au) were obtained from sputtered foils, and the XPS peaks have values of $Cu_{2p_{3/2}} = 931.77 \text{eV}$, $Ag_{3d_{5/2}} = 367.46 \text{eV}$ and Au $4f_{7/2}$ = 83.30eV, with the VBM for each showed a change of ±0.09eV from Fermi level. Samples were cleaved and loaded into intro chamber the night before measuring. One of the cons of this work will be shown in the survey scans, where strong overlaps of C1s (B.E. = 284.6eV) and SeLMM Auger peaks occurs (Figure 28). This overlap made charge correction via adventitious carbon to be difficult, which was a problem for this work. Charge correction was needed to locate the position of the VBM of the polycrystalline samples, therefore, the Mg Ka dual source was used for the core of this work (Chapter 5). The mono source indeed has its advantages for XPS study, where one of the pros for using the mono source is due to the reduction in X-ray line width, which ultimately results in narrower XPS peaks and consequently better chemical state information. However, this work needed a way of charge correction, therefore, mono source was limited to initial photoemission studies.



Figure 28 XPS survey spectra of CuInSe₂, AgInSe₂ and CuGaSe₂ samples

7.1 Valence Band and Atomic Concentration of Polycrystalline CuInSe₂, AgInSe₂ and CuGaSe₂ Materials

The valence band spectra of CuInSe₂, AgInSe₂ and CuGaSe₂ samples are depicted in Figure 29. The resolution of all VBs is clearly more resolved than the VB-derived regions measured by Mg K α X-rays from Chapter 5. It should be reminded that each VBM was shifted to 0eV (Fermi level), because of the inability C1s charge

correction. The VB of AgInSe₂ clearly shows the nonbonding Ag4d peak, with antibonding from Ag4d-Se4p hybridization to the right of the nonbonding Ag4d peak. The overall valence feature resembles the valence features from Chapter 5, with a dominating nonbonding Ag4d peak, and a suppressed antibonding and bonding peak (with small In-Se bonding overlapping Ag-Se bonding).

The VB for both CuInSe₂ and CuGaSe₂ have very similar valence features. The resemblance verifies the insignificance Ga alloys have on the VB features, as described in Chapter 4. The composition for CuGaSe₂ in Figure 29 however, does not correspond with the trend we noticed from our Mg K α X-ray study in Chapter 5. Figure 21a shows the increase in GGI from 0.0 to 0.8 (with no Ag), which showed an increase in OVC-like composition. The GGI = 1.0 was not performed for Mg K α , however we would suggest the trend to follow the group I poor as GGI increases, therefore we consider the surface composition in Figure 29 for CuGaSe₂ is related to a bad cleave. We did not further investigate this sample with the Mono source, and the CuInSe₂ and AgInSe₂ did show OVC-like composition, as shown in Figure 29.



Figure 29 XPS valence band, spectra of CuInSe₂, AgInSe₂ and CuGaSe₂ samples.



Figure 30 XPS surface composition of CuInSe₂, AgInSe₂ and CuGaSe₂. (Composition error $\pm 6.0\%$)

7.2 Core Levels of Polycrystalline AgInSe₂, CuInSe₂ and CuGaSe₂

XPS core levels of detailed scans of Cu2*p*, Ag3*d* In3d, Ga2*p* and Se3*d* were measured and are depicted in Figure 31-35, with binding energies recorded in Table 4. The most notable change in peak position is Se3d (Figure 31). For CuInSe₂, the Se3d_{5/2} peak has a measured binding energy position of 53.5eV. The spectra above and below the CuInSe₂ are Se3d detailed scans of AgInSe₂ and CuGaSe₂ (Figure 31). The change in peak positions can be explained by the differences in the structural parameters a and c (lattice constants), u (anion displacement) and $2\eta \equiv c/a$ (tetragonal deformation). The differences in bond lengths, for example Cu-Se and In-Se in CIS, leads to an anion displacement $u \neq \frac{1}{4}$, where u is defined as:

$$u = \frac{1}{4} + \frac{\left(R_{AC}^2 - R_{BC}^2\right)}{a^2} \tag{6}$$

where R_{AC} and R_{BC} are the bond lengths of I-VI and II-VI, and a is the lattice constant. When $u < \frac{1}{4}$ in CuInSe₂, $R_{AC} < R_{BC}$, which simply means the Se atom is closer to Cu than it is to In. This slight difference, along with the other structural parameters all contribute to the change in binding energy. For AgInSe₂, Se3d_{5/2} shifts to lower binding energies than both CuInSe₂ and CuGaSe₂. This shift is concordance with the calculated anion displacement of AgInSe₂ u > 1/4, which simply means the Se atom is closer to In than it is to Ag, as oppose to CIS and CGS [63].

Reported binding energies of $In3d_{5/2}$ in CuInSe₂ is found to vary from 444.1eV to 444.7eV [40]. It was found that the shift in $In3d_{5/2}$ peak to higher binding energies is a result of In-rich compounds [40]. No aggressive changes noticed for our measured $In3d_{5/2}$ in AgInSe₂ and CuInSe₂ – similarly for Cu2 $p_{3/2}$ for CuGaSe₂ and CuInSe₂ (Figures 32 and 33).



CasaXPS (K. Jones)

Figure 31 XPS photoemission peak of Se3*d* for CuInSe₂, AgInSe₂ and CuGaSe₂ samples



CasaXPS (K. Jones)

Figure 32 XPS photoemission peak of In3*d* for CuInSe₂ and AgInSe₂ samples



CasaXPS (K. Jones)

Figure 33 XPS photoemission peak of Cu2p for CuInSe₂and CuGaSe₂ samples



CasaXPS (K. Jones)

Figure 34 XPS photoemission peak of Ag3*d* for AgInSe₂ sample



CasaXPS (K. Jones)

Figure 35 XPS photoemission peak of $Ga2p_{3/2}$ for CuGaSe₂ sample

Table 4XPS binding energy positions of $Ag3d_{5/2}$, $Cu2p_{3/2}$, $In3d_{5/2}$, $Ga2p_{3/2}$ and
Se3d for AgInSe2, CuInSe2 and CuGaSe2 samples

Sample	Regions and Binding Energy Positions (eV)							
	Ag3d _{5/2}	Cu $2p_{3/2}$	In3d5/2	Ga $2p_{3/2}$	Se3d			
AgInSe ₂	366.8		443.8		53.1			

CuInSe ₂	931.2	444.1		53.5
CuGaSe ₂	931.4		1116.9	53.7

In this section, we showed the VB of AgInSe₂, CuInSe₂ and CuGaSe₂ by monochromatic Al K α X-rays, and the binding energy positions of Ag4d_{5/2}, Cu2p_{3/2}, In3d_{5/2}, Ga2p_{3/2} and Se3d. It should be noted that AgGaSe₂ sample was attempted but had serious charging issues. Similar charging issues were noticed for CuGaSe₂; however, we were able to record data on the third attempt. The charging seems to be related to long x-ray exposure time to samples with slightly wider bandgaps of (Ag,Cu)(In,Ga)Se₂, with CuGaSe₂ and AgGaSe₂ having E_g of 1.68 and 1.81-eV [65]. The use of a dual source or a neutralizer could alleviate the charging issue [58], in which the bulk of this dissertation used the standard Mg K α x-ray dual source. The main advantage is the auto charge correction, which allows most semiconductors and metals to be measured with no special sample preparation.

Chapter 8

PHOTOEMISSION STUDY OF POLYCRYSTALLINE AGGASE₂, AGINSE₂, CUINSE₂, AND CUGASSE₂ (hv = 1253.6eV, Mg Kα DUAL SOURCE)

8.1 Surface Reconstruction of Polycrystalline AgGaSe₂, AgInSe₂, CuInSe₂, and CuGaSe₂

In this chapter, we wanted to verify that changes on cleaved-samples (polycrystalline AgGaSe₂, AgInSe₂, CuInSe₂ and CuGaSe₂ samples) over time would still show OVC-like compositions. We lightly sputtered each cleaved sample and recorded the surface composition overtime. Each sample was surveyed at different time intervals, ranging from 0 to 12+ hours. Committing to only surveys allowed for all samples to have a quick scan, without any charging issues. Samples CuInSe₂ and AgInSe₂ both showed stronger group I-poor composition than samples CuGaSe₂ and AgGaSe₂. For this study however, we were after any changes of the surface over time, which we did not see any significant changes, except for one case (CuGaSe₂) where the surface composition seems to settle after 5 hours.

Samples AgGaSe₂ and CuGaSe₂ both showed a slight increase in group I composition on the surface. This increase in Cu agrees with high formation energy of Ga_{Cu} antisite defect, as described in Chapter 1. For AgGaSe₂, a similar increase in Ag concentration was noticed, as in the case for CuGaSe₂. This suggest that there is also a high formation energy of Ga_{Ag} , since the surface composition CuGaSe₂ and AgGaSe₂ are roughly the same. As of now, however, there is no data supporting this claim of a high defect formation energy of Ga_{Ag} antisite defect, therefore remains as a speculation based off our measured XPS data.

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Figure 36 XPS surface composition of AgGaSe₂, CuGaSe₂, AgInSe₂ and CuInSe₂. Compositions recorded at different time intervals. (Composition error \pm 6.0%)

8.2 Core Levels of Polycrystalline (Ag,Cu)(In,Ga)Se₂

Polycrystalline samples studied received photoemission by MgK α X-rays. Each sample was loaded the night before with a minimum of 12 hours in between load and data collection. Samples were cleaved and collected as-is, with no sputtering done on the surface. No sputtering allowed for C1s charge correction, which was done for each region studied. The XPS regions of Ag3 $d_{5/2}$, Cu2 $p_{3/2}$, Ga2 $p_{3/2}$, In3 $d_{5/2}$, and Se3pwere studied and the binding energies are shown in Figures 37-41.

Figure 37 shows the peak positions of $\text{Cu}2p_{3/2}$ of samples with varying AAC and GGI ratios. The black horizontal dotted line indicates the CuInSe₂ sample, measured with a peak position of 931.57eV. The change in peak positions for Cu2 $p_{3/2}$ is in concordance with changes noticed in the measured bond lengths of R_{I-Se}(Å) of similar AAC and GGI ratios [42]. The shift in Cu2 $p_{3/2}$ peak position to higher energies suggest a stronger Cu-Se bond, hence a shorter bond of Cu-Se [40]. In the cases of AAC = 0.0, the increase in GGI ratios shows an increase in binding energy,
ranging from 931.57 to 931.89eV. This agrees with the R_{I-Se} bond lengths, of samples with AAC = 0.00, shortens at higher GGI ratios. Increasing AAC mostly shows a higher shift in binding energy for $Cu_{2p_{3/2}}$ [42]. From the measured bond lengths, increasing AAC shows an increase in R_{I-Se} bond lengths (with GGI = 0.0 and varying GGI ratios), which should mean the binding energy shift for corresponding $Cu_{2p_{3/2}}$ should be at lower peak positions. It is interesting to mention that the peak positions of Ag3 $d_{5/2}$ in Figure 38 almost mimic the energy shifts of Cu2 $p_{3/2}$ in every AAC and GGI ratio (except for when there is no Ag or no Cu). The red horizontal dotted line indicates the AgInSe₂ sample, measured with a peak position of 367.67eV (Figure 38). The trend of $Cu_{2p_{3/2}}$ and $Ag_{3d_{5/2}}$ peak shifts are similar and correspond to the changes in bond lengths of R_{Cu-Se} and R_{Ag-Se} at different GGI ratios [42]. Based off calculations of R_{I-Se} in CuInSe₂ and AgInSe₂, R_{Ag-Se} bond length is 0.16Å greater than R_{Cu-Se}; and measured values of R_{I-Se} in CuInSe₂ and AgInSe₂, R_{Ag-Se} bond length is 0.20Å. This means, for every short RAg-Se in (Ag,Cu)(In,Ga)Se2 system, there is a shorter R_{Cu-Se} bond length. A similar trend in bond lengths R_{I-Se} for AgGaSe₂ and CuGaSe₂ were noticed [42], however, long x-ray exposure for these samples lead to aggressive charging effects, therefore were not included in this work.



Figure 37 XPS Cu2p_{3/2} peak position for Ag and Ga fractions of (Ag,Cu)(In,Ga)Se₂. The black dotted horizontal line indicates the position of CuInSe₂ sample.



Figure 38 XPS Ag3d_{5/2} peak position for Ag and Ga fractions of (Ag,Cu)(In,Ga)Se₂. The red dotted horizontal line indicates the position of AgInSe₂ sample.

Figure 39 shows the binding energy position of $In3d_{5/2}$ of different AAC and GGI ratios. The red and black horizontal line correspond to the baseline AgInSe₂ and CuInSe₂ sample peak position, with measured values of 444.58 and 444.39eV. For sample AAC = 0.3 and GGI = 0.0, the In3 $d_{5/2}$ peak shifts downward to 444.21eV. Following the same reasoning as before with Cu XPS peak position, lower binding energies suggest weaker bonds, which weaker bonds corresponds to wider In-Se bond lengths. The subtle shift in binding energies agrees with the bond length distance of R_{In-Se} being slightly greater with AAC = 0.3/GGI = 0.0 than AAC = 0.0/GGI = 0.0 [42].

In almost every case, the $In3d_{5/2}$ peak position is above the black dotted line in Figure 39 (CuInSe₂). This suggest that the In-Se bond length in CuInSe₂ is shorter at higher GGI ratios, which agrees with R_{III-Se} bond length values. The Ga2*p*_{3/2} peak follows the same trend as $In3d_{5/2}$, which means the Ga-Se bond length should also decrease at higher GGI. When comparing bond length values In-rich and Ga-rich compounds of CIGS (i.e. In-rich GGI = 0.0 and 0.3, Ga-rich GGI = 1.0 and 0.8), it was noticed that R_{III-Se} is greater in In-rich conditions, which suggest that the bond length of R_{In-Se} is greater than R_{Ga-Se} in In-rich and Ga-rich conditions [42]. There is no horizontal line in Figure 40 (Ga2p_{3/2} XPS peaks) because the baseline CuGaSe₂ and AgGaSe₂ samples undergone severe charging issues, mostly due to long exposure to Mg K α X-rays.



Figure 39 XPS In3d_{5/2} peak position for Ag and Ga fractions of (Ag,Cu)(In,Ga)Se₂



Figure 40 XPS Ga2p_{3/2} peak position for Ag and Ga fractions of (Ag,Cu)(In,Ga)Se₂

In Figure 41, the Se3*d*_{5/2} positions are recorded, with the red and black horizontal line representing the AgInSe₂ and CuInSe₂ Se3*d*_{5/2} peak position (54.08 and 54.07eV respectively). Binding energy position at higher peak positions suggest stronger bonding, corresponding to shorter I-Se and III-Se bond lengths [42]. In the Ag-Cu-In-Ga-Se system, the bonds from shortest to longest are: (experimented and calculated) Ga-Se (AGS) < Ga-Se (CGS) < Cu-Se (CGS) < Cu-Se (CIS) < In-Se (CIS) < In-Se (AIS) < Ag-Se (AGS) < Ag-Se (AGS) [42, 66, 67]. In Figure 41, majority of the peaks are above the red and black horizontal lines, which suggest stronger bonds like Cu-Se and Ga-Se are more likely to exist at higher GGI and AAC.



Figure 41 XPS Se3d_{5/2} peak position for Ag and Ga fractions of (Ag,Cu)(In,Ga)Se₂

This section sums up the binding energy positions of cleaved $(Ag,Cu)(In,Ga)Se_2$ recorded by Mg K α X-rays. We discussed that the inclusion of Ag and Ga in CuInSe₂ disrupts the effective anion displacement, thereby changing the magnitude of various bond strengths in the material [42], which directly affects the binding energy position of Ag3*d*, Cu2*p*, In3*d*, Ga2*p*, and Se3*d*. Changes in binding energy however does not explain the differences in OVC-like compositions to (Ag,Cu)(In,Ga)Se₂ compositions, therefore was not included in the bulk of the work.

Chapter 9

DISCUSSION

In Chapter 4, we used angle-resolved photoemission spectroscopy on three single crystals: CuInSe₂ (001), Cu(In,Ga)Se₂ (001), and AgInSe₂ (112). Each sample was prepared on a GaAs substrate, in which samples with an (001) orientation grew on a GaAs (100) and the sample with (112) grew on GaAs (111) substrate. We performed photon dependence (hv = 17 - 40eV) perpendicular to the surface normal, which permitted the Γ -T- Γ photoemission path for (001) oriented samples, and C- Γ -C for the (112) oriented sample. Each sample, we measured the VBM at the Γ -point, where the following positions were obtained: $CuInSe_2 VBM = 0.58eV$, $Cu(In,Ga)Se_2$ VBM = 0.52eV, and $AgInSe_2 VBM = 1.24eV$. The single crystal study helped verify that CuInSe₂ and Cu(In,Ga)Se₂ samples have similar valence features, and the position of the VBM is not affected by the Ga addition, but only the amount of Cu atoms. It was also found that the related bands from Ag4d-Se4p hybridization sits much lower than the bands from Cu3d-Se4p hybridization. This resulted into a VBM further below the Fermi level for AgInSe₂ than for CuInSe₂/Cu(In,Ga)Se₂. Therefore, the single crystal study suggests that if Cu atoms were replaced by Ag atoms in the Cu-In-Ga-Se system, the VBM may shift further below the Fermi level

In Chapter 5, x-ray photoelectron spectroscopy and energy dispersive spectroscopy were performed on polycrystalline samples, with varying Ag and Ga fraction in the Ag-Cu-In-Ga-Se system. For surface study, each sample was prepared on a Mo-coated soda lime glass, which was cleaved prior to photoemission study. Bulk related compositions were measured after deposition, as-is. The results reported showed a phase segregation between the bulk and surface, where the surface resembled an OVC-like composition and bulk resembled a (Ag,Cu)(In,Ga)Se₂ composition. We later investigated Mg K α -derived VBs and measured the position of the VBM. We noticed that the VBM for polycrystalline samples with and without Ag does not shift as much from the Fermi level. With the addition of Ga however, the shift in the VBM was more pronounced, but only for certain conditions. Two things must be met for a pronounce shift in VBM: (1) Ag must be alloyed to the Cu-In-Ga-Se system. Without Ag, the increase in Ga content has little impact to the shift of the VBM (2) GGI ratio must be greater than 0.3. For GGI ratios less than 0.3, even when alloyed with Ag, the VBM has values around $\sim 0.3 \text{eV}$ – much further above the VBM of GGI > 0.3 (average VBM ~ 0.89eV). The study of polycrystalline samples however contradicts the single crystal study. Before, from the single crystal study, we said that the change in Ga content does not affect the valence band, thereby not affecting the position of the VBM. However, the major changes in the VBM for the polycrystalline samples were mostly due to a difference in Ga content. Since we know that the position of the VBM is governed by the amount of Cu3d-Se4p and Ag4d-Se4p hybridizations [25], we believe that the surface may be changing at different Gafractions, which could ultimately have different phases occurring at different Gafractions.

Additional work in Chapter 5 looked at the VB features from Mg K α photons. Unfortunately, the VBs only resembled Ag-rich and Cu-rich like valence features (i.e. AgInSe₂ and CuInSe₂). We believe this is mostly due the low photoionization cross section of Cu3d and Ag4d at hv = 1253.6eV. To obtain more Ag-like and Cu-like valence features, a different photon energy is required. For Ag4d, the best photon energy is hv = 40.8eV, He II lamp or synchrotron radiation. Our work was limited to another photon energy that permitted more Cu-like valence band, which used hv = 120eV.

In Chapter 6, we used soft x-rays from synchrotron radiation, with a photon energy hv = 120eV. This part of the work confirmed that increasing GGI ratios does indeed lead into surface changes. We verified that Cu-poor like valence features (i.e. CuIn₃Se₅) can be obtain at low GGI ratios and shows an increase in Cu-rich like valence features (i.e. $CuInSe_2$) at higher GGI, when AAC = 0.3. From our surface studies, we identified two extremes: when GGI = 0.3, the VBM is around ~0.3eV, and when GGI > 0.3, the VBM is around 0.9eV. We studied two samples from the two extreme cases from our XPS study, one with GGI = 0.3 and the other GGI = 0.5, both with AAC = 0.5. We again noticed the change VB features with differing GGI ratios, but the opposite change was shown. Now, the Cu-rich like VB appears for the low GGI = 0.3, and Cu-poor like VB for high GGI = 0.5. The supposed contradiction however can be explained simply by comparing two groups of samples: samples with GGI = 0.3 and samples with GGI 0.5. First, the GGI = 0.3 samples. The VB in Figure 25b and 26a both have GGI = 0.3, with AAC = 0.3 and 0.5 respectively. We noticed that the VB for AAC = 0.3 resembled an OVC-like VB (Figure 25b), which agrees with the decrease in group I surface composition in Figure 21a. When AAC = 0.5, the VB in Figure 26a shows stronger Cu-rich like VB features, which also agrees with the increase in group I composition in Figure 21a. From this study, we confirmed that the sample from GGI = 0.3 does indeed have a more Cu-rich like valence feature than the GGI = 0.5 sample, which agrees with the positions of their corresponding VBM, when AAC = 0.5. The large shift in the VBM around 0.9eV is believed to be affected by the

electronic properties Ag-related OVCs mostly, however, as suggested, lower photon energies needs to be acquired to probe the contribution of Ag-d orbitals in the VB.

Chapter 10

CONCLUSION AND FUTURE WORK

The ordered vacancy compound (OVC) of (Ag,Cu)(In,Ga)Se₂, is primarily in the form of (Ag,Cu)(In,Ga)₃Se₅ and (Ag,Cu)(In,Ga)₅Se on the surface. This OVC naturally increases the energy barrier at the buffer/absorber by shifting the valence band maxima (VBM) of the surface to energies further below the Fermi level. The position of the VBM is governed mostly by the amount of Cu3d-Se4p hybridizations and small amounts of Ag4d-Se4p hybridizations and can be tuned easily by exchanging the amount of Cu and Ag atoms.

In this work, we successfully identified a phase segregation between the surface and bulk, with the surface mostly $(Ag,Cu)(In,Ga)_3Se_5$ and $(Ag,Cu)(In,Ga)_5Se_8$ like composition and the bulk $(Ag,Cu)(In,Ga)Se_2$ composition. ARPES on single crystals revealed that the VBM position of AgInSe₂ is roughly 0.72eV further below the VBM of CuInSe₂/Cu(In,Ga)Se₂. We later performed valence band scans on polycrystalline samples by XPS and confirmed that Ag alloys does indeed have a VBM slightly further away from the Fermi level than without Ag, however, the change in the VBM position does not change much with different Ag-fraction, but with Ga-fraction. With the addition of Ga, it was noticed that the VBM sits at two scenarios: when GGI = 0.3, and when GGI > 0.3. It was then believed that Ga content was affecting the amount of surface Cu3d-Se4p hybridizations and Ag4d-Se4p hybridizations, which should show distinctive valence features, if the right photon energy was selected.

We were able to show the changes in Cu3d-Se4p hybridizations by using a photon energy of hv = 120eV. This photon energy helped confirmed that Cu-poor like

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valence features were indeed forming at lower GGI ratios and increased to Cu-rich like valence features as GGI increased – when AAC = 0.3. We also confirmed the two extreme cases, when GGI = 0.3 and GGI > 0.3, when AAC = 0.5. The sample from GGI = 0.3 does indeed have a more Cu-rich like valence feature than the GGI = 0.5 sample, which agrees with the positions of their corresponding VBM. The large shift in the VBM around 0.9eV is believed to be affected mostly by the electronic properties Ag-related OVCs mostly, however, as suggested, lower photon energies needs to be acquired to probe the contribution of Ag-d orbitals in the VB.

For future work, we strongly recommend a detailed study of Ag-d VBs, derived by He II photons or 40.8eV equivalent photons by synchrotron radiation. Our work shows evidence of Ag-OVCs, by the photon excitations used did not permit a detailed study of the changes in Ag-d related valence features. We also believe a theoretical study is needed for the common defects associated with the competing compounds on the surface. Our work shows that the VB changes along with related Ag- and Ga-fractions, but a stronger explanation of why they change could be determined from the defect formation energies in the Ag-Cu-In-Ga-Se system.

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Appendix A

DEVICE PERFORMANCE

A.1 Cu(In,Ga)Se₂/CdS Interface

As opposed to homojunction cells (like silicon solar cells) that require n- or ptype dopant to form the p-n junction, a heterojunction is created between n-type CdS and p-type CIGS [1-5]. The band diagram in Figure 42 depicts the band alignment of ZnO/CdS/CIGS, with energy band gaps of 3.2eV/2.4eV/1.14eV [22,27]. The conduction band of CIGS sits higher than CdS, and ZnO conduction band sits below CdS, closer to the Fermi level. At the CdS/CIGS interface, a conduction band offset (ΔE_C) in the form of a spike is formed (Figure 42) [1-5]. A spike at an interface is usually detrimental for a solar cell [1-4], models show however, that if ΔE_C is less than 0.5eV [28-30], electrons can transport across the interface assisted by thermionic emission, in which for CdS/CIGS, this $\Delta E_C = 0.3eV$ [31].

The OVCs of stoichiometric Cu-chalcopyrite materials and plays a critical role in interface recombination in CIGS solar cells (Figure 43). This phenomenon is supported by the work of [33], which they verified the importance of OVCs by a careful growth of CIGS absorber without V_{Cu} . The growth details are mentioned in [32], in which showed the full devices without OVC layer suffered and resulted into poorer device performance. In our work, we showed that replacing some Cu atoms with Ag atoms would shift the VBM further below the Fermi level of ACIGS materials, therefore, could lead possible lead to a decrease in interface recombination due to a lower VBM. Certain conditions need to be met, however. The first condition of course is that Ag must be added, but the main condition seems to be that GGI ratio needs to be greater than 0.3. With the Ag addition and GGI > 0.3, the VBM can shift much further below the Fermi level as shown in Figure 42.

The device performance of each sample is listed in Table 5. The best device has a GGI ratio of 0.3 and AAC ratio of 0.3.



Figure 42 Band diagram of ZnO/CdS/CIGS [22,27]. Band bending in the form of a spike $\Delta E_C = 0.3 \text{eV}$ [31]



Figure 43 Band diagram of ZnO/CdS/CIGS a) electrons recombining with holes, b) OVC layer inducing a downward shift in VBM

Bulk GGI and AAC Ratio	Voc (V)	Jsc (mA/cm2)	FF (%)	Eff (%)
GGI(0.0)AAC(0.0)	0.471	36	72.7	12.3
GGI(0.0)AAC(0.3)	0.463	36.9	74.2	12.3
GGI(0.0)AAC(1.0)	0.081	25.7	34.6	0.7
GGI(0.3)AAC(0.0)	0.661	29.4	75.8	14.7
GGI(0.5)AAC(0.0)	0.71	26.3	72.1	13.5
GGI(0.8)AAC(0.0)	0.748	12.5	65.1	5.7
GGI(0.3)AAC(0.3)	0.637	30.8	77.1	14.9
GGI(0.5)AAC(0.3)	0.598	25	69.9	10.4
GGI(0.8)AAC(0.3)	0.693	21	64.3	8.7
GGI(0.3)AAC(0.5)	0.676	25.81	75.7	13.1
GGI(0.5)AAC(0.5)	0.752	25.8	70.3	13.1
GGI(0.8)AAC(0.5)	0.731	17.6	64.4	8
GGI(0.3)AAC(0.8)	0.683	27.1	69	12.2
GGI(0.5)AAC(0.8)	0.788	23.2	72.1	12.9
GGI(0.8)AAC(0.8)	0.861	16.5	72.1	10.1

Appendix B

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