To my family
ACKNOWLEDGMENTS

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<td>Ag-Cu-In-Ga-Se</td>
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<td>AFM</td>
<td>Atomic force microscopy</td>
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<td>ALD</td>
<td>Atomic layer deposition</td>
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<td>CALPHAD</td>
<td>Calculation of phase diagram</td>
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<td>CIGS</td>
<td>Cu(In$_{1-x}$Ga$_x$)Se$_2$</td>
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<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
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<td>DEZn</td>
<td>Diethylznic</td>
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<td>DSC</td>
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<td>DTA</td>
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<td>$E_g$</td>
<td>Band gap of a semiconductor</td>
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<td>FF</td>
<td>Fill factor</td>
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<td>GIXRD</td>
<td>Grazing incidence X-ray diffraction</td>
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<tr>
<td>ICP-AES</td>
<td>Inductively coupled plasma atomic emission spectroscopy</td>
</tr>
<tr>
<td>$J_{SC}$</td>
<td>Short-circuit current density</td>
</tr>
<tr>
<td>J-V</td>
<td>Current density-voltage</td>
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<td>NREL</td>
<td>National renewable energy laboratory</td>
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<td>PV</td>
<td>Photovoltaics</td>
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<tr>
<td>PVD</td>
<td>Physical vapor deposition</td>
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<tr>
<td>QE</td>
<td>External quantum efficiency</td>
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<tr>
<td>RTA</td>
<td>Rapid thermal annealing</td>
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<td>SEM</td>
<td>Scanning electron spectroscopy</td>
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<tr>
<td>SGTE</td>
<td>Scientific Group Thermodata Europe</td>
</tr>
<tr>
<td>TEGa</td>
<td>Triethylgallium</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron spectroscopy</td>
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>TMA</td>
<td>Trimethylaluminum</td>
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<td>TMIn</td>
<td>Trimethylindium</td>
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<td>UV-Vis</td>
<td>Ultraviolet–visible spectroscopy</td>
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<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<td>XRD</td>
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The thermodynamic database for the Ag-Cu-Ga-Se quaternary system was optimized against all available experimental data using the CALPHAD (CALculation of PHAse Diagram) method in order to aid the development of (Ag,Cu)(In,Ga)Se$_2$ selenization processes. The Bragg-Williams random mixing model, sublattice model and ionic liquid model were used to simulate the Gibbs free energy of the system. A set of consistent parameters was obtained by the CALPHAD method, and reasonable agreement was reached between the thermodynamic properties for various phases and phase relations of this system.

Zinc Oxysulfide (ZnO$_{1-x}$S$_x$) thin film was deposited using Atomic Layer Deposition (ALD) on CIGS thin film substrate, serving as an alternative buffer layer material to CdS for wide-bandgap CIGS thin film solar cells. XPS studies of the deposited films indicated that the concentration of sulfur in the buffer layer film deviated negatively from the precursor pulse ratio. The deposited film had a polycrystalline structure and the conformality of the deposited film was confirmed. Cells were fabricated and tested with variable buffer layer composition and thickness. The highest efficiency, 11.58%, was achieved with 0.9 H$_2$S pulse fraction. The efficiency decreases with decreasing and
increasing S concentration, reaching 0% at S/(S+O) ratio of 0.5. A lower fill factor and short circuit current density is primarily responsible for the reduced performance, which may be caused by parasitic resistances induced by recombination at the absorber/buffer layer interface or the conduction bandgap offset.

In and Ga were doped into ZnO thin film. The comparable minimum resistivity 1.65 x 10^{-3} \, \Omega \cdot \text{cm} was reached using 0.1 and 0.05 TMIn and TEGa pulse fraction for ZnO:In and ZnO:Ga, respectively. For the samples with minimum resistivity, the ZnO:In shows high carrier concentration but low mobility while ZnO:Ga shows high mobility but relatively lower carrier concentration. The efficiency of complete cells using ZnO:In and ZnO:Ga as TCO materials was measured as 6.03% and 11.51%. The cell with ZnO:Ga shows better $V_{OC}$ and $J_{SC}$ because the Ga-doped ZnO shows better transmission and its larger bandgap and moderate carrier concentration may lead to a more favorable band offset at the interface.
CHAPTER 1
INTRODUCTION

Background

Since the past few centuries, the demand of the energy has grown exponentially and is expected to grow further in future due to the increasing population and the technology development of the whole world. Although in 2015, the energy demand increased by only 0.9%, which is the slowest rate since 1998, it still put a lot of pressure on the conventional energy sources such as oil, gas and coal because this type of energy counts up to more than 80% energy consumption in the world. On the contrary, renewable energy counts less than 10%. Among all different kinds of renewable energy, hydroelectric energy reached the shares of global primary energy consumption 6.8% and the others are around 2.5% (Figure 1-1).

The increasing utilization of traditional fossil fuel will not meet the energy demand because it is nonrenewable and has very limited quantity. Furthermore, the consumption traditional fossil fuel releases large amount CO$_2$, which is a huge concern in terms of the environment protection. The increasing concentration of CO$_2$ in atmosphere causes the rise of the temperature and the acidification of ocean. CO$_2$ absorbs the infrared part of radiation from the earth and re-radiates it back to the earth, creating the effect of “greenhouse”. Erratic weather patterns and submerging of certain areas due to melting of ice at poles could happen if the greenhouse effect cannot be controlled in future.

In order to meet the increasing demand of energy while minimize the damage to the environment, it is necessary to utilized renewable or green energy source. And solar energy is a promising energy source. Compared to other type of renewable energy
source such as hydroelectricity, wind energy, solar energy is abundant and widely spread all over the world. Thus, the utilization of solar energy would be low cost and unrestricted geographically. Furthermore, during the use of solar energy, no waste and emission is generated and the operating and maintenance cost is relatively low.

There are several different photovoltaics materials, which can convert the solar energy directly to electricity such as Crystalline Si, thin-film CIGS and CdTe, single-junction GaAs etc. as shown in Figure 1-2. Among all these materials, CIGS thin film solar cell has the advantage of low manufacture cost, suitability for flexible substrate and better resistance to heat. Currently, the CIGS thin film technology has demonstrated laboratory solar cell efficiency 22.3%. This performance approaches that of the Si solar cell technology, but lacks significantly in large-scale production. The average commercial module performance is about 12%, and thus a large gap exists between the laboratory state of the art solar cells, and power modules from production. So the question is what are the technical barriers and the cost reduction opportunities that need to be tackled to both increase module efficiency and reduce manufacturing cost.

**Problem Statement**

The chalcopyrite alloy Cu(In_{1-x}Ga_x)Se_2 has received tremendous success as an absorber for thin film PV devices, demonstrating the highest efficiency of any polycrystalline thin film material [1]. The absorber composition of this champion cell, however, is not at the bandgap energy. This has motivated research on alloying Ag with Cu to increase the bandgap energy while also increasing cell efficiency. The substitution of Ag for Cu in CIGS absorber layers shifts the bandgap energy higher and towards the optimal value (1.4 eV) while decreasing materials cost. In addition to increasing the
bandgap, researchers have begun investigating \((\text{Ag}_{x}\text{Cu}_{1-x})(\text{In}_{x}\text{Ga}_{1-x})\text{Se}_2\) alloys as a means to reduce processing temperature, improve crystalline quality, improve wetting, and attain greater power conversion efficiencies [2, 3].

The synthesis process of CIGS has been well-studied [4-8] and several researches have been done on the assessment of \(\text{Cu-In-Ga-Se}\) system [9-17] to aid the optimization of the synthesis process of CIGS. The phase relation change during the synthesis process of CIGS is complicated and the implementation of Ag would cause change of the material phase and reaction temperature. However, the effect of the Ag addition on the phase relation change is not clear, which causes the difficulties to optimize the synthesis reaction pathway for the ACIGSe. Therefore, the thermodynamic description of ACIGSe system is of interest to better understand the absorber synthesis process.

Furthermore, with this substitution and higher bandgap, an alternative buffer layer material to CdS is needed to retain a favorable band alignment with the absorber. For CdS buffer layer, it has been shown that an electrically resistive \(i\)-ZnO layer is beneficial for reducing the shunts effect [18]. However, the extra layer not only reduce the photon transmission but also increasing the manufacturing cost. Therefore, eliminating \(i\)-ZnO layer would simplify the fabrication process and beneficial for the cost control. Extensive studies have been done on the alternative Cd-free buffer layer materials [19-24]. Zinc Oxysulfide \(\text{(ZnO}_{1-x}\text{S}_x)\) is a candidate buffer layer material since its electrical and optical properties are tunable by varying the oxygen to sulfur ratio in the film. Furthermore, the wider bandgap of \(\text{ZnO}_{1-x}\text{S}_x\) compared to CdS and the thinner film possible with conformal ALD compared with conventional chemical bath deposited
CdS, promises higher transmission especially in high wavelength range. It has been applied on various solar materials as a buffer layer using different deposition technique [22, 25, 26]. Among all these deposition technique, atomic layer deposition shows significant advantage due to its strong capability of thickness, doping concentration and film conformality control. Furthermore, ALD usually requires low deposition temperature and generate less waste. This would minimize the degradation of the cell performance induced by the thermal diffusion [27].

Beside the buffer layer, the properties of transparent conducting oxides (TCO) can affect the performance of the solar cell because it not only conducts the photocurrent generated from the underlying cell but also, in the meantime, transmits the photon to the absorber layer. Therefore, good transmission and low resistivity are two favorable properties of TCO for photovoltaic application. Stadler et al. [28] did a comprehensive review on various TCO materials including ITO, ZnO:Al etc. These n-type TCOs are important for thin film solar cell production and have been extensively studied [29-33].

Among all these TCO materials, ZnO based material has drawn a lot of attention for PV application due to its wide bandgap of 3.3 eV [34]. Compared with Al depant, Ga and In can be a better dopant candidates due to the relatively smaller difference between their ion radius and Zn$^{3+}$ ion radius. Both In (ZnO:In) and Ga-doped ZnO (ZnO:Ga) has been studied using various deposition method such as sputtering [35-42], chemical vapor Deposition [43-46], chemical spray [47-49], pulsed laser deposition [50, 51] and sol-gel method [52-54]. Compared to the deposition technique mentioned above, atomic payer deposition (ALD) shows many advantage such as the ability to
finely control the doping level and film thickness, typically lower deposition temperature, good film uniformity and conformality. There are several studies about ZnO:Ga using ALD with various Ga precursor, such as trimethylgallium (TMGa) [55], gallium(III) isopropoxide (GTIP) [56] and triethylgallium (TEGa) [57-59]. However, studies on ZnO:In were much less. Hsia et al. and Kim et al. used trimethylindium (TMIn) [60] with N₂O and dimethylamino-dimethylindium (DMLDMIn) [61] with H₂O for atomic layer deposition respectively. Although these studies developed the deposition process, the deposition using CIGS/CdS bilayer substrate has never been conducted before. Furthermore, the high deposition temperature (above 300 °C) leads to the degradation of the solar cell [27].

Present Contribution

Present contribution contains three parts: the assessment and thermodynamic modeling of Ag-Cu-In-Ga-Se system, the use of atomic layer deposition (ALD) to form ZnO₁₋ₓSₓ as buffer layer and ZnO:Ga/In as TCO layer, the effect of rapid thermal annealing on the complete cell.

The Ag-Cu system was reassessed in Chapter 2. A new self-consistent model was established based on newly published Cu activity data in the FCC solid phase. In Chapter 3, on the basis of thermochemical and phase boundary data, the Ag-Se binary system was thermodynamically assessed and modeled. The 2-sublattice and 3-sublattice models were used to model the low and high temperature phase of the intermetallic compound Ag₂Se, respectively, based on their special order-disorder structure transition. DFT calculation was used to calculate the Gibbs free energy of formation of the end members in the models. A set of modeling parameters was obtained by the CALPHAD method and reasonable agreement was reached between
the thermodynamic properties for various phases and phase relations of this system. In Chapter 4 and Chapter 5, an assessment of the thermochemistry and phase equilibria of the Ag-Cu-Se, Ag-Ga-Se, Ag-In-Se and higher order system was performed based on available experimental data and predictions of temperature dependence of the Gibbs energies of formation for the intermetallic compounds. With the complete thermodynamic database, the implications for selenization of metal precursors are explored.

In Chapter 6, rapid thermal annealing studies were conducted on SS/Mo/CIGS/CdS/ITO/Ag devices as a function of anneal time in dry N₂ in the temperature range 50 to 200 °C, as well as in humidified N₂ (85% RH) at 85 °C. Interestingly, dry N₂ annealing produced an enhancement in cell performance for low thermal budget, predominantly due to increased J_{SC}, and to a lesser extent higher V_{OC}. As examples, CIGS cell efficiency increased by 1.8±0.8% after annealing at 50 °C for 300s and 2.0±2.3% when annealed at 100 °C for 600s. At higher anneal temperature or longer time the cell performance deteriorated with significant decrease in FF and V_{OC}. The results for the 85% RH at 85 °C anneals were similar to the dry anneal studies but with less dramatic changes. Cell performance results after dark annealing indicate light-soaking effects induced by the lamp are not important at these relatively short anneal times. Measurement of quantum efficiency for the annealed samples supports the assumption that the buffer layer/absorber interface degrades at a relatively low temperature and that ITO degradation takes place at higher thermal budgets.

In Chapter 7, Zinc Oxysulfide (ZnO_{1-x}S_x) thin film was deposited using Atomic Layer Deposition (ALD) on CIGS thin film substrate, serving as an alternative buffer
layer material to CdS for wide-bandgap CIGS thin film solar cells. XPS studies of the deposited films indicated that the concentration of sulfur in the buffer layer film deviated negatively from the precursor pulse ratio. The surface morphology and film structure were examined using SEM and XRD, respectively. Results showed that the deposited film had a polycrystalline structure and the conformality of the deposited film was excellent. Cells were fabricated and tested with variable buffer layer composition and thickness. The highest efficiency, 11.58%, was achieved with 90.9% S/(S+O) ratio. The efficiency decreases with decreasing and increasing S concentration, reaching 0% at S/(S+O) ratio of 0.5. A lower fill factor and short circuit current density is primarily responsible for the reduced performance, which may be caused by parasitic resistances induced by recombination at the absorber/buffer layer interface or the conduction bandgap offset.

Doping of ZnO with In during ALD by periodic exposure to TMIn was studied with an emphasis on the structural properties of the films (Chapter 8). XRD results show compressive stress in the film induced by the larger In atom, which leads to smaller grain size. Based on these results stacked layers of ZnOS/ZnO:In and sputtered sputtered ZnOS/ZnO:Al were deposited on CIGS thin films to compare the performance of the ALD TCO to that of our standard TCO. The complete cell with ZnO:In as TCO shows relatively low $J_{SC}$ and $R_{se}$ compared with the cell using sputtered ZnO:Al as TCO. In Chapter 9, In and Ga-doped ZnO thin films with various doping level were deposited using atomic layer deposition on Si (100), borosilicate glass and CdS/CIGS/Mo/Stainless Steel substrate. The properties of ZnO:In and ZnO:Ga were characterized and the performance of the complete cell was tested and analyzed.
ZnO:Ga was found to be a better TCO material than ZnO:In. Both films show minimum resistivity around $1.65 \times 10^{-3} \ \Omega \cdot \text{cm}$ but ZnO:Ga shows relatively lower carrier concentration and higher carrier mobility compared to ZnO:In. XRD spectra reveal that both films exhibit hexagonal ZnO structure. In and Ga dopants induce compressive and tensile stress to the film, respectively. Compared to ZnO:Ga, ZnO:In shows less transmission and smaller bandgap due to the higher free carrier concentration, higher doping level and less bonding strength. The conduction band offset of ZnO:In/CdS and ZnO:Ga/CdS was measured as 0.8 eV and 0.23 eV, respectively. The complete solar cell with ZnO:In as TCO layer shows lower efficiency due to the relatively lower $J_{\text{SC}}$ and $V_{\text{OC}}$. This can be attributed to the relatively lower transmission and higher conduction band offset at the ZnO:In/CdS interface.
World primary energy consumption grew by a below-average 1.0% in 2015, the slowest rate of growth since 1998 (other than the decline in the aftermath of the financial crisis). Growth was below average in all regions except Europe & Eurasia. All fuels except oil and nuclear power grew at below-average rates. Oil remains the world’s dominant fuel and gained global market share for the first time since 1999, while coal’s market share fell to the lowest level since 2005. Renewables in power generation accounted for a record 2.8% of global primary energy consumption.

Figure 1-1. Change of the source of energy consumption worldwide [62].

Figure 1-2. Research cell efficiency records.
CHAPTER 2
THERMODYNAMIC OPTIMIZATION OF THE AG-CU SYSTEM

CIGS based solar cells have shown more than 20% photovoltaic (PV) conversion efficiency [63, 64]. In order to further increase their efficiencies and minimize their production costs, Ag can be added to substitute part of Cu to form a PV material with larger band gap [65, 66]. However, the reaction pathway during the synthesis process of CIGS is complicated and adding Ag into CIGS makes it even more difficult to be optimized. Fully understanding the Ag-Cu-In-Ga-Se thermodynamic system and phase equilibrium will be helpful in discovering the most efficient reaction pathway. In this work, the Ag-Cu system was thermodynamically optimized as a part of the complete database and a good agreement between the calculated thermodynamic properties and experimental data was archived.

Ag-Cu System in Literature

Phase Diagram

According to extensive experimental results, the phase diagram of Ag-Cu system is a simple eutectic diagram without any miscibility gap in the liquid phase. In the current work, the maximum solubility of Cu in Ag and Ag in Cu are assessed as 0.100 and 0.046 in mole fraction of Cu and Ag, respectively. The calculated phase diagram and the comparison with selected experimental data [67-69] are shown in Figure 2-2A. Special points from selected previous assessment work and from the current work are shown in Figure 2-2B.

The liquid phase of Ag-Cu system has been investigated by many groups since 1875 [67, 70-78]. Various experimental methods such as DTA, EMF measurements, pyrometry, etc. were used in these measurements and no miscibility gap was reported.
Among these values, the experimental data from Heycock et al. [70] were widely accepted since it has been confirmed by other experimental results obtained from using high purity metal and low oxygen contamination from Rosina et al. [67, 76]. The detailed experimental values were collected in Subramanian et al. [67].

The most recent eutectic point was reported at 1053K in Bienzle et al. [69]. Before that, several groups [70-72, 79-81] measured the eutectic temperature ranging from 1050.15 K to 1053 K with various methods [67]. In this work, the eutectic temperature 1052.1±0.08 K from Moser et al. [81] was used as suggested by Subramanian et al. [67] because the eutectic temperature purposed by in Bienzle et al. [69] was extrapolated whereas Moser et al. [81] carefully measured the temperature with high purity metal. The composition of eutectic point reported as 0.399±0.002 in mole fraction of Cu by Hansen [82] was used for optimization in this work because according to Subramanian et al. [67], previous experimental results were all in a small range between 0.398 and 0.410 of Cu in mole fraction. Bahari et al. [83] reinvestigated the Ag-Cu system by using Tamman plot. A similar results as Subramanian et al. [67] were obtained.

The solidus and solvus of Ag-Cu system have been reported by many groups [71-73, 75, 76, 78, 80, 84-88]. No intermetallic compounds were reported in previous work. Selected experimental data are summarized in Elliott et al. [86]. The experimental data on Cu-rich side generally show good agreement while on the Ag-rich side there was significant scattering in the data. The most recent solidus and solvus was reported by Bienzle et al. [69]. In order to adopt the thermodynamic data measured in Bienzle et al. [69], these constitutional data were used for optimization in the current work but with
relative lower weight because they were estimated by extrapolating EMF value to zero. Witusiewicz et al. [68] reported another set of solidus and solvus data measured by Sommer [89]. However, these data are unpublished. Due to a lack of detailed experimental method and condition, they were not used for optimization in current work.

**Thermodynamic Properties**

Several researchers [75, 90, 91] have conducted measurement of the thermodynamic properties of Ag-Cu system in solid phase. The experimental data measured before 1990 were summarized by Subramanian et al. [67]. Besides these summarized data, the activities of Cu and integral thermodynamics data of the solid phase on Ag-rich side were measured by Bienzle et al. [69] with EMF measurement by using high purity metal. In this work, the enthalpy of mixing in solid phase at 1052 K from Subramanian et al. [67] were used since these data were in good agreement with previous experimental results [75]. Furthermore, other newly measured thermodynamic data from Bienzle et al. [69] including the enthalpy of mixing in solid phase at 1053K and the activity of Cu in solid phase at various temperatures were used.

Subramanian et al. [67] completed a summary about the thermodynamic properties in the liquid phase and some of the measurements were repeated. The published results are identical to previous work [92-98]. After that, the enthalpies of mixing in liquid phase of Ag-Cu system were re-determined using a new in-situ mixing technique at 1375±2 K by Fitzner et al. [99].

**Thermodynamic Modeling**

Before the current work, several groups have assessed the thermodynamic database of Ag-Cu system [68, 100-104]. Researches have shown that Murray et al. [100], Lim et al. [102] and Kusoffsky [103] generate deviation from the experimental
data [67, 68]. Currently, the data or the thermodynamic data reported by Hayes et al. [101] was widely used in other thermodynamic assessment research. However, the calculated data using Hayes et al. [101] shows noticeable deviation compared with experimental values reported in by Bienzle et al. [69] and Fitzner et al. [99]. Although the results from Witusiewicz et al. [68] and He et al. [104] can fit the thermodynamic values from Fitzner et al. [99], their calculated results do not show satisfactory agreement with the experimental data reported by Bienzle et al. [69].

**Thermodynamic Models**

**Pure Elements**

The description of the Gibbs energy of pure Ag and Cu was taken from the most recent complication Dinsdale [105]. They were modeled by using the following equation with different sets of parameters for corresponding temperature intervals:

\[
^\circ G - H^{SER} = A + BT + C T \ln T + DT^2 + ET^{-1} + FT^3 + IT^7 - JT^{-9}
\]

where \( H^{SER} \) means enthalpy of standard element reference referring to the enthalpy of the stable state of the pure element at 298.15 K, \( T \) is the absolute temperature and A~J are the coefficients.

**Liquid Phase and Solid Phase**

Extensive experiments have shown that there is no miscibility gap in the liquid phase and no stoichiometric compound was found in the solid phase. In this work, the disordered liquid phase and \( \alpha \) phase (fcc-A1) of Ag-Cu system are described by Bragg-Williams random mixing model. The Gibbs energy of these phases can be expressed as:

30
\[ G^\phi = x_A^{\phi} G_A^\phi + x_B^\phi G_B^\phi + RT \left( x_A \ln x_A + x_B \ln x_B \right) + ^{XS} G^\phi \]  \tag{2-2}

where \( \phi \) refers to the phase to be described, \( x \) means element mole fraction and \(^{XS} G^\phi\) can be described with a simple Redlich–Kister polynomial expansion:

\[ ^{XS} G^\phi = x_A x_B \sum_{v=0}^{n} v L^\phi_{A,B} (x_A - x_B)^v \]  \tag{2-3}

where \( v L^\phi_{A,B} \) refers to the interaction coefficient for phase \( \phi \) in an A-B binary system. In the current work, these parameters are expressed as the first two terms of Equation 2-3:

\[ v L^\phi_{A,B} = a^\phi + b^\phi T \]  \tag{2-4}

where \( a \) and \( b \) are the parameters for each phase \( \phi \) to be optimized with PANDAT 8.1 software.

**Result and Discussion**

The thermodynamics parameters of the binary Ag-Cu binary system were optimized with Optimization Function in the PANDAT 8.1 software. For the rough search process, all experimental values including phase equilibrium data, enthalpy of mixing and partial molar activity in liquid phase, components activity at various temperature and enthalpy of mixing on silver-rich side in solid phase, are taken into consideration. Finally, in the normal optimization process, the constitutional data on Ag-solvus were excluded because these data are calculated by extrapolating the EMF value to zero and based on the assumption that the concentration of Cu is nearly zero, which could generate large error especially for these points near 0.1 mole fraction of Cu. The phase diagram calculated using optimized database in this study was shown in Figure 2-1.

Figure 2-2A illustrates the comparison between the calculated phase diagram and the experimental phase equilibrium data. An enlarged phase diagram in the range
of 0 to 0.11 mole fraction of Cu is plotted in Figure 2-2B. The optimized thermodynamic parameters are summarized in Table 2-2. The calculated phase diagram generally shows a good agreement with the experimental phase equilibrium data. However, as shown in Figure 2-2B, on the Ag-rich side in fcc-A1 phase, the solidus and solvus deviate from some of the experimental data because the composition-temperature data proposed by Bienzle et al. [69] were extrapolated. The extrapolation for solvus was based on the assumption that the concentration of Cu in Ag was very small and thus can be neglectable. Therefore, these data may have relatively lower accuracy and need to be confirmed by other methods, e.g. dilatometric measurements, DTA etc.

Table 2-1 shows the calculated and experimental special points in the Ag-Cu system including melting points, eutectic reaction and maximum solubility. It is worth noting that most of these calculated points show good agreement with the experimental data except the maximum solubility of Cu on silver-rich side. This is because first, on the silver-rich side, the experimental data were significantly scattered and secondly, in order to match with the measured activity data by Bienzle et al. [69], the extrapolated maximum solubility of Cu in Ag in the same work, which was not reconfirmed by other experimental means, was used for optimization.

The activity of Cu on the silver-rich side in FCC phase and selected integral thermodynamic value are plotted in Figure 2-3 and Figure 2-4. Compared with the activity calculated with Hayes et al. [101], the cooper activity curves generated with current work show better agreement with the experimental data measured by Bienzle et al. [69] except one data point at 0.04 mole fraction of copper at 1053 K, which is considered as statistical outlier and thus was used with less weight.
The comparison between calculated and experimental excess Gibbs free energy and partial molar activity in liquid phase at 1400 K are illustrated in Figure 2-5 and Figure 2-6, respectively. These experimental values, which have a good agreement with previous experiment results, are taken from Subramanian et al. [67]. Figure 2-5 shows that the excess Gibbs free energy curve generated with the optimized database in current work has a good agreement with the experimental data. However, the calculated curve from Hayes et al. [101] shows negative deviation from the experimental value and its maximum value shifts to the silver-rich side, which is different from the fact that the experimental data show symmetry about 0.5 mole fraction of copper. Compared with the curve calculated with Hayes et al. [101], the optimized database generates better agreement with the experimental data in both value and symmetry aspects.

The calculated and experimental data [99] of enthalpy of mixing in the liquid phase at 1375±2 K are plotted in Figure 2-7. As shown in the figure, the calculated enthalpy curve is identical to the experimental data, while there is a large discrepancy between the curve calculated with Hayes et al. [101] and the experimental data [99].

The phase diagram of Ag-Cu system is an exception of the Hume-Rothery theory because limited solubility is shown on both Ag-rich and Cu-rich side. The main reason can be that the atomic radii difference between silver and copper is 12.5%, which is very close to the empirical value proposed by Hume-Rothery 14%-15% [106]. When Ag atoms substitute the solvent Cu atoms or vice versa, extra energy will be required since relatively large lattice distortion takes place due to the difference atomic sizes of silver and copper. Therefore, the completely solution is not thermodynamically favorable for Ag-Cu system.
Summary

The thermodynamic database for the binary Ag-Cu binary system was optimized based on available experimental data using the CALPHAD (CALculation of PHAse Diagram) method. The Bragg-Williams random mixing model was used to describe both liquid phase and fcc-A1 phase. The latest measured activity of Cu and enthalpy of mixing were used in optimization process. A simple eutectic Ag-Cu phase diagram was reached using the optimized database. The calculated thermodynamic properties and phase diagram in the current work shows better agreement with the latest experimental data than those generated from previous databases.
### Table 2-1. Special Points in the Ag-Cu System

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Composition mole fraction of Cu</th>
<th>Temperature K</th>
<th>Reaction type</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag ↔ L</td>
<td>0</td>
<td>1234.98</td>
<td>Melting</td>
<td>[67]</td>
</tr>
<tr>
<td>L ↔ (Ag) + (Cu)</td>
<td>0.100 0.399 0.954</td>
<td>1052.25</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.129 0.416 0.955</td>
<td>1054.4</td>
<td></td>
<td>[101]</td>
</tr>
<tr>
<td></td>
<td>0.121 0.398 0.953</td>
<td>1053.4</td>
<td>Eutectic</td>
<td>[68]</td>
</tr>
<tr>
<td></td>
<td>0.141 0.397 0.951</td>
<td>1055.79</td>
<td></td>
<td>[104]</td>
</tr>
<tr>
<td></td>
<td>0.136 0.398 0.952</td>
<td>1054</td>
<td></td>
<td>[100]</td>
</tr>
<tr>
<td></td>
<td>0.141 0.399 0.951</td>
<td>1052.25</td>
<td></td>
<td>[67]</td>
</tr>
<tr>
<td></td>
<td>0.134 0.399 0.078</td>
<td>1053.05</td>
<td></td>
<td>[83]</td>
</tr>
<tr>
<td>Cu ↔ L</td>
<td>1</td>
<td>1357.77</td>
<td>Melting</td>
<td>[67]</td>
</tr>
</tbody>
</table>

### Table 2-2. Thermodynamic model parameters of the Ag-Cu system

<table>
<thead>
<tr>
<th>Phase</th>
<th>Thermodynamic Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>( L_{\text{Ag,Cu}}^{0} = 14144.1 - 0.3690T )</td>
</tr>
<tr>
<td></td>
<td>( L_{\text{Ag,Cu}}^{1} = -1381.51 + 1.4017T )</td>
</tr>
<tr>
<td></td>
<td>( L_{\text{Ag,Cu}}^{2} = 1462.21 )</td>
</tr>
<tr>
<td>fcc-A1</td>
<td>( L_{\text{Ag,Cu}}^{0} = 26579 - 3.3516T )</td>
</tr>
<tr>
<td></td>
<td>( L_{\text{Ag,Cu}}^{1} = -9626.37 + 7.7262T )</td>
</tr>
<tr>
<td></td>
<td>( L_{\text{Ag,Cu}}^{2} = 7380.9 )</td>
</tr>
</tbody>
</table>
Figure 2-1. Assessed Ag-Cu phase diagram.
Figure 2-2. Assessed Ag-Cu phase diagram and enlarged phase diagram between 0 and 0.11 in mole fraction of Cu with selected experimental data. The black line is the assessed phase boundary.
Figure 2-3. Activity of Cu in solid phase on silver-rich side (reference state: fcc-A1 phase of Cu). ■ [69] 950 K, ● [69] 1000 K ▲ [69] 1100 K ▼ [69] 1053 K ♦ [69] 1150 K. Blue lines are the activity calculated using the database from [101]. Red lines refer to the activity derived from the optimized database from current work. Black line indicates Raoult’s Law.
Figure 2-4. Enthalpy of mixing of Ag-Cu system in solid phase. The solid square (■) indicates experimental data measured by [69] and red line the data calculated from [101]. Black line refers to the Enthalpy derived from this study.
Figure 2-5. Excess Gibbs free energy of Ag-Cu system in liquid phase at 1400 K. The solid square (■) indicates experimental data measured by [67] and the red dash line refers to Hayes et al. [101]. The black curve is extract from the database assessed in this study.
Figure 2-6. Activity of Ag and Cu in liquid phase at 1400 K (reference state: liquid phase of Ag and Cu, respectively). □, O is the activity of Ag and Cu, respectively, taken from [67]. The blue dash line refers to [101] and the red line is the activity calculated using the optimized database in this study.
Figure 2-7. Enthalpy of mixing of Ag-Cu system in liquid phase at 1375±2 K. The solid square (■) indicates experimental data measured by [99] and the red dash line refers to [101]. The black line is the curved extracted from the optimized database in this study.
CHAPTER 3
THERMODYNAMIC OPTIMIZATION OF THE AG-SE SYSTEM

CuIn\(_{x}\)Ga\(_{1-x}\)Se\(_2\) (CIGS) based solar cells have been confirmed showing a 22.3% photovoltaic (PV) conversion efficiency – one of the highest efficiencies of PV thin film materials [107]. The addition of Ag to substitute part of Cu can adjust the bandgap closer to the theoretical optimum band gap 1.4 eV for Air Mass (AM) 1.5 solar spectrum for further increasing the conversion efficiencies [65, 66, 108]. The prediction of phase equilibrium using the Ag-Cu-In-Ga-Se (ACIGS) thermodynamic database will be helpful in discovering the most efficient reaction pathway and process conditions, making the present Ag-Se system vital important. Furthermore, the low temperature phase, α-Ag\(_2\)Se, is a narrow bandgap semiconductor and the high temperature phase, β-Ag\(_2\)Se, is a superionic conductor [109-111]. Both of them are widely used in photographic films, thermochromic materials, and photochargeable secondary batteries [112].

The phase diagram and thermochemical properties of Ag-Se system were extensively studied [113-116] and previously reviewed [117-119], but the thermodynamic model has not been established yet, which makes it difficult to predict the effect of Ag on the phase relationships of the CIGS material. In this study, the thermodynamic model was set up using CALPHAD (calculation of phase diagram) approach [ref] combined with DFT (density functional theory) calculations based on evaluation of experimental data in the Ag-Se system. A five-sublattice model is applied for the high temperature phase of Ag\(_2\)Se compound based on the study of its disordered structure with large vacancy occupancy [120, 121]. The Gibbs energy of formation of endmembers in the sublattice model was obtained using DFT calculations. A two-sublattice model was used for low temperature phase of Ag\(_2\)Se and the Gibbs free
energy of formation was also calculated with DFT approach for the endmembers. A good agreement between the calculated phase diagram and thermodynamic properties with experimental data were archived using the self-consistent thermodynamic model established in this work.

**Literature Review**

**Phase Diagram**

The latest Ag-Se phase diagram was constructed by Karakaya et al. [117] as shown in Figure 3-1. According to this evaluation, the Ag-Se system contains one intermetallic compounds Ag\(_2\)Se with two polymorphs of \(\alpha\)-Ag\(_2\)Se with orthorhombic structure at low temperatures (space group \(P\bar{2}_1\bar{2}_1\bar{2}_1\), < 405.42 K) and \(\beta\)-Ag\(_2\)Se with body-centered cubic (bcc) structure at high temperatures (space group \(Im\bar{3}m\), > 405.42 K), two terminal solid phase face-centered cubic (fcc) fcc-Ag and trigonal-Se, and two miscibility gaps in the liquid phase.

Several investigations determined the liquid phase equilibrium. The existence of two miscibility gaps in the liquid phase was reported by Friedrich [122] and Pellini [123], and was confirmed by Houphouet-Boigny et al. [124] as shown in Figure 3-2. Ohno et al. [125], Tsuchiya et al. [126] and Wiggett et al. [127] measured the phase boundaries of the miscibility gaps using conductivity measurement, \(\gamma\)-ray attenuation and sample quenching method, respectively. These three measurements show large discrepancy, except the composition and temperature of the monotectic reaction between the liquid, fcc-Ag and \(\beta\)-Ag\(_2\)Se phase. Ohno et al. [125] and Tsuchiya et al. [126] proposed a converged miscibility gap in Ag-rich liquid phase, while Wiggett et al. [127] proposed that the boundary of miscibility gap does not converge even at high temperatures.
Friedrich et al. [128] showed a very small solubility (less than 0.27 at.% Se) of Se in fcc-Ag without details. Therefore, it is not considered in the present modeling work. No solubility of fcc-Ag in Trigonal-Se was reported. Extensive studies have been conducted for the phase equilibrium and thermodynamic properties of $\alpha$-Ag$_2$Se and $\beta$-Ag$_2$Se phases. The melting temperature of $\beta$-Ag$_2$Se was measured using thermal analysis [123], differential thermal analysis (DTA) [129] and conductivity measurement [125] and these results show a good consistency as 1170 K, 1167 K and 1168 K, respectively. Measured transition temperatures between $\alpha$-Ag$_2$Se and $\beta$-Ag$_2$Se are mostly consistent except for the data obtained by Voronin et al. [130], who used electromotive force (EMF) measurement in solid electrolyte (AgCl) or a glycerol solution with constant stirring to get the transformation temperature of 397.5 K. However, Echmaeva et al. [131], Nasar et al. [132] and Feng et al. [133], using EMF measurement, reported a higher transformation temperature as 405.5 K, 406 K and 407.7 K, respectively. The transformation temperature of 406±1 K was recently reported by Asadov et al. [134] using microstructural and X-ray analysis.

Oehsen et al. [115] reported a small deviation from stoichiometry in $\alpha$-Ag$_2$Se and $\beta$-Ag$_2$Se phases, and the homogeneity range was determined using the solid state galvanic cell Ag/Ag$_3$Rbi$_5$/Ag$_2$+eSe/C between 348 K and 463 K. Grønvold et al. [135] investigated thermodynamic properties of the $\alpha$-Ag$_2$Se and $\beta$-Ag$_2$Se transformation region using adiabatic calorimetry and proposed a different phase diagram around this phase transformation region.
Thermodynamic Properties

The standard Gibbs energy of formation ($\Delta_f G^0_{298,Ag_2Se}$) and the standard enthalpy of formation ($\Delta_f H^0_{298,Ag_2Se}$) of Ag$_2$Se was extensively studied using EMF measurement [115, 130-133] and adiabatic calorimetry [135]. These results show good consistency, except that the standard Gibbs energy of formation of $\alpha$-Ag$_2$Se reported by Olin et al. [136] shows a slightly lower value (2 kJ·mol$^{-1}$). The enthalpy of transformation from $\alpha$-Ag$_2$Se to $\beta$-Ag$_2$Se has been measured using differential scanning calorimetry (DSC) [114, 130, 133, 137] and adiabatic calorimetry [135, 138]. The results from DSC scatter are between 6.06 kJ·mol$^{-1}$ and 7.68 kJ·mol$^{-1}$ while the value obtained with adiabatic calorimetry shows good consistency at ~7 kJ·mol$^{-1}$. These experimental data were summarized in Table 3-1 and Table 3-2. Blachnik et al. [139] determined the activity of Se in liquid phase at 1273 K using the modified dew point method.

Thermodynamic Models

Unary Phases

The description of Gibbs energies for pure Ag was taken from the compilation by Dinsdale [105] and that of Se was taken from Chang [140] using the following equation:

$$G^\rho_i - H^\text{SER}_i = A + BT + CT\ln T + DT^2 + ET^{-1} + FT^3 + IT^{-7} - JT^{-9}$$

(3-1)

where $H^\text{SER}$ represents the standard element reference (SER) referring to the enthalpy of the stable state of the pure element at 298.15 K and 1 bar, $T$ the absolute temperature, and $A \sim J$ the modeling parameters.

Liquid Phases

For liquid phase, the ionic-liquid two sub-lattice model was used by the following expression:
\[ G_m^o = y_{Ag^+} y_{Se^{2-}} G_{Ag^+:Se^{2-}}^o + Q y_{Va} y_{Ag^+} G_{Ag^+:Se^{2-}}^o + Q y_{Se} G_{Se}^o + \]
\[ + RT \left( P y_{Ag^+} \ln y_{Ag^+} + Q (y_{Se^{2-}} \ln y_{Se^{2-}} + y_{Va} \ln y_{Va} + y_{Se} \ln y_{Se}) \right) \]  \hspace{1cm} (3-2)

where \( G_{Ag^+:Se^{2-}}^o \) is the Gibbs energy of formation for liquid \( \text{Ag}_2\text{Se} \). \( G_{Ag^+}^o \) and \( G_{Se}^o \) are the Gibbs energies of formation of liquids Ag and Se, respectively. The values of P and Q are determined using:

\[ P = 2 y_{Se^{2-}} + Q y_{Va} \]  \hspace{1cm} (3-3)

\[ Q = 1 y_{Ag^+} \]  \hspace{1cm} (3-4)

where the value 2 in Equation 3-3 and 1 in Equation 3-4 are the charges of \( \text{Se}^{2-} \) and \( \text{Ag}^+ \) ion, respectively. The term \( \sum_{\nu=0}^{n} y_{Ag^+} \nu L_{Ag^+:Se^{2-}:Va} (y_{Se^{2-}} - y_{Va})^{\nu} \) refers to the interaction between \( \text{Se}^{2-} \) and vacancy (Va) on the Ag-rich side of the system and \( \sum_{\nu=0}^{n} y_{Ag^+} \nu L_{Ag^+:Se^{2-}:Se} (y_{Se^{2-}} - y_{Se})^{\nu} \) indicates the interaction between \( \text{Se}^{2-} \) and neutral Se atoms on the Se-rich side of the system. These two terms are expressed by the following expression:

\[ ^\nu L = a_{\nu} + b_{\nu} T \]  \hspace{1cm} (3-5)

where \( a_{\nu} \) and \( b_{\nu} \) are modeling parameters to be determined in the present work using available experimental data.

**Non-stoichiometric Compound \( \text{Ag}_2\text{Se} \)**

The low temperature phase \( \alpha-\text{Ag}_2\text{Se} \) shows an orthorhombic structure with space group of \( P2_12_12_1 \). In this structure, two Ag atoms are crystallographically independent and are distributed between the Se layers [141]. However, at high temperatures, the \( \beta- \)
Ag\textsubscript{2}Se shows bcc structure with space group of \textit{Im\textoverline{3}m}. In this structure, Se anions are arranged in bcc packing of 2a Wyckoff site and Ag cations locates partially in three kinds of interstitial positions: the octahedral 6b site, the tetrahedral 12d site, and the triangular 24h site [120, 121]. Small homogeneity range was reported in both \(\alpha\)-Ag\textsubscript{2}Se and \(\beta\)-Ag\textsubscript{2}Se [114, 115, 135]. Based on these structure information, \(\alpha\)-Ag\textsubscript{2}Se phase was described by a two-sublattice model \((\text{Ag, Va})_{2/3}(\text{Se, Va})_{1/3}\) and \(\beta\)-Ag\textsubscript{2}Se phase can be described by the sublattice model based on the experimentally measured structure [120],

\[
(Ag, Va)_6(Ag, Va)_{12}(Ag, Va)_{24}(Se)_2 \quad (3-6)
\]

where the four subscripts correspond to Wyckoff sites 6b, 12d, 24h, and 2a of space group \(\text{Im\overline{3}m}\), respectively. Since there are 44 atom sites in the lattice, it is easier to model the structure by assuming the whole lattice as one atom site. Thus the model can be modified to

\[
(Ag, Va)_{3/22}(Ag, Va)_{3/11}(Ag, Va)_{6/11}(Se)_{1/22} \quad (3-7)
\]

Based on the results of DFT calculation, for the convenience of modeling, the model was further modified as following

\[
(Ag, Va)_{3/22}(Ag, Va)_{2/11}(Ag, Va)_{1/11}(Ag, Va)_{6/11}(Se)_{1/22} \quad (3-8)
\]

The details can be found in section Calculations of Gibbs Energy.

The Gibbs energy of \(\alpha\)-Ag\textsubscript{2}Se phases are described using the following expression:

\[
G^{\alpha-\text{Ag}_2\text{Se}} = \text{ref} G^{\alpha-\text{Ag}_2\text{Se}} + \text{id} G^{\alpha-\text{Ag}_2\text{Se}} + \text{ex} G^{\alpha-\text{Ag}_2\text{Se}}
\]

(3-9)
Each term in Equation 3-9 is expressed using the expressions:

\[
\text{ref } G^{a-Ag_2Se} = y^{\text{ref}}_{\text{Ag}} y^{\text{ref}}_{\text{Se}} G^{a-Ag_2Se}_{\text{Ag}_{\text{ref}} \text{Se}_{\text{ref}}} + y^{\text{ref}}_{\text{Va}} y^{\text{ref}}_{\text{Se}} G^{a-Ag_2Se}_{\text{Va}_{\text{ref}} \text{Se}_{\text{ref}}} + y^{\text{ref}}_{\text{Ag}} y^{\text{ref}}_{\text{Va}} G^{a-Ag_2Se}_{\text{Ag}_{\text{ref}} \text{Va}_{\text{ref}}} 
\]

(3-10)

\[
\text{id } G^{a-Ag_2Se} = RT (2 y_{\text{Ag}}^2 \ln(y_{\text{Ag}}^2) + 2 y_{\text{Va}}^2 \ln(y_{\text{Va}}^2) + y_{\text{Se}}^2 \ln(y_{\text{Se}}^2) + y_{\text{Va}}^2 \ln(y_{\text{Va}}^2))
\]

(3-11)

\[
\text{ex } G^{a-Ag_2Se} = y_{\text{Se}}^2 y_{\text{Va}}^2 \sum_{v=0}^{L'} L'_{v} \text{Se}_{v} \text{Va}_{v} + y_{\text{Ag}}^2 y_{\text{Va}}^2 \sum_{v=0}^{L'} L'_{v+L'} \text{Ag}_{v} \text{Va}_{v}
\]

(3-12)

The Gibbs energy of β-Ag2Se phases are described using the similar expression but with five sublattices. The \( L' \) terms in Equation 3-12 are the interaction parameters between the constitutions on the corresponding sublattices and were optimized in this work.

**Calculations of Gibbs Energy**

Experimental data in the literature combined with DFT based first-principles calculations were employed to obtain Gibbs energy of the non-stoichiometric α-Ag2Se and β-Ag2Se phases. The DFT calculation were conducted by our collaborator, Shun-Li Shang and Zi-Kui Liu in the department of materials science and engineering at the Pennsylvania State University. First-principles calculations in the present work were conducted by Vienna Ab-initio Simulation Package (VASP 5.4.1) [142, 143] with the electron-ion interaction described by the projector augmented wave method [144]. The generalized gradient approximation developed by Perdew-Burke-Ernzerhof (PBE) [145] together with the van der Waals correction of the D3 method (i.e., PBE+D3) [146], were selected to describe the exchange-correlation (X-C) energy functional. In addition, the improved GGA-PBE for densely packed solids and their surfaces, i.e., the PBEsol [147], was also employed, since both PBE+D3 and PBEsol could describe well structural as well as phonon properties of chalcogenides [148].
During VASP calculations, eleven electrons \((5s^14p^6)\) were treated as valence electrons for Ag and six \((4s^24p^4)\) for Se. The employed plane wave cutoff energies, \(k\)-points meshes, and the smearing methods for Ag\(_2\)Se as well as Ag and Se are shown in Table 3-3. For each structure of interest (especially the low energy structures of \(\beta\) phase), its equilibrium properties (for example, energy, volume, and bulk modulus) were determined by fitting the DFT energy versus volume \((E-V)\) data points according to a four-parameter Birch-Murnaghan equation of state (EOS) [149],

\[
E(V) = a_1 + a_2V^{-2/3} + a_3V^{-4/3} + a_4V^{-2}
\]  

(3-13)

where \(a_1, a_2, a_3,\) and \(a_4\) are fitting parameters. Seven or eight data points within the volume range of \(-10\% < (V-V_0)/V_0 < 10\%\) were typically used for the present EOS fittings. Other details of DFT calculations are the same as our previous calculations [148].

Figure 3-3 shows the relative energies for some low energy structures of Ag\(_3\)Se\(_2\), Ag\(_4\)Se\(_2\), Ag\(_5\)Se\(_2\) in terms of \((Ag, Va)_6(Ag, Va)_{12}(Ag, Va)_{24}(Se)_2\) (see Equation 3-6), where the reference states are the lowest energy structures of Ag\(_3\)Se\(_2\) and Ag\(_5\)Se\(_2\), and the employed X-C functional is PBEsol. It is seen that Ag\(_4\)Se\(_2\) (\(\beta\)-Ag\(_2\)Se) is more stable with respect to Ag\(_3\)Se\(_2\) and Ag\(_5\)Se\(_2\), agreeing with Oliveria et al. [150]. It is found that the lowest energy structure of Ag\(_4\)Se\(_2\) is the configuration with 4 Ag atoms in site 12d \((1/3\) site occupancy by Ag, not shown here), and this structure is set as the stable structure of Ag\(_4\)Se\(_2\) (\(\beta\)-Ag\(_2\)Se). Therefore, for the convenience of thermodynamic modeling, the second lattice \((Ag, Va)_{3/11}\) in Equation 3-7 can be treated as \((Ag, Va)_{1/11}(Ag, Va)_{2/11}\) and the endmember \((Va)_{3/22}(Va)_{2/11}(Ag)_{1/11}(Va)_{6/11}(Se)_{1/22}\) refers to the stoichiometric \(\beta\)-Ag\(_2\)Se. Thus, the model for \(\beta\)-Ag\(_2\)Se phase can be modified as shown in Equation 3-8.
The second lowest structure of Ag$_4$Se$_2$ is the configuration with one Ag in site 6b, two Ag in site 12d, and one Ag in site 24d. We hence conclude that Ag atoms in β-Ag$_2$Se occupy all of the sites 6b, 12d, and 24h, but the major one is the site 12d. The present finding agrees well with experimental observation [120, 150].

Relative energies for various endmember compounds in α and β phases are shown in Table 3-4, where the reference states are fcc-Ag and Trigonal-Se. Since the Wyckoff sites 6b, 12d, and 24h in β-Ag$_2$Se cannot be fully occupied by Ag, otherwise, the distance between some Ag-Ag atomic pairs are quite small (<1Å), resulting in unreasonably large energy. DFT calculations fail for some of these structures, for example, the three interstitial sites (6b, 12d, and 24d) are fully occupied by Ag.

For the assumed compounds of β-Ag$_6$Se$_2$ (site 6b fully occupied by Ag), β-Ag$_{12}$Se$_2$ (site 12d fully occupied by Ag), β-Ag$_{24}$Se$_2$ (site 24h fully occupied by Ag), and β-Ag$_{18}$Se$_2$ (both sites 6b and 12d fully occupied by Ag), the predicted relative energies are 13.9, 91.73, 20.12, 150.532 kJ/mol-atom (see data in Table 3-4), respectively.

Thermodynamic Modeling and Results

Thermodynamic optimization for Ag-Se system was conducted using the Pandat Software. Phase diagram and thermodynamics properties were calculated using the Poly-3 module in Thermo-Calc Software. The optimization procedure is shown as following. Firstly, the Gibbs energy of stoichiometric Ag$_2$Se was derived based on the available experimental data. The terminal phases, fcc-Ag and Trigonal-Se, were treated as unary phases as no mutual solubility was reported. The interaction parameters of liquid phase were then optimized using the phase equilibrium data including liquid phase and thermodynamic properties of liquid phase. The data published by Ohno et al. [125] and Tsuchiya et al. [126] were not used in this optimization since their phase
boundary data derived from liquid physical properties show large uncertainty and inconsistent with the measured Se activity in liquid phase [151]. Secondly, the Gibbs energy of the endmembers of α-Ag₂Se and β-Ag₂Se phases obtained from DFT calculations was used for the endmembers in the sublattice model for the α-Ag₂Se and β-Ag₂Se phases (Table 3-5). All the available experimental data were used together to finalize the parameters in the model.

The thermodynamic parameters of the Ag–Se system modelled in the present work are listed in Table 3-5. Calculated Ag–Se phase diagram is presented in Figure 3-2 along with the experimental data [122, 123, 125-127, 152]. A good agreement between the experimental data and the calculated results was generally achieved except for the phase boundary of β-Ag₂Se in equilibrium with liquid phase around 900-1000 K due to the scattered experimental data in the literature. It lies close to the data of Pellini et al. [123] at the region between 0.35-0.39 at.% Se. With Se content increasing, the calculated phase boundary moves close to the data reported by Pelabon et al. [152]. Calculated miscibility gap in Ag-rich liquid phase shows a good agreement with the data measured using the sample quenching method [127].

The enlarged phase diagram superimposed with experimental data [114, 115, 123, 135, 153, 154] between 33.28 and 33.35 in at.% Se is shown in Figure 3-4. The calculated homogeneity range of Ag₂Se shows a good agreement with the experimental data measured by coulometric titrations with the solid state galvanic cell Ag/Ag₄RbI₅/Ag₂⁺δSe/C [115], except the boundary of β-Ag₂Se in equilibrium with Se solid phases. It is worth noting that there is a two-phase field of α-Ag₂Se and β-Ag₂Se phases during Ag₂Se phase transition reported by Oehsen et al. [115]. As shown in
Figure 3-5, the calculated two-phase equilibrium region agrees with experimental data by Oehsen et al [115]. The calculated phase diagram differs from the one proposed by Grønvold et al. [135], where the proposed phase boundaries were extrapolated instead of direct measurement.

Table 3-6 shows the temperatures and compositions of the experimental and calculated values for all invariant reactions. A good agreement was generally achieved. For reaction L3 (Se rich liquid phase as shown in Figure 3-2) $\leftrightarrow \beta$-Ag₂Se+Trigonal-Se, Karakaya et al. [117] reported that this reaction could be a congruent melting of Se. However, based on the phase equilibrium data reported by Pellini et al. [123], the temperature that $\beta$-Ag₂Se+liquid transforms to $\beta$-Ag₂Se+Se is 490 K, which is lower than the Se melting temperature of 494.2 K [136]. This indicates the existence of a eutectic reaction. In this work, the eutectic composition and temperature of liquid were calculated as $x$(Liquid, Se)=0.9714 and $T$=489.75 K, respectively, agreeing with the experimental data by Pellini et al. [155].

Calculated activities of Se and Ag at 1273 K were compared with experimental data of Blachnik et al. [139] as shown in Figure 3-6. The calculated values fit the experimental data well in the region of Se atomic fraction larger than 0.312, but in the region of Se atomic fraction smaller than 0.312, the calculated values are lower than the experimental data. The discrepancy may due to the relatively low accuracy of the vapor pressure measurements while the vapor pressure is low.

The measured and calculated standard enthalpies of formation, standard entropies and standard Gibbs energy of formation for the intermetallic compound Ag₂Se
agrees well as shown in Table 3-1. The calculated value agrees with all of the experimental data as the deviation of the experimental data is small.

The temperature and enthalpy of $\alpha$-Ag$_2$Se to $\beta$-Ag$_2$Se transformation are calculated as 405.42 K and 7.71 kJ/mol as shown in Table 3-6 and Table 3-2, respectively. The experimentally measured enthalpy of this transformation scatters between 6.06 kJ·mol$^{-1}$ and 7.71 kJ·mol$^{-1}$, and the values obtained using DSC [114, 130, 133, 137] scatter and deviate significantly from the data measured by adiabatic methods, which could be attributed to the hysteresis effect during heating or cooling. The calculated heat capacity is in excellent agreement with the measured ones as shown in Figure 3-7.

**Summary**

A self-consistent thermodynamic description for the Ag–Se system was firstly established in this work. The ionic-liquid model and sublattice model were used for the liquid phase and the intermetallic compounds Ag$_2$Se, respectively. The Gibbs energy of the endmember with stoichiometric composition in $\alpha$-Ag$_2$Se and $\beta$-Ag$_2$Se phases was derived from the experimentally measured thermodynamic properties. The Gibbs free energy of the endmembers off-stoichiometric composition was calculated using first-principle calculations and was directly used in the sublattice model. The calculated phase diagram and thermodynamic properties demonstrate a reasonable agreement with the measured data available in the literature.
**Table 3-1. Summary of experimentally-measured thermodynamic properties of Ag\(_2\)Se**

<table>
<thead>
<tr>
<th>Compound</th>
<th>(-\Delta_f G^\circ), kJ·mol(^{-1})</th>
<th>(S^\circ), J·K(^{-1})·mol(^{-1})</th>
<th>(-\Delta_f H^\circ), kJ·mol(^{-1})</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Ag(_2)Se</td>
<td>49.47</td>
<td>149.99</td>
<td>42.73</td>
<td>[131]</td>
</tr>
<tr>
<td></td>
<td>48.9</td>
<td>148.2</td>
<td>42.7</td>
<td>[132]</td>
</tr>
<tr>
<td></td>
<td>49.19</td>
<td>150.08</td>
<td>42.41</td>
<td>[130]</td>
</tr>
<tr>
<td></td>
<td>49.59</td>
<td>149.2</td>
<td>43.09</td>
<td>[130]</td>
</tr>
<tr>
<td></td>
<td>49.02</td>
<td>155.54</td>
<td>40.62</td>
<td>[115]</td>
</tr>
<tr>
<td></td>
<td>46.9</td>
<td>149.9</td>
<td>40.1</td>
<td>[136]</td>
</tr>
<tr>
<td></td>
<td>49.41</td>
<td>151.03</td>
<td>42.36</td>
<td>[135]</td>
</tr>
<tr>
<td></td>
<td>49.24</td>
<td>154.6</td>
<td>41.12</td>
<td>[133]</td>
</tr>
<tr>
<td></td>
<td>49.47</td>
<td>149.98</td>
<td>42.73</td>
<td>This Work</td>
</tr>
<tr>
<td>β-Ag(_2)Se</td>
<td>47.43</td>
<td>169.01</td>
<td>35.02</td>
<td>[131]</td>
</tr>
<tr>
<td></td>
<td>47.58</td>
<td>169.44</td>
<td>35.04</td>
<td>[130]</td>
</tr>
<tr>
<td></td>
<td>47.48</td>
<td>169.09</td>
<td>35.05</td>
<td>[135]</td>
</tr>
<tr>
<td></td>
<td>47.64</td>
<td>169.57</td>
<td>35.06</td>
<td>[133]</td>
</tr>
<tr>
<td></td>
<td>47.52</td>
<td>169.38</td>
<td>35.00</td>
<td>[115]</td>
</tr>
<tr>
<td></td>
<td>47.87</td>
<td>148.2</td>
<td>42.7</td>
<td>[132]</td>
</tr>
<tr>
<td></td>
<td>47.43</td>
<td>169</td>
<td>35.01</td>
<td>This Work</td>
</tr>
</tbody>
</table>

**Table 3-2. Summary of experimentally-measured enthalpy of transition of Ag\(_2\)Se**

<table>
<thead>
<tr>
<th>(\Delta_{trans} H_m^0) (kJ·mol(^{-1}))</th>
<th>Method</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.06</td>
<td>DSC</td>
<td>[133]</td>
</tr>
<tr>
<td>6.82 ± 0.2</td>
<td>Adiabatic</td>
<td>[135]</td>
</tr>
<tr>
<td>7.37</td>
<td>DSC</td>
<td>[130]</td>
</tr>
<tr>
<td>7.68 ± 0.1</td>
<td>DSC</td>
<td>[114]</td>
</tr>
<tr>
<td>6.8 ± 0.14</td>
<td>DSC</td>
<td>[137]</td>
</tr>
<tr>
<td>7.0 ± 0.6</td>
<td>Adiabatic</td>
<td>[138]</td>
</tr>
<tr>
<td>7.71 ± 0.55</td>
<td>EMF</td>
<td>[131]</td>
</tr>
<tr>
<td>7.12</td>
<td>compilation</td>
<td>[156]</td>
</tr>
<tr>
<td>7.06</td>
<td>compilation</td>
<td>[157]</td>
</tr>
<tr>
<td>7.71</td>
<td>Evaluated</td>
<td>This Work</td>
</tr>
</tbody>
</table>
Table 3-3. Details of DFT calculations for each compound including the space group, total atoms in the supercell, \( k \)-points mesh, cutoff energy (\( E_{\text{cut}} \) in eV), and the smearing method.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space group</th>
<th>Atoms</th>
<th>( k )-mesh</th>
<th>( E_{\text{cut}} )^a</th>
<th>Smear^b</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-Ag(_2)Se</td>
<td>( P2_12_12_1 )</td>
<td>12</td>
<td>13\times9\times8</td>
<td>250 360</td>
<td>1 -5</td>
</tr>
<tr>
<td>( \beta )-Ag(_2)Se</td>
<td>( I\overline{m}3m )</td>
<td>2 ~ 44^c</td>
<td>12\times12\times12</td>
<td>250 360</td>
<td>1 -5</td>
</tr>
<tr>
<td>Ag</td>
<td>( Fm\overline{3}m )</td>
<td>1</td>
<td>29\times29\times29</td>
<td>360</td>
<td>1 -5</td>
</tr>
<tr>
<td>Se</td>
<td>( P3_121 )</td>
<td>3</td>
<td>23\times23\times16</td>
<td>210 360</td>
<td>1 -5</td>
</tr>
</tbody>
</table>

^a The energy of 250 (or 210) eV used for structural relaxations and the energy of 360 eV for final calculations.

^b The same as the settings used in VASP code, the number “1” represents the Methfessel-Paxton method for structural relaxations and “-5” the tetrahedron method with Blöchl corrections for final calculations to get accurate energy.

^c Atomic numbers depend on vacancy included in \((\text{Ag},\text{Va})_6(\text{Ag},\text{Va})_{12}(\text{Ag},\text{Va})_{24}(\text{Se})_2\).

Table 3-4. Relative energy (\( \Delta E \), kJ/mole-atom) with respect to fcc-Ag and Trigonal-Se from DFT calculations.

<table>
<thead>
<tr>
<th>Material</th>
<th>Method</th>
<th>( \Delta E )</th>
<th>4a-Ag (( \alpha )) or 6b-Ag (( \beta ))</th>
<th>4a-Ag (( \alpha )) or 12d-Ag (( \beta ))</th>
<th>4a-Se (( \alpha )) 24h-Ag (( \beta ))</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-Ag(_2)Se</td>
<td>PBE+D3</td>
<td>-9.936</td>
<td>Ag</td>
<td>Ag</td>
<td>Se</td>
<td>Stable phase at low T</td>
</tr>
<tr>
<td></td>
<td>PBEsol</td>
<td>-5.869</td>
<td>Ag</td>
<td>Ag</td>
<td>Se</td>
<td></td>
</tr>
<tr>
<td>( \alpha )-Ag</td>
<td>PBE+D3</td>
<td>0.518</td>
<td>Ag</td>
<td>Ag</td>
<td>Va</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PBEsol</td>
<td>0.561</td>
<td>Ag</td>
<td>Ag</td>
<td>Va</td>
<td></td>
</tr>
<tr>
<td>( \alpha )-Se</td>
<td>PBE+D3</td>
<td>22.869</td>
<td>Va</td>
<td>Va</td>
<td>Se</td>
<td>E-V data points are scattering</td>
</tr>
<tr>
<td></td>
<td>PBEsol</td>
<td>21.468</td>
<td>Va</td>
<td>Va</td>
<td>Se</td>
<td></td>
</tr>
<tr>
<td>( \beta )-Ag(_2)Se</td>
<td>PBE+D3</td>
<td>-4.127</td>
<td>Va</td>
<td>Partial Ag</td>
<td>Va</td>
<td>The lowest energy structure</td>
</tr>
<tr>
<td></td>
<td>PBEsol</td>
<td>-3.196</td>
<td>Va</td>
<td>Partial Ag</td>
<td>Va</td>
<td></td>
</tr>
<tr>
<td>( \beta )-Se</td>
<td>PBE+D3</td>
<td>53.402</td>
<td>Va</td>
<td>Va</td>
<td>Va</td>
<td>Bcc-Se</td>
</tr>
<tr>
<td></td>
<td>PBEsol</td>
<td>43.164</td>
<td>Va</td>
<td>Va</td>
<td>Va</td>
<td></td>
</tr>
<tr>
<td>( \beta )-Ag(_6)Se(_2)</td>
<td>PBE+D3</td>
<td>13.937</td>
<td>Ag</td>
<td>Va</td>
<td>Va</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PBEsol</td>
<td>22.092</td>
<td>Ag</td>
<td>Va</td>
<td>Va</td>
<td></td>
</tr>
<tr>
<td>( \beta )-Ag(_{12})Se(_2)</td>
<td>PBE+D3</td>
<td>91.738</td>
<td>Va</td>
<td>Ag</td>
<td>Va</td>
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<td></td>
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<td>97.680</td>
<td>Va</td>
<td>Ag</td>
<td>Va</td>
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</tr>
<tr>
<td>( \beta )-Ag(_{24})Se(_2)</td>
<td>PBE+D3</td>
<td>20.119</td>
<td>Va</td>
<td>Va</td>
<td>Ag</td>
<td></td>
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<tr>
<td></td>
<td>PBEsol</td>
<td>20.653</td>
<td>Va</td>
<td>Va</td>
<td>Ag</td>
<td></td>
</tr>
<tr>
<td>( \beta )-Ag(_{18})Se(_2)</td>
<td>PBE+D3</td>
<td>150.532</td>
<td>Ag</td>
<td>Ag</td>
<td>Va</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PBEsol</td>
<td>149.370</td>
<td>Ag</td>
<td>Ag</td>
<td>Va</td>
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Table 3-5. Optimized parameters for the Ag–Se system (J/mol-formula as shown in the model)

<table>
<thead>
<tr>
<th>Phase</th>
<th>T (K)</th>
<th>Function</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>298.15&lt;T&lt;1234.93</td>
<td>$G_{\text{Liquid}}^{\text{Ag}_1\text{Va}} = 3815.574+109.310992<em>T-23.8463314</em>T<em>LN(T)\cdot0.001790585</em>T**2$</td>
<td>[105]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-3.98587E-07<em>T**3-12011</em>T**(-1)-1.034E-20*T**7$</td>
<td></td>
</tr>
<tr>
<td>Liquid</td>
<td>1234.93&lt;T&lt;3000</td>
<td>$G_{\text{Liquid}}^{\text{Ag}_1\text{Va}} = -3587.111+180.964657<em>T-33.472</em>T*LN(T)$</td>
<td></td>
</tr>
<tr>
<td>Liquid</td>
<td>298.15&lt;T&lt;918</td>
<td>$G_{\text{Liquid}}^{\text{Se}} = -9809.19613+288.813417<em>T-52.4</em>T<em>LN(T)+0.024925</em>T**2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$-5.455E-06*T**3$</td>
<td></td>
</tr>
<tr>
<td>Liquid</td>
<td>918&lt;T&lt;1150</td>
<td>$G_{\text{Liquid}}^{\text{Se}} = 8433.1372-78.4769299<em>T+5.399</em>T<em>LN(T)-0.035945</em>T**2$</td>
<td>[140]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$+5.2016666E-06*T**3$</td>
<td></td>
</tr>
<tr>
<td>Liquid</td>
<td>1150&lt;T&lt;1500</td>
<td>$G_{\text{Liquid}}^{\text{Se}} = 7460.61988+192.646347<em>T-36</em>T*LN(T)$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>298.15&lt;T&lt;6000</td>
<td>$G_{\text{Liquid}}^{\text{Ag}_1\text{Se}_2} = \text{GAG2SEB} + 19233.4 - 15.867*T$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0 $L_{\text{Ag}_1\text{Se}_2}^{\text{Va}}$</td>
<td>$-6216.24+25.9082*T$</td>
<td>This Work</td>
</tr>
<tr>
<td></td>
<td>1 $L_{\text{Ag}_1\text{Se}_2}^{\text{Va}}$</td>
<td>$-14971.24+9.23549*T$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2 $L_{\text{Ag}_1\text{Se}_2}^{\text{Va}}$</td>
<td>$75.1145$</td>
<td></td>
</tr>
<tr>
<td>fcc-Ag</td>
<td>298.15&lt;T&lt;3000</td>
<td>$G_{\text{FCC-Ag}} = \text{GHSERAG}$</td>
<td>[105]</td>
</tr>
<tr>
<td>trigonal-Se</td>
<td>298.15&lt;T&lt;1500</td>
<td>$G_{\text{TRIGONAL-Se}} = \text{GHSERSE}$</td>
<td>[140]</td>
</tr>
<tr>
<td>α-Ag₂Se</td>
<td>298.15&lt;T&lt;1000</td>
<td>$G_{\alpha\text{-Ag}_2\text{Se}} = 0.3333333 * \text{GAG2SEA}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0 $G_{\text{Ag}_1\text{Va}}$</td>
<td>$0.3333333 * \text{GHSERAG} + 345.3333$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0 $G_{\text{Va}_1\text{Se}}$</td>
<td>$0.66666667 * \text{GHSERAG} + 345.3333$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0 $G_{\alpha\text{-Ag}_2\text{Se}}$</td>
<td>$0.3333333 * \text{GHSERSE} + 7623$</td>
<td>This Work</td>
</tr>
<tr>
<td></td>
<td>0 $L_{\alpha\text{-Ag}_2\text{Se}}^{\text{Va}_1\text{Se}_2}$</td>
<td>$153.1419 + 34.6824*T$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0 $L_{\alpha\text{-Ag}_2\text{Se}}^{\text{Va}_1\text{Se}_2}$</td>
<td>$7151.8425 + 1.9268*T$</td>
<td></td>
</tr>
</tbody>
</table>

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Table 3-5. Continued

<table>
<thead>
<tr>
<th>Phase</th>
<th>T (K)</th>
<th>Function</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-Ag₂Se</td>
<td>298.15&lt;T&lt;1000</td>
<td>( G_{\beta-\text{Ag}_{2}\text{Se}}^{\text{VA:AG:VA:VA:SE}} = 0.0454545*G\text{AG2SEB} )</td>
<td>This Work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( G_{\beta-\text{Ag}_{2}\text{Se}}^{\text{VA:VA:VA:VA:SE}} = 0.0454545*\text{GBCCSE} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( G_{\beta-\text{Ag}_{2}\text{Se}}^{\text{VA:AG:AG:VA:SE}} = 0.272727*\text{GHSERAG}+0.0454545*\text{GHSERSE}+29189.33445 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( G_{\beta-\text{Ag}_{2}\text{Se}}^{\text{AG:AG:AG:VA:SE}} = 0.5454545*\text{GHSERAG}+0.0454545*\text{GHSERSE}+11888.49817; )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( G_{\beta-\text{Ag}_{2}\text{Se}}^{\text{AG:AG:AG:VA:SE}} = 0.409091*\text{GHSERAG}+0.0454545*\text{GHSERSE}+68423.64321 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( 0L_{\beta-\text{Ag}<em>{2}\text{Se}}^{\text{VA:AG:VA:VA:SE}} = 991.365+45.1980*T ) ( \dagger ) ( L</em>{\beta-\text{Ag}_{2}\text{Se}}^{\text{VA:AG:VA:VA:SE}} = -990.0392+49.1137*T )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( 0L_{\beta-\text{Ag}_{2}\text{Se}}^{\text{AG:AG:AG:VA:SE}} = 2503.43453+28.72093*T )</td>
<td></td>
</tr>
<tr>
<td>GHSERAG</td>
<td>298.15&lt;T&lt;1234.93</td>
<td>-7209.512+118.202<em>T-23.8463</em>T<em>LN(T)-0.00179</em>T^2-3.9859E-07<em>T^3-12011</em>T^-1</td>
<td>[105]</td>
</tr>
<tr>
<td></td>
<td>1234.93&lt;T&lt;3000</td>
<td>-15095.252+190.266404<em>T-33.472</em>T<em>LN(T)+1.412E+29</em>T^-9</td>
<td></td>
</tr>
<tr>
<td>GHSERSE</td>
<td>298.15&lt;T&lt;760</td>
<td>-6657.653+92.5397<em>T-19.14</em>T<em>LN(T)-0.0123</em>T^2+2.6767E-06*T^3</td>
<td>[140]</td>
</tr>
<tr>
<td></td>
<td>760&lt;T&lt;1500</td>
<td>-9059.16586+150.334216<em>T-28.552</em>T*LN(T)</td>
<td></td>
</tr>
<tr>
<td>GBCCSE</td>
<td>298.15&lt;T&lt;800</td>
<td>-6709.819+152.4568<em>T-28.1882</em>T<em>LN(T)+3.2189E-3</em>T^2</td>
<td>[105]</td>
</tr>
<tr>
<td></td>
<td>800&lt;T&lt;1000</td>
<td>-1.6453E-6<em>T^3+72177</em>T^-1</td>
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<tr>
<td></td>
<td>1000&lt;T&lt;1608</td>
<td>-5531.567+131.735<em>T-24.913</em>T<em>LN(T)-0.573E-3</em>T^2-0.86E-6*T^3</td>
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<td>1608&lt;T&lt;3200</td>
<td>230161.408-2004.054685<em>T+276.7666402</em>T*LN(T)</td>
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<td>-167.120107E-3<em>T^2+15.637371E-6</em>T^3-33783257*T^-1</td>
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<tr>
<td>GAG2SEA</td>
<td>298.15&lt;T&lt;406</td>
<td>-64345.3904+298.6623<em>T-64.63765</em>T<em>LN(T)-0.026365</em>T^2</td>
<td>This Work</td>
</tr>
<tr>
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<td>406&lt;T&lt;1500</td>
<td>-83910.6916+458.2582<em>T-84.83965</em>T<em>LN(T)-0.00175</em>T^2</td>
<td></td>
</tr>
<tr>
<td>GAG2SEB</td>
<td>298.15&lt;T&lt;1500</td>
<td>GAG2SEA + 7710-19.0175*T</td>
<td></td>
</tr>
<tr>
<td>Reaction</td>
<td>Composition (at.% Se)</td>
<td>T(K)</td>
<td>Reaction Type</td>
</tr>
<tr>
<td>----------</td>
<td>-----------------------</td>
<td>------</td>
<td>---------------</td>
</tr>
<tr>
<td>L1↔Ag+L2</td>
<td>12/0/31.3</td>
<td>1163</td>
<td>Monotectic</td>
</tr>
<tr>
<td></td>
<td>8.2/0/31.2</td>
<td>1163</td>
<td></td>
</tr>
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<td></td>
<td>11/0/31</td>
<td>1163</td>
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</tr>
<tr>
<td></td>
<td>7.6/0/30.7</td>
<td>1163.01</td>
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</tr>
<tr>
<td>L2↔Ag+β-Ag₂Se</td>
<td>32/0/33.3</td>
<td>1113</td>
<td>Eutectic</td>
</tr>
<tr>
<td></td>
<td>30.876/0/33.3</td>
<td>1112.53</td>
<td></td>
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<tr>
<td>L2↔β-Ag₂Se</td>
<td>33.3</td>
<td>1170</td>
<td>Congruent</td>
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<td>33.3</td>
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<td>33.3</td>
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<td>33.3</td>
<td>1170.12</td>
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<tr>
<td>L2↔β-Ag₂Se+L3</td>
<td>44.5/33.3/95.5</td>
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<td>97.14/33.3/100</td>
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<tr>
<td>β-Ag₂Se↔α-Ag₂Se</td>
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</table>
Figure 3-1. Ag-Se phase diagram assessed by Karakaya et al. [117] and summarized by Predel et al. [118].
Figure 3-2. Calculated phase diagram of the Ag–Se system in the present work in comparison with experimental data [122, 127, 152, 155].
Figure 3-3. Low relative energies of $\beta$ phase (see Equation 3-13) with compositions of Ag$_3$Se$_2$, Ag$_4$Se$_2$ and Ag$_5$Se$_2$, where the reference states are the lowest energies of Ag$_3$Se$_2$ and Ag$_5$Se$_2$, respectively.
Figure 3-4. Calculated phase diagram in the Ag–Se system near the Ag$_2$Se polymorphic transformation region in comparison with experimental data [114, 115, 135, 153, 154].
Figure 3-5. Calculated phase diagram near the invariant reaction $\beta$-$\text{Ag}_2\text{Se} \leftrightarrow \text{Ag} + \alpha$-$\text{Ag}_2\text{Se}$. 
Figure 3-6. Calculated activities of Ag and Se at 1273 K in comparison with experimental data [151].
Figure 3-7. Calculated heat capacity of Ag$_2$Se versus temperature in comparison with experimental data [135].
Energy is the underlying factor to human economic activity, and more energy is projected to be needed in the near future and photovoltaics provide a means to supply that energy. CIGS based solar cells have been confirmed showing 21% photovoltaic (PV) conversion efficiency \[159\]. In order to further increase their efficiencies and minimize their production costs, Ag can be added to substitute part of Cu to form a PV material with larger band gap \[65, 66\]. However, the reaction pathway during the synthesis process of CIGS is complicated and adding Ag into CIGS makes it even more difficult to be optimized. Fully understanding the Ag-Cu-In-Ga-Se thermodynamic system and phase equilibrium will be helpful in discovering the most efficient reaction pathway. In this work, the Ag-Cu-Se system was thermodynamically optimized as a part of the complete database and a good agreement between the calculated thermodynamic properties and experimental data was archived.

**Ag-Cu-Se System in Literature**

**Ag-Cu System**

The Ag-Cu system was optimized \[67, 101, 160\] against phase equilibrium data \[67\], the enthalpy of mixing in liquid \[92\]. In the most recent assessment, as shown in Chapter 2, the measurements of Cu activity in fcc-A1 (Ag) phase using electro-motive force (EMF) measurement were used. The calculated solidus of fcc-A1 Ag phase are shown close to the data reported by Sommer et al. \[89\] This set of thermodynamics database was used directly without any modification for this ternary phase evaluation because firstly, no more new data was reported and also, the EMF measurements
provides more accuracy than other phase equilibrium measurements such as DTA or microanalysis.

**Ag-Se System**

The Ag-Se system was firstly assessed in this work and the details of this model was presented in Chapter 3. Before this assessment, only Karakaya et al. [117] proposed a phase diagram based on the available phase equilibrium data. The Ag-Se system contains one intermetallic compounds Ag$_2$Se with two polymorphs of $\alpha$-Ag$_2$Se with orthorhombic structure (low temperature) and $\beta$-Ag$_2$Se with body-centered cubic structure (high temperature), two terminal solid phase FCC-Ag and Trigonal-Se, and two miscibility gaps in the liquid phase.

Several investigations have been conducted to determine the liquid phase equilibrium. The existence of two miscibility gaps in the liquid phase on was firstly reported by Friedrich [122] and Pellini [123] and was confirmed by Houphouet-Boigny et al. [124] The composition of the two miscibility gap was reported between 11-31 at.% Se at 1163 K and 45-95 at.% Se at 889 K, respectively. Ohno et al. [125], Tsuchiya et al. [126] and Wiggett et al. [127] measured the phase boundaries of the miscibility gap using conductivity measurement, gamma-ray attenuation and sample quenching method, respectively. The results from these three measurements show large discrepancy, except the composition and temperature of the monotectic reaction between the liquid, FCC-Ag and $\beta$-Ag$_2$Se phase. Ohno et al. [125] and Tsuchiya et al. [126] proposed a converged miscibility gap in Ag-rich liquid phase, while Wiggett et al. [127] proposed that the boundary of miscibility gap does not converge rapidly.
Friedrich et al. [128] showed small solubility (less than 0.27 at.% Se) of Se in FCC-A without more detail. Therefore, it is not considered in this assessment. No solubility of FCC-Ag in Trigonal-Se was reported. Extensive studies have been conducted for the phase equilibrium and thermodynamic properties of α-Ag\textsubscript{2}Se and β-Ag\textsubscript{2}Se phase. The melting temperature of β-Ag\textsubscript{2}Se was measured using thermal analysis [123], DTA [129] and conductivity measurement [125], and the results show good consistency as 1170 K, 1167 K and 1168 K, respectively. However, the measured transition temperature between α-Ag\textsubscript{2}Se and β-Ag\textsubscript{2}Se shows large discrepancy. Voronin et al. [130] used EMF measurement in solid electrolyte (AgCl) or a glycerol solution with constant stirring to get the transformation temperature of 397.5 K. However, Echmaeva et al. [131], Nasar et al. [132] and Feng et al. [133] using EMF measurement, reported a higher transformation temperature as 405.5 K, 406 K and 407.7 K, respectively. The transformation temperature of 406±1 K was recently reported by Asadov et al. [134] using microstructural and X-ray analysis.

Oehsen et al. reported small deviation from stoichiometry in α-Ag\textsubscript{2}Se and β-Ag\textsubscript{2}Se phase, and the homogeneity range was determined using the solid state galvanic cell Ag/Ag\textsubscript{3}RbI\textsubscript{5}/Ag\textsubscript{2}+δSe/C between 348 K and 463 K. Grønvold et al. [135] investigated the thermodynamic properties of the transformation region using adiabatic calorimetry and proposed a different phase diagram around the α-Ag\textsubscript{2}Se and β-Ag\textsubscript{2}Se phase transformation region.

Most of studies regarding the thermodynamic properties of Ag-Se system focused on the intermetallic compound Ag\textsubscript{2}Se. The standard Gibbs energy of formation \((\Delta_f G_{298,\text{Ag}_2\text{Se}}^0)\) and the standard enthalpy of formation \((\Delta_f H_{298,\text{Ag}_2\text{Se}}^0)\) was extensively
studied using EMF measurement [115, 130-133] and adiabatic calorimetry [135]. Their results show good consistency, except that the results for α-Ag₂Se from Olin et al. [136] show a slightly lower value (2 kJ·mol⁻¹) for the standard Gibbs energy of formation. The enthalpy of transformation from α-Ag₂Se to β-Ag₂Se has been measured using DSC [114, 130, 133, 137] and adiabatic calorimetry [135, 138]. The results from DSC scatter between 6.06 kJ·mol⁻¹ and 7.68 kJ·mol⁻¹ while the value obtained with adiabatic calorimetry show good consistency at ~7 kJ·mol⁻¹. The experimental data are summarized in Table 3-1 and Table 3-2. Blachnik et al. [139] determined the activity of Se in liquid phase at 1273K by measuring the vapor pressure using modified dew point method.

Besides the experimental data mentioned above, no new experimental data is available. In this model, the intermetallic compound Ag₂Se was modeled based on its lattice structure, which gives the physical meaning to the extrapolation to the ternary phases. The model was directly used in this ternary assessment without further modification.

**Cu-Se System**

There are several investigations in terms of the Cu-Se system [15, 71, 161]. The latest assessment was done by Du et al. [15]. However, they used the associate model for their thermodynamic database, which is different from the ionic liquid model used for Ag-Cu and Ag-Se system. Thus, it is not used in this ternary system assessment. Shen et al. [162] reassessed the system in 2016. The homogeneity range of α-Gu₂Se₃ was

This binary system consists of two terminal phases, FCC-A1 Cu and TRIGONAL_A8 Se. Three intermetallic compounds Cu₃Se₂, CuSe, CuSe₂ were confirmed. The liquid phase of this system exhibits two miscibility gaps. In the
most recent assessment [163], the compound CuSe₂, CuSe and Cu₃Se₂ were treated as line compound. The homogeneity range of both \( \alpha\)-Cu₂ₓSe (low temperature phase) and \( \beta\)-Cu₂ₓSe (high temperature phase) were modeled using sublattice model based on their lattice structure. The calculated thermodynamic properties of these intermetallic compounds agrees with the available experimental data, including the standard enthalpies of formation and entropies, heat capacity etc. To sum up, a set of self-consistent thermodynamic parameters describing the Gibbs energy of each individual phase as a function of composition and temperature were obtained. The calculated phase diagram and thermo-chemical properties including enthalpy, entropy and chemical potentials agree well with the experimental values, thus it is used in this ternary assessment without further modification.

**Ag-Cu-Se System**

**Phase diagram**

Agaev et al. [164] firstly constructed the phase diagram for Ag₂Se-Cu₂Se system over the temperature range 600-1200 °C. The detailed phase diagram was shown in Figure 4-1. In this assessment, the ternary compound AgCuSe was proposed. This compound shows a phase transition from \( \beta\)-AgCuSe to \( \alpha\)-AgCuSe at 200 °C. At 760 °C, \( \alpha\)-AgCuSe shows incongruent melting. There is one eutectic point shown at 730 °C and two eutectoid reactions was reported at Ag₂Se-rich and Cu₂Se-rich portion respectively. One thing worth noticing is that, in this proposed phase diagram, both Ag₂Se and Cu₂Se shows considerably large solubility with each other, but no detailed experimental data was shown. In this assessment, only the liquidus was measured using thermal analysis, which leaves the proposed phase relation in the solid phase questionable.
Another complete different pseudo binary phase diagram was proposed by Schäfer et al. [165] as shown in Figure 4-3. The phase boundary was determined using Differential Thermal Analysis. In this assessment, no solubility was found for both terminal phases Ag$_2$Se and Cu$_2$Se, which was further confirmed by Chen et al. using XRD [166]. The intermetallic compound AgCuSe melts at 750 °C congruently. Two erected reaction was measured at 728 °C and 745 °C on Ag$_2$Se-rich and Cu$_2$Se-rich side. Compared to Agaev et al. and Asano et al., the phase equilibrium data shown in Schäfer et al. are more reliable due to the lack of specific experimental detail and missing intermetallic compound in Agaev et al. and Asano et al, respectively.

One important feature of Ag-Cu-Se system is the liquid miscibility gap at high temperature. The monotectic solubility gaps extend across the entire system. Asano et al. [167] determined the tie line in the miscibility gap at 1473 K as shown in Figure 4-2. Besides the phase equilibrium data in the liquid phase, Asano et al. also reported several isopleth diagram. However, the existence of the ternary compound AgCuSe was not shown in any of the phase diagrams. Thus, their isopleth diagram was not considered in this assessment.

**Ternary compound AgCuSe**

AgCuSe exists as an uncommon mineral, eucairite, in nature [168]. Although it has been studied by many researchers [161, 169-174], it was shown in the phase diagram proposed by three investigators [164, 165, 175]. AgCuSe has two different crystal structures: disordered high-temperature structure (α-phase) and ordered low-temperature structure (β-phase). The high-temperature α-phase was characterized as cubic structure. In this structure, the Ag and Cu cations randomly distributed over
tetrahedral and trigonal site and the Se anions forming an fcc lattice [176]. In terms of the structure of the low-temperature β-phase, Earley et al. [168] reported a tetragonal structure but later, Frueh et al. [169] using XRD, reported a pseudo-tetragonal orthorhombic structure based on fives subcells with tetragonal unit stacking along one a-axis. No homogeneity range was reported for this compound. The available experimental data was summarized in

The phase transformation temperature has been studied by several investigators [161, 169, 176-178]. Trots et al. [177] reported the transformation temperature as 464 K and 480 K using DSC cooling and heating, respectively. Frueh et al. [169] did not state specific temperature but the transformation temperature range was determined between 463.15 K and 468.15 K according to the XRD analysis. The result measured with DSM-2M DSC by Glazov [161] shows that AgCuSe undergoes the phase transition at 484 K, which is close to the results reported by Trots et al. derived from the DSC heating curve. The same method was also used by Chrisafiss et al. [176] and the temperature was determined as 474.9 K. Balapanov et al. [178] reported a relatively higher transition temperature as 603 K using EMF. The reason could be the extra 0.1% Ag added to the sample, which results in the low purity of the sample. Thus, this value was not considered in this assessment.

The thermodynamic properties of AgCuSe was incomplete. The only available data was the standard heat of formation -49.95±9.5 kJ/mol and entropy 156±3 J/mol for the β-AgCuSe. The heat capacity of β-AgCuSe was also reported in the range between 298 K and 480 K [161].
Thermodynamic Models

Unary Terminal Phases

The description of the Gibbs energy of pure Ag, Cu and Se was taken from the most recent compilation Dinsdale [105] and Change [140]. They were modeled by using the following equation with different sets of parameters for corresponding temperature intervals:

\[ G_i^\phi - H_i^{SER} = A + BT + CT\ln T + DT^2 + ET^{-1} + FT^3 + IT^7 - JT^{-9} \]  

(4-1)

where \( H_i^{SER} \) means enthalpy of standard element reference referring to the enthalpy of the stable state of the pure element at 298.15 K, T is the absolute temperature and A~J are the coefficients.

Liquid Phases

For the liquid phase, the ionic-liquid two sub-lattice model was used by the following expression:

\[ G_m^\phi = y_{Ag^\cdot} y_{Se^\cdot} G_{Ag^\cdot;Se^\cdot}^\cdot + y_{Cu^\cdot} y_{Se^\cdot} G_{Cu^\cdot;Se^\cdot}^\cdot + y_{Ag^\cdot} y_{Cu^\cdot} y_{Se^\cdot} G_{Ag^\cdot,Cu^\cdot;Se^\cdot}^\cdot + y_{Ag^\cdot} y_{Se^\cdot} y_{Cu^\cdot} G_{Ag^\cdot;Se^\cdot,Cu^\cdot}^\cdot + \]

\[ + Q y_{Va^\cdot} y_{Ag^\cdot} G_{Ag^\cdot}^\cdot + Q y_{Va^\cdot} y_{Cu^\cdot} G_{Cu^\cdot}^\cdot + Q y_{Sc^\cdot} G_{Sc}^\cdot + RT (P y_{Ag^\cdot} \ln y_{Ag^\cdot} + P y_{Cu^\cdot} \ln y_{Cu^\cdot} + Q (y_{Sc^\cdot} \ln y_{Sc^\cdot} + y_{Va^\cdot} \ln y_{Va^\cdot} + y_{Se^\cdot} \ln y_{Se^\cdot})) \]

\[ + y_{Ag^\cdot} y_{Sc^\cdot} y_{Va^\cdot} L_{Ag^\cdot;Sc^\cdot;Va^\cdot} + y_{Cu^\cdot} y_{Sc^\cdot} y_{Va^\cdot} L_{Cu^\cdot;Sc^\cdot;Va^\cdot} + y_{Ag^\cdot} y_{Sc^\cdot} y_{Se^\cdot} L_{Ag^\cdot;Sc^\cdot;Se^\cdot} + y_{Cu^\cdot} y_{Sc^\cdot} y_{Se^\cdot} L_{Cu^\cdot;Sc^\cdot;Se^\cdot} \]

\[ \quad + y_{Cu^\cdot} y_{Ag^\cdot} y_{Se^\cdot} L_{Cu^\cdot;Ag^\cdot;Se^\cdot} + y_{Cu^\cdot} y_{Ag^\cdot} y_{Sc^\cdot} y_{Va^\cdot} L_{Cu^\cdot;Ag^\cdot;Sc^\cdot;Va^\cdot} \]

(4-2)

where \( G_{Ag^\cdot;Se^\cdot}^\cdot \) and \( G_{Cu^\cdot;Se^\cdot}^\cdot \) is the Gibbs energy of formation of liquid \( Ag_2Se \) and \( Cu_2Se \), respectively. \( G_{Ag^\cdot}^\cdot \), \( G_{Cu^\cdot}^\cdot \) and \( G_{Sc^\cdot}^\cdot \) are the Gibbs energies of formation per mole of atoms of liquids Ag, Cu and Se, respectively. The value of \( P \) and \( Q \) are determined using:

\[ P = 2 y_{Sc^\cdot} + Q y_{Va^\cdot} \]  

(4-3)

\[ Q = l (y_{Ag^\cdot} + y_{Cu^\cdot}) \]  

(4-4)
where the number 2 in Equation 4-3 and 1 in Equation 4-4 is the charge of Se and Ag or Cu ion, respectively. The term \( L_{\text{Ag}^+:\text{Se}^{2-}:\text{Va}} \) refers to the interaction between \( \text{Ag}^+ \) and \( \text{Se}^{2-} \) on the Ag-rich side on the system and \( L_{\text{Ag}^+:\text{Se}^{2-}:\text{Se}} \) indicates the interaction between \( \text{Ag}^+ \), \( \text{Se}^{2-} \) and Se atoms on the Se-rich part of the system. \( L_{\text{Cu}^+:\text{Se}^{2-}:\text{Va}} \) and \( L_{\text{Cu}^+:\text{Se}^{2-}:\text{Se}} \) indicates the interaction between \( \text{Cu}^+ \) and \( \text{Se}^{2-} \). \( L_{\text{Ag}^+:\text{Cu}^+:\text{Se}^{2-}:\text{Va}} \) and \( L_{\text{Ag}^+:\text{Cu}^+:\text{Se}^{2-}:\text{Se}} \) indicates the ternary interaction between \( \text{Ag}^+ \), \( \text{Cu}^+ \) and \( \text{Se}^{2-} \). These terms are expressed by the following expression:

\[
\ell L_{\A,\B}^{\phi} = a^\phi v + b^\phi T
\]  

(4-5)

where \( a^\phi v \) and \( b^\phi v \) are the terms which was assessed in this work using available experiment data.

**Compound Phases**

In the Ag-Cu-Se system, all compounds exist as selenide. There compounds CuSe, CuSe\(_2\) and Cu\(_3\)Se\(_2\) were treated as line compound [162]. The Ag\(_2\)Se and Cu\(_2\)Se shows certain homogeneous range and was modeled using sublattice model described as the model mentioned in Chapter 3 and (Cu, Va\(_1\))(Se, Va\(_1\))(Cu\(_1\)), respectively. The ternary compound AgCuSe was modeled using sublattice model (Ag\(_1\))(Cu\(_1\))(Se\(_1\)) and no vacancy site was added into the model since no homogeneity rage was reported. The Gibbs energy of AgCuSe was expressed using the following equation:

\[
\ell G_{\text{AgCuSe}}^{\phi} = G_{\text{AgCuSe}}^{\phi} - H_{\text{AgCuSe}}^{\text{SER}} = a + bT + cTlnT + dT^2 + eT^{-1} + fT^3
\]  

(4-6)
Results and Discussion

Optimization Results

Thermodynamic optimization for Ag-Cu-Se system was conducted and the phase diagram and thermodynamics properties are calculated using Parrot and Poly-3 Module in Thermo-Calc Software., respectively [179]. The optimization procedure is shown as following. Firstly, the optimized Ag-Cu, Ag-Se, Cu-Se binary thermodynamic database was combined as one database. The ternary compound AgCuSe and the parameters $L_{Ag^+,Cu^+,Se^2-}$ for the liquid phase was optimized against available pseudo-binary Ag$_2$Se-Cu$_2$Se experiment data. The standard enthalpy of formation and the standard entropy along with the heat capacity data was used to derive the Gibbs energy of β-AgCuSe as a function of temperature (noted as GAGCUSEB). Then, another function $a+b*T$ was added to the function GAGCUSEB to express the Gibbs energy of α-AgCuSe. The value of a and b were determined together with the liquid parameter $L_{Ag^+,Cu^+,Se^2-}$ using the transformation and melting temperature of AgCuSe and other phase equilibrium data in the liquid phase. Finally, the liquid parameter $L_{Ag^+,Cu^+,Se^2-,V_a}$ were optimized against the available ternary liquidus data and tie line of the liquid miscibility gap at 1473.15 K.

The thermodynamic parameters of the Ag–Cu-Se system evaluated in the present work are listed in Table 4-2. The calculated Ag$_2$Se-Cu$_2$Se pseudobinary phase diagram is presented in Figure 4-4, along with the experimental data [164, 165]. A good agreement between the experimental data and the assessment was achieved generally. The liquid phase equilibrium at the Ag$_2$Se-rich portion, due to the scattered experimental data. The measured and calculated invariant reaction using the optimized database was listed in Table 4-3.
Glazov et al. [161] calculated the standard enthalpy of formation and the standard entropy of $\beta$-AgCuSe as $-49.95\pm1.5$ kJ/mol and $156.3\pm3.0$ J/mol·K, respectively, by using the thermodynamic quantities for silver and copper selenides reported by other investigators. The standard enthalpy of formation of $\beta$-AgCuSe was calculated as $-52.8$ kJ/mol and the standard entropy was calculated as $151.7$ J/mol·K. The deviation between calculated enthalpy of formation in this work and Glazov et al. can be considered reasonable because other than directly measurement, the value in Glazov et al. was calculated using the thermodynamic quantities of two terminal compounds from other literature, which may increase the inaccuracy of the results. Good agreement was reached between the standard entropy calculated in this work and Glazov et al. The calculated heat capacity of $\beta$-AgCuSe agrees with the experimental data as shown in Figure 4-5.

One of the most important features of Ag-Cu-Se system is the extent of the miscibility gap from Ag-rich to Cu-rich portion of the diagram. The calculated isothermal diagram at 1473.1 K shows good agreement with the measured experimental data by Asano et al. as shown in Figure 4-6. The relatively large deviation shown at the Cu, Se-rich corner of the diagram is attributed to the disagreement of the measured miscibility gap boundary of Cu-Se binary system and the Ag-Cu-Se system. An isopleth diagram with 15 wt.% of Se was calculated and shown in Figure 4-7. Generally, a good agreement between calculated and experimental data was reached. However, some disagreement was found at 1100 K between 5 and 20 wt.% Cu. Furthermore, the calculated liquidus at Cu-rich part shows higher temperature than the measured data. The deviation can be explained by the missing of the ternary compound AgCuSe in the
diagram proposed by Asano et al., which will definitely result in the wrong phase relation and equilibrium for this ternary system.

**Isopleth Diagram Prediction**

Several isopleth diagram with different Ag/(Ag+Cu) ratio were calculated using the optimized database in this work. The isopleth diagram is helpful in understanding the possible composition and reaction path way of Ag+Cu salinization process. Figure 4-8 shows the isopleth diagram with Ag/(Ag+Cu)=0.79 and the Se mole fraction ranges from 0 to 0.33. At 800 K, starting from the composition with pure Ag and Cu, the Cu composition in the two miscibility gap will react with Se first, forming β-Cu$_2$Se (region 11). As more Se incorporating in to the sample, the mole fraction of Cu in FCC_A1 phase will keep decreasing and eventually below the maximum solubility of Cu in Ag, leading to the disappearance of the miscibility gap in FCC_A1 phase (region 7). Then, the β-Cu$_2$Se and Ag continues to react with Se forming α-AgCuSe (region 12) until there are only Ag and α-AgCuSe existing in the sample (region 13). Then the rest Ag will be further selenized forming β-Ag$_2$Se. Other Cu-related compounds, such as CuSe, Cu$_2$Se$_3$ and CuSe$_2$, will not form when the Se composition in the sample is less than 0.33 mole fraction. The order of the reactions are shown as following:

\[
\begin{align*}
2Cu + Se & \longleftrightarrow \beta - Cu_2Se \\
\beta - Cu_2Se + 2Ag + Se & \longleftrightarrow 2\alpha - AgCuSe \\
2Ag + Se & \longleftrightarrow \beta - Ag_2Se
\end{align*}
\]  

(4-7)

The other two isopleth diagram of Ag/(Ag+Cu)=0.5 and Ag/(Ag+Cu)=0.2 shown in Figure 4-9 and Figure 4-10 reveals the same salinization reaction order and one thing worth noticing is the shit of FCC_A1+CU2SE_B two-phase region to the higher Se mole fraction position due to the decreasing Ag composition.
The calculated isothermal diagram of Ag-Cu-Se system at 873 K is shown in Figure 4-11. According to the diagram, there is a miscibility gap extending from Cu-rich to Ag-rich region with Se mole fraction between 0.95 and 0.52. At the metal-rich region, Cu tends to react with Se before Ag gets selenized and the ternary compound will not appear until all the Cu in FCC_A1 phase is selenized to β-Cu₂Se.

**Summary**

A self-consistent thermodynamic description for the Ag-Cu–Se system is presented using the two sublattice ionic-liquid model for the liquid phase and sublattice model for intermetallic compound with disordered high-temperature structure (α-phase) and ordered low-temperature structure (β-phase). A consistent set of thermodynamic parameters was derived. The calculated phase diagram and thermodynamic properties demonstrate a reasonable agreement with the measured data available in the literature.
### Table 4-1. Phase transformation temperature of AgCuSe

<table>
<thead>
<tr>
<th>Transition Temperature (K)</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>464</td>
<td>Cooling</td>
<td>Trots [177]</td>
</tr>
<tr>
<td>480</td>
<td>Heating</td>
<td>Trots [177]</td>
</tr>
<tr>
<td>463.15-468.15</td>
<td>XRD</td>
<td>Frueh [169]</td>
</tr>
<tr>
<td>484</td>
<td>DTA</td>
<td>Glazov [161]</td>
</tr>
<tr>
<td>603</td>
<td>EMF</td>
<td>Balapanov [178]</td>
</tr>
<tr>
<td>474.92±0.2</td>
<td>DSC</td>
<td>Chrisafiss [176]</td>
</tr>
<tr>
<td>467.9</td>
<td>Optimized</td>
<td>This Work</td>
</tr>
</tbody>
</table>

### Table 4-2. Optimized parameters for the Ag–Cu-Se system (J/mol of formula)

<table>
<thead>
<tr>
<th>Phase</th>
<th>T (K)</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>298.15&lt;T&lt;3000</td>
<td>( ^0L_{Ag^+,Cu^{-}:Se^2-} = \frac{632.414908+24.3881633}{T} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( ^1L_{Ag^+,Cu^{-}:Se^2-} = \frac{110.936806+3.03105875}{T} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( ^2L_{Ag^+,Cu^{-}:Se^2-} = \frac{3474.36122+9.32945441}{T} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( ^0L_{Ag^+,Cu^{-}:Se^2-,Va} = \frac{5212.6880+10.0832}{T} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( ^1L_{Ag^+,Cu^{-}:Se^2-,Va} = -15119.4779 )</td>
</tr>
<tr>
<td>( ^{\beta} )AgCuSe</td>
<td>298.15&lt;T&lt;6000</td>
<td>( AGCUSEB )</td>
</tr>
<tr>
<td>( ^{\alpha} )AgCuSe</td>
<td>298.15&lt;T&lt;6000</td>
<td>( AGCUSEB + \frac{2786.59231-5.95494290}{T} )</td>
</tr>
<tr>
<td>AGCUSEB</td>
<td>298.15&lt;T&lt;6000</td>
<td>( \frac{-68723.6822+145.040701\times T-38.7450941\times T^{LN(T)}}{T^{2}}+0.0745867623\times T^{2}-191060.284\times T^{(-1)}+0.0000191216\times T^{3} )</td>
</tr>
</tbody>
</table>

### Table 4-3. Calculated and measured Invariant reaction for Ag\(_2\)Se and Cu\(_2\)Se pseudo binary system.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>T (K)</th>
<th>Composition x(Ag)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid→( ^{\beta} )-Ag2Se+( ^{\alpha} )-AgCuSe</td>
<td>1003</td>
<td>0.42</td>
<td>0.6666667</td>
</tr>
<tr>
<td></td>
<td>1004</td>
<td>0.4254</td>
<td>0.6666667</td>
</tr>
<tr>
<td>Liquid→( ^{\beta} )-Cu2Se+( ^{\alpha} )-AgCuSe</td>
<td>1015</td>
<td>0.3</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1017</td>
<td>0.289</td>
<td>0</td>
</tr>
<tr>
<td>( ^{\alpha} )-AgCuSe↔Liquid</td>
<td>1042</td>
<td></td>
<td>Cooling [177]</td>
</tr>
<tr>
<td></td>
<td>1054</td>
<td></td>
<td>Heating [177]</td>
</tr>
<tr>
<td></td>
<td>1003</td>
<td></td>
<td>[161]</td>
</tr>
<tr>
<td></td>
<td>1026</td>
<td></td>
<td>[165]</td>
</tr>
<tr>
<td></td>
<td>1023</td>
<td>0.3333333</td>
<td>This Work</td>
</tr>
</tbody>
</table>
Figure 4-1. Pseudobinary phase diagram of Ag$_2$Se and Cu$_2$Se proposed by Agaev et al.
Figure 4-2. The miscibility gap in liquid phase of Ag-Cu-Se system at 1473 K proposed by Asano et al.
Figure 4-3. Pseudobinary phase diagram Ag$_2$Se-Cu$_2$Se proposed by Schafer et al.
Figure 4-4. Calculated Ag$_2$Se-Cu$_2$Se pseudo binary phase diagram.
Figure 4-5. Calculated Heal Capacity of $\beta$-AgCuSe along with experimental data. ■ Glazov et al. [161]
Figure 4-6. Isothermal diagram of Ag-Cu-Se system at 1247.15 K (1200 °C) along with experimental data.
Figure 4-7. Calculated Isothet Diagram with 15 wt.% Se superimposed with experimental data.
Figure 4-8. Calculated Isopleth Diagram of Ag/(Ag+Cu)=0.79

1. LIQUID
2. L1+L2
3. CU2SE_B+LIQUID
4. LIQUID+CU2SE_B+LIQUID
5. FCC_A1+LIQUID+LIQUID
6. FCC_A1+CU2SE_B+LIQUID
7. FCC_A1+CU2SE_B
8. FCC_A1+CU2SE_B+LIQUID
9. FCC_A1+LIQUID
10. LIQUID+AG2SE_B+FCC_A1
11. CU2SE_B+FCC_A1+FCC_A1
12. AGCUSE_A+FCC_A1+CU2SE_B
13. FCC_A1+AGCUSE_A
14. AGCUSE_A+FCC_A1+AG2SE_B
15. FCC_A1+FCC_A1+CU2SE_A
16. FCC_A1+CU2SE_A+AGCUSE_A
17. FCC_A1+AGCUSE_B+AG2SE_A
18. FCC_A1+AGCUSE_A+LIQUID
19. AGCUSE_A+LIQUID+FCC_A1
20. FCC_A1+LIQUID
21. AGCUSE_B+FCC_A1+CU2SE_B
22. AGCUSE_B+FCC_A1+AG2SE_B
Figure 4-9. Calculated Isopleth Diagram of $\text{Ag}/(\text{Ag}+\text{Cu})=0.5$
Figure 4-10. Calculated Isopleth Diagram of Ag/(Ag+Cu)=0.7
Figure 4-11. Calculated Isothermal Diagram of Ag-Cu-Se system at 873 K.
CHAPTER 5
THERMODYNAMIC OPTIMIZATION OF THE AG-GA-SE, AG-IN-SE AND HIGHER ORDER SYSTEM

Literature Review

Ag-Ga-Se System

Palarnick et al. firstly published a pseudobinary Ag$_2$Se-Ga$_2$Se phase diagram [180], in which a γ phase was reported between 690-850 K at Ga$_2$Se$_3$ rich region. Based on this assessment, Feigelson [181] did further study mainly focused on the phase equilibrium between the β phase and the liquid phase using single crystal AgGaSe$_2$ and the homogeneity range was firstly reported. Mikkelsen [182] did extensive study on full range of this pseudo binary system using differential thermal analysis, x-ray diffraction, and crystal growth studies. A new compound Ag$_9$GaSe$_6$ was reported and its homogeneity range was measured. A full summary of the work above can be found in Prince et al. [183]. Zhu et al. successfully synthesized high quality AgGaSe$_2$ single crystal using Bridgman Technique and confirmed the solubility of Ag$_2$Se in Ga$_2$Se$_3$ [184]. The maximum solubility shows the composition Ag$_{7}$Ga$_{11}$Se$_{14}$. Furthermore, the detailed homogeneity range of AgGaSe$_2$ was measured by Zhu et al. The results are identical as reported by Badikov et al. [185]. The isothermal section at 300 K, vertical sections of AgGaSe$_2$-Se and Ag$_9$GaSe$_6$-Se were also measured using DTA, XRD, Microhardness measurements [186].

Möller and Neumann et al. published two identical papers [187, 188] reporting the heat capacity of AgGaSe$_2$ in the range of 300-500 K. Sharma et al. also reported a set of heat capacity data between 0-900 K estimated using ab initio calculations. The data reported by Sharma et al. are almost double value reported by Möller and Neumann et al. The difference may be caused by the error of the experiment or the
immature calculation method used in their research. Therefore, the accuracy of these two sets of data needed to be evaluated. There are only two reports in terms of the thermodynamic properties of AgGaSe$_2$ and Ag$_9$GaSe$_6$ as listed in Table 5-1 [189]. The melting point and the enthalpy of melting of AgGaSe$_2$ was measured as 819-844 °C and 16.6 kcal/mol using DTA [190].

**Ag-In-Se System**

The only available summary of Ag-In-Se system was conducted by Schmid et al. [191]. The Gibbs free energy of formation for AgIn$_5$Se$_8$ and AgInSe$_2$ was reported as -850 kJ/mol and -188 kJ/mol [192, 193]. However, Aristi et al. [194] reported a complete different value as 242±25.12 kJ/mol. Later, Hiroaki et al. [190] reported the melting and transformation temperature of AgInSe$_2$ as 771 °C and 654-667 °C and the heat of melting and transformation was determined as 11 and 3.87 kcal/mol. The heat capacity of AgInSe$_2$ within the range of 0-300 K was reported by Kopytov et al. with the density functional theory using the pseudopotential method [195]. However, Sharma et al. reported complete different value within the range of 0-800 K [196]. Therefore, similar as AgGaSe$_2$, the accuracy of these two sets of data thus were evaluated in this assessment.

The pseudobinary system Ag$_2$Se-In$_2$Se$_3$ was reported by several researchers. Rigan et al. [197] reported the homogeneity range for AgInSe$_2$ and δ phase, as well as the phase boundary for the liquid phase for the first time. Olekseyuk et al. map out the phase diagram for the full pseudo binary system [198]. The phase relation of the system at 450 °C was reported by Chen et al. [163].
Thermodynamic Models

Unary Terminal Phases

The description of the Gibbs energy of pure Ag, Ga, In and Se was taken from the most recent complication Dinsdale [105] and Change [140]. They were modeled by using the following equation with different sets of parameters for corresponding temperature intervals:

\[
G_i^\circ = G_i^\circ - H_i^{SER} = A + BT + CT\ln T + DT^2 + ET^{-1} + FT^3 + IT^{-7} - JT^{-9}
\]  

(5-1)

where \(H_i^{SER}\) means enthalpy of standard element reference referring to the enthalpy of the stable state of the pure element at 298.15 K, T is the absolute temperature and A~J are the coefficients.

Liquid Phases

For the liquid phase, the ionic-liquid two sub-lattice model was used by the following expression:

\[
G_m^\circ = y_{Ag^2Se^2} G_{Ag^2Se^2}^\circ + y_{Ga^2Se^3} G_{Ga^2Se^3}^\circ + y_{In^2Se^3} G_{In^2Se^3}^\circ + y_{Se^2} y_{Ga^2Se} G_{Ga^2Se^2}^\circ + y_{Se^2} y_{In^2Se} G_{In^2Se^2}^\circ + y_{Se^2} y_{Se^2} G_{Se^2}^\circ \\
+ Q_{y_{Ag}} y_{Ag} G_{Ag}^\circ + Q_{y_{Ga}} y_{Ga} G_{Ga}^\circ + Q_{y_{In}} y_{In} G_{In}^\circ + Q_{y_{Se}} y_{Se} G_{Se}^\circ \\
+ RT(P_{y_{Ag}} \ln y_{Ag} + P_{y_{Ga}} \ln y_{Ga} + P_{y_{In}} \ln y_{In} + P_{y_{Se}} \ln y_{Se})) \\
+ y_{Ag^2Se^2} y_{y_{Se^2}} L_{Ag^2Se^2} + y_{Ga^2Se^3} y_{y_{Se^2}} L_{Ga^2Se^3} + y_{In^2Se^3} y_{y{Se}^2} L_{In^2Se^3} + y_{Se^2} y_{y_{Se}} L_{Se} \\
+ y_{Ga^2Se} y_{y_{Se^2}} L_{Ga^2Se^2} + y_{In^2Se} y_{y_{Se^2}} L_{In^2Se^2} + y_{Se^2} y_{y_{Se}} L_{Se} \\
\]  

(5-2)

where \(G_{Ag^2Se^2}^\circ\) and \(G_{Ga^2Se^3}^\circ\) is the Gibbs energy of formation of liquid Ag\(_2\)Se and Ga\(_2\)Se\(_3\) or In\(_2\)Se\(_3\), respectively. \(G_{Ag^2Se}^\circ\), \(G_{Ga^2Se^2}^\circ\) and \(G_{Se^2}^\circ\) are the Gibbs energies of formation per mole of atoms of liquids Ag, Ga, In and Se, respectively. The value of P and Q are determined using:

\[
P = 2y_{Se^2} + Q_{y_{y_{Se}}} \]

(5-3)
\[ Q = I(y_{Ag^+} + y_{Ga(In)^{3+}}) \]  

where the number 2 in Equation 5-3 and 1 in Equation 5-4 is the charge of Se and Ag or Ga(In) ion, respectively. The term \( L_{Ag^+\cdot Se^{2-}\cdot Va} \) refers to the interaction between \( Ag^+ \) and \( Se^{2-} \) on the Ag-rich side on the system and \( L_{Ag^+\cdot Se^{2-}\cdot Se} \) indicates the interaction between \( Ag^+, Se^{2-} \) and Se atoms on the Se-rich part of the system. \( L_{Ga(In)^{3+}\cdot Se^{2-}\cdot Va} \) and \( L_{Ga(In)^{3+}\cdot Se^{2-}\cdot Se} \) indicates the interaction between \( Ga(In)^{3+} \) and \( Se^{2-} \). \( L_{Ag^+\cdot Ga(In)^{3+}\cdot Se^{2-}\cdot Va} \) and \( L_{Ag^+\cdot Ga(In)^{3+}\cdot Se^{2-}\cdot Se} \) indicates the ternary interaction between \( Ag^+, Cu^+ \) and \( Se^{2-} \). These terms are expressed by the following expression:

\[ \nu L_\nu^{\delta} = a_\nu^{\phi} + b_\nu^{\phi}T \]  

where \( a_\nu^{\phi} \) and \( b_\nu^{\phi} \) are the terms which was assessed in this work using available experiment data.

**Compound Phases**

In the Ag-Ga-Se and Ag-In-Se system, all compounds exist as selenide. The Gibbs energy of the stoichiometric compound was expressed using the following equation:

\[ \nu G_\nu^{\phi} = G_\nu^{\phi} - H_\nu^{\phi} = a + bT + cT\ln T + dT^2 + eT^{-1} + fT^3 \]  

The vacancy site was added using sublattice model accordingly. For \( AgGaSe_2 \), the model \( (Ag,Ga)_1(Ga)_1(Se)_2(Se,Va)_1 \) was used in order to add solubility of \( Ga_2Se_3 \) in to \( AgGaSe_2 \) phase. The last sublattice \( (Se,Va) \) indicates the Se atoms sitting on the interstitial site. The \( Ag_9GaSe_6 \) was directly treated as line compound since no solubility was reported. \( AgInSe_2 \) and \( AgIn_5Se_8 \) was also treated as line compounds due to lack of
thermodynamic data. And their Gibbs energy was estimated based on the available phase diagram and phase relation.

**Assessment Results**

**Ag-Ga-Se System**

The calculated standard Gibbs energy of formation, standard enthalpy of formation and standard entropy of AgGaSe\(_2\) and Ag\(_9\)GaSe\(_6\) are listed in Table 5-1 and a good agreement between the experimental data and calculated value generally. It is worth noting that there is relatively large difference between the calculated and experimental value of the standard Gibbs energy of formation because according to the phase relation, the Gibbs energy of Ag\(_9\)GaSe\(_6\) has to meet the following relation in order to be stable:

\[
\frac{1}{5}G_{\text{AgGaSe}_6} > 1.8G_{\text{AgGaSe}_2} - 0.8G_{\text{GaSe}_3}
\] (5-7)

Therefore, the value reported by Babanly et al. does not make Ag\(_9\)GaSe\(_6\) stable at 298.15 K. Thus this value was discarded in this assessment. Also Aresti et al. stated that there could be over estimation in terms of the heat of formation of AgGaSe\(_2\). Therefore, this value was assessed using less weight in this study. The Gibbs free energy of AgGaSe\(_2\) and Ag\(_9\)GaSe\(_6\) as the function of temperature was plot in Figure 5-1. Both of the assess Gibbs energy follows the relation with the terminal compounds. And the heat capacity of AgGaSe\(_2\) superimposed with experimental data are shown in Figure 5-2. A good agreement between calculated value and experimental data is achieved.

Figure 5-3 shows the calculated AgGaSe\(_2\)-Se isopleth diagram. Babanly et al. [186] does not measure the composition in the liquid miscibility gap region. However, according the caution, two liquid miscibility gap was found in the isopleth diagram.
Figure 5-4. Shows the calculated pseudobinary Ag$_2$Se-Ga$_2$Se phase diagram. The calculated results agree with the experimental data well. One thing worth noticing is that Mikkelsen et al. [182] does not report any phase change in terms of the binary Ga$_2$Se$_3$, which was proven by Ider et al. and Zheng et al. [16, 17]. Therefore, the two phase $\delta+\delta'$ region was an estimation and need to be confirmed by experiment in future. The optimized parameters are listed in Table 5-2.

**Ag-In-Se System**

Due to lack of experimental data, especially the thermodynamics data of two ternary compounds AgInSe$_2$ and AgIn$_5$Se$_8$. It is impossible to model the whole system under the current experimental data availability. However, based on the available data and phase relation. It is possible for us to make an estimation of the Gibbs energy and the value can be confined in a small range. As shown in Figure 5-5, the calculated AgInSe$_2$ shows good agreement with Sharma et al. and the data from Kopytov et al. is too low [195, 196]. The calculated standard Gibbs energy of formation, standard enthalpy of formation and standard entropy of AgInSe$_2$ are shown in Table 5-1. The standard enthalpy of formation of AgInSe$_2$ agrees with the data from Aresti et al but there are 29.97 kJ/mol difference between the experimental and calculated data in term of the standard Gibbs energy of formation [193]. According to the phase relation, the Gibbs free energy of the compound in Ag-In-Se system has the following relation:

$$G_{\text{AgInSe}_2} < 0.5G_{\text{Ag}_2\text{Se}} + 0.5G_{\text{In}_2\text{Se}_3}$$

(5-8)

$$1/3G_{\text{AgIn}_5\text{Se}_8} < 1/3G_{\text{AgInSe}_2} + 2/3G_{\text{In}_2\text{Se}_3}$$

(5-9)

$$1/3G_{\text{AgIn}_5\text{Se}_8} > 5/3G_{\text{AgInSe}_2} - 2/3G_{\text{Ag}_2\text{Se}}$$

(5-10)
The value reported from Peraldo et al. does not fit the relation above and thus was not considered in the assessment. The estimated Gibbs free energy of AgInSe$_2$ and AgIn$_5$Se$_9$ is shown in Figure 5-6 and the calculated Gibbs energy match the relation mentioned above. The calculated isothermal diagram at 450 °C (Figure 5-7) shows good agreement with experimental data from Chen et al. [163].

**Higher Order System and Practical Application**

The experimental reported for higher order system is rare. The most important property is the complete solubility of AgInSe$_2$ and AgGaSe$_2$ [199]. And the solubility of Ag in CuInSe$_2$ or Cu in AgInSe$_2$ has not been reported. Therefore, the higher order system is a combination of the system previously assessed, including Ag-Cu-Ga-In [10], Cu-Ga-In-Se [13, 14, 16, 17, 162] and the subsystems Ag-Cu, Ag-Se, Ag-Cu-Se, Ag-Ga-Se and Ag-In-Se described in this work. And with the assessed thermodynamic database, the phase relation can be redacted. However, due to the large freedom, it is impossible to directly plot the phase relation of the quinary system unless some of the conditions are restrained. The phase change during the selenization process can be calculated by set the fixed value of temperature, pressure, the ratio between some of the elements in the system. Several different phases were involved during the selenization and these phases named with Greek letters are intruded as following. ξ phase refers to the phase of Ag, Cu, In and Ga metal in HCP structure. γ phase and η_HT phase refer to the metal alloys with the composition of (Ag,Cu)$_9$(In,Ga)$_4$ and (Ag,Cu)$_2$(Ga,In)$_2$, respectively. α phase is the compound (Ag,Cu)(Ga,In)Se$_2$ that were desired for PV material. Phase β is described as comprised of 3 compounds, Cu$_2$In$_4$Se$_7$, Cu$_8$In$_{18}$Se$_{32}$ and Cu$_{7}$In$_{19}$Se$_{32}$, but is considered to be a defect chalcopyrite structure of
solid solutions within a composition range bounded by the compounds CuInSe\textsubscript{2}, and CuIn\textsubscript{5}Se\textsubscript{8} [200].

An example for the calculation was performed for T=450 °C, metal group I/III=1, Ga/III=0.25 and the value for Ag/I was set at 1, 0.75 and 0.25. Figure 5-8 shows the salinization process when Ag/I=1. α phase does not appear until x(se) is over 0.05 and Se first tends to react with the liquid alloy forming ξ phase and GaSe. InSe and FCC metal alloy phase appears during the salinization process but eventually they will react with the Se, forming α phase. A surge of α phase fraction can be observed with x(se)>0.35, due to the reaction:

\[ \text{InSe + FCC(Ag, Ga, In) + Se} \rightarrow \alpha \]  

Once x(se) reach 0.5, the only phase that exists is AgIn\textsubscript{0.75}Ga\textsubscript{0.25}Se\textsubscript{2} and further Se incorporation will not have at even higher Se composition.

Another calculation was performed on the same condition but Ag/I ratio was changed to Cu-rich value 0.25 and the result is shown in Figure 5-9. Similar as the results in Figure 5-8, at the initial state, the liquid metal phase is unavoidable. However, instead of ξ phase, γ phase coexists with the liquid phase in the sample. These two phases can directly react with Se, forming α phase. η\_HT phase appears at x(Se)=0.1 but eventually will be selenized completely at x(Se)=0.32. One thing worth noticing is although at x(Se)=0.5, it is possible to get single α phase, it is possible for further selenization to take place, forming β phase and Ag\textsubscript{9}GaSe\textsubscript{6}. Therefore, when selenizing Cu-rich ACIG alloy, it is very important to control the Se incorporation quantitatively in order to avoid the formation of undesired phases.
The third calculation was performed for the same condition except the Ag/I was set as 0.25 which indicates the Cu-poor condition (Figure 5-10). Different from the case with no Cu, at the initial state the alloy contains γ which allows the formation of α phase at the beginning of the selenization. GaSe is not observed in the selenization process. The other phase behaves similar as the case with no Cu. And single α phase was reached at x(Se)=0.5 with the composition of Ag_{0.75}Cu_{0.25}In_{0.75}Ga_{0.25}Se_2. No further selenization happens with increasing Se composition.

Based on the calculation results, the existence of Cu aids the formation of γ phase which can directly reaction with Se forming α phase. It will also prevent the formation of GaSe compounds at the beginning of selenization. However, for the alloy with Cu-rich composition, the selenization process needs to be carefully controlled in order to prevent the formation of unwanted phases such as β and Ag_9GaSe_6 defect phase, which may reduce the film quality.
Table 5-1. Thermodynamic properties of the ternary compounds in Ag-Ga-Se system.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta_f G^0(298)$</th>
<th>$\Delta_f H^0(298)$</th>
<th>$S^0(298)$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ/mole</td>
<td>J·K$^{-1}$·mole$^{-1}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AgGaSe$_2$</td>
<td>237±3.4</td>
<td>239±5.6</td>
<td>159.6±11.2</td>
<td>[189]</td>
</tr>
<tr>
<td></td>
<td>238.733</td>
<td>239.836</td>
<td>164.12</td>
<td>This Work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>446.31±75.36</td>
<td></td>
<td>[194]</td>
</tr>
<tr>
<td>Ag$_9$GaSe$_6$</td>
<td>433±4.1</td>
<td>413.1±10.9</td>
<td>742.9±32.5</td>
<td>[189]</td>
</tr>
<tr>
<td></td>
<td>594.965</td>
<td>413.104</td>
<td>742.88</td>
<td>This Work</td>
</tr>
<tr>
<td>AgInSe$_2$</td>
<td>242±25.12</td>
<td>-</td>
<td></td>
<td>[194]</td>
</tr>
<tr>
<td></td>
<td>188</td>
<td>-</td>
<td>-</td>
<td>[193]</td>
</tr>
<tr>
<td></td>
<td>219.97</td>
<td>241.8</td>
<td>94.56</td>
<td>This Work</td>
</tr>
</tbody>
</table>
Table 5-2. Optimized parameters of Ag-Ga-Se and Ag-In-Se system.

<table>
<thead>
<tr>
<th>Phase</th>
<th>T (K)</th>
<th>Parameters</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgGaSe₂</td>
<td>298.15-1500</td>
<td>$G_{AgGaSeVa} = AGGASE2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$G_{GaSeVa} = AGGASE2-GHSERAG+GHSERGA-32000$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$G_{AgGaSe} = AGGASE2+GHSERSE+150000$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$G_{GaSeVa} = AGGASE2+GHSERSE-GHSERAG+GHSERGA+118000$</td>
<td></td>
</tr>
<tr>
<td>Ag₉GaSe₆</td>
<td>298.15-1500</td>
<td>$G_{AgGaSe} = 141202.0408235+384.8805008<em>T-402.3287064</em>T*LN(T)$</td>
<td>This Work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$+0.9340918* T^2 - 88870821.8500238<em>T^{(-1)} - 0.0000929</em>T^3$</td>
<td></td>
</tr>
<tr>
<td>AgInSe₂</td>
<td>298.15-940</td>
<td>$G_{AgInSe} = -316042.0580943+1319.0419596<em>T-211.6533333</em>T*LN(T)$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>940-6000</td>
<td>$G_{AgInSe} = -530253.5899855+1546.9264869<em>T-211.6533333</em>T*LN(T)$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$+0.0208000<em>T^2+291840.0000000</em>T^{(-1)}-0.0000194*T^3$</td>
<td></td>
</tr>
<tr>
<td>AgIn₅Se₈</td>
<td>298.15-6000</td>
<td>$G_{AgInSe} = 2*G_{InSe} - 40000$</td>
<td></td>
</tr>
<tr>
<td>AGGASE2</td>
<td>298.15-1500</td>
<td>-3.45897715E+05+2.26386543E+03<em>T-3.94855834E+02</em>T*LN(T)</td>
<td>[201]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+5.06907797E-01<em>T^2+3.65989337E+06</em>T^{(-1)}-1.66884947E-04*T^3</td>
<td></td>
</tr>
<tr>
<td>In₂Se₃</td>
<td>298.15-6000</td>
<td>-367289.95332+708.53899<em>T-135.62187</em>T<em>LN(T)-0.00715</em>T^2</td>
<td>[140]</td>
</tr>
<tr>
<td>GHSERSE</td>
<td>298.15-760</td>
<td>-6657.653+92.539696<em>T-19.14</em>T<em>LN(T)-0.12295</em>T^2+2.6766666E-06*T^3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>760-1500</td>
<td>-9059.16586+150.334216<em>T-28.552</em>T*LN(T)</td>
<td></td>
</tr>
<tr>
<td>GHSERAG</td>
<td>298.15-1234.93</td>
<td>-7209.512+118.202013<em>T-23.8463314</em>T*LN(T)</td>
<td>[105]</td>
</tr>
<tr>
<td></td>
<td>1234.93-3000</td>
<td>-.01790585<em>T^2-3.98587E-07</em>T^3-12011*T^(-1)</td>
<td></td>
</tr>
<tr>
<td>GHSERGA</td>
<td>298.15-302.9</td>
<td>-21312.3346+585.26385<em>T-108.2288</em>T*LN(T)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>+.22715565<em>T^2-1.1857525E-04</em>T^3+439953.9*T^(-1)</td>
<td></td>
</tr>
<tr>
<td>Phase</td>
<td>T (K)</td>
<td>Parameters</td>
<td>Reference</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
<td>----------------------------------------------------------------------------</td>
<td>-----------</td>
</tr>
</tbody>
</table>
| GHSERGA | 302.9-4000  | \begin{align*}
-6978.97846+132.50245&T-26.06929&T\cdot\ln(T)+1.5059995E-04&T^2 \\
-4.01731667E-08&T^3-118332.1&T^{-1}+1.645E+23&T^{-9}
\end{align*} | [105]     |
| Liquid  | 298.15-6000 | \begin{align*}
\mathcal{L}_{\text{Ag}^+\cdot\text{Ga}^2+\cdot\text{Se}^2}^0 &= 2.75771911E+05-3.23203376E+02&T \\
\mathcal{L}_{\text{Ag}^+\cdot\text{Ga}^2+\cdot\text{Se}^2}^1 &= -3.26259868E+04 \\
\mathcal{L}_{\text{Ag}^+\cdot\text{Ga}^2+\cdot\text{Se}^2}^2 &= -4.05694892E+04 \\
\mathcal{L}_{\text{Ag}^+\cdot\text{Ga}^2+\cdot\text{Se}^2}^0 &= 51252.36503-15.5499973 \\
\mathcal{L}_{\text{Ag}^+\cdot\text{Ga}^2+\cdot\text{Se}^2}^0 &= -83162.8242
\end{align*} | This Work |
Figure 5-1. Gibbs free energy of AgGaSe$_2$, Ag$_9$GaSe$_6$ and the two terminal compounds Ag$_2$Se and Ga$_2$Se$_3$. 
Figure 5-2. Heat Capacity of AgGaSe$_2$ with experimental data. Sharma et al. [202] and Neumann et al. [187, 188].
Figure 5-3. AgGaSe$_2$-Se cross section superimposed with experimental data from Babanly et al. [186].
Figure 5-4. Calculated pseudobinary system of Ag$_2$Se-Ga$_2$Se$_3$ with experimental data from Mikkelsen et al. [182].
Figure 5-5. Heat Capacity of AgInSe$_2$ superimposed with experimental data Sharma et al. [196] and Kopytov et al. [195].
Figure 5-6. Gibbs energy of AgInSe$_2$ as the function of temperature.
Figure 5-7. Isothermal diagram of Ag-In-Se system at 450 °C superimposed from the experimental data from Chen et al. [163].
Figure 5-8. Phase fraction change with the increasing Se composition. Ag/I=1, I/III=1, Ga/III=0.25. T=450 °C.
Figure 5-9. Phase fraction change with the increasing Se composition. Ag/I=0.25, I/III=1, Ga/III=0.25. T=450 °C.
Figure 5-10. Phase fraction change with the increasing Se composition. Ag/I=0.75, I/III=1, Ga/III=0.25. T=450 °C.
CHAPTER 6
THE EFFECT OF RAPID THERMAL ANNEALING ON THE PERFORMANCE OF CIGS CELLS WITH AN ITO LAYER

Literature Review

CIGS thin film cells are an attractive choice for use in photovoltaic applications because of their higher power efficiency and potential lower production cost [203]. CIGS cells use transparent conducting oxides such as Al:ZnO (AZO) and indium-tin-oxide (ITO) as the window layer. AZO is often preferred due to its lower cost, but reaction with H$_2$O has raised reliability concerns [204]. Although less expensive AZO is generally selected as the transparent window layer for commercial CIGS production, ITO is still considered a better window layer material for its outstanding electrical and optical properties (e.g., low resistivity ($\sim 2 \times 10^{-4}$ $\Omega$ cm) and high transparency (>80%) [205], wide band gap energy (3.5–4.3 eV) and long-term stability at high temperature in humid environments [206]).

Several investigations have been conducted on diffusion across the CdS/CIGS interface [207, 208]. Krishnan et al. showed that the solid solution $\gamma$-CuCd$_2$(Ga$_x$In$_{1-x}$)Se$_4$ reaction product appears when the sample temperature is elevated to $\sim$400 °C [5]. Study of the degradation process on completed device and the interaction between ITO and CdS after annealing are, however, less studied. Martel et al. showed that during the deposition of CdS on ITO using e-beam evaporation, S and In diffuses into ITO and CdS layer, respectively [209]. Furthermore, the diffusion rate for each element was determined as $10^{-17}$ cm$^2$/s [210] at $T=$ 150 °C. This study reports on degradation of a completed CIGS device as a function of anneal temperature and time with ITO as the window layer. The change in electrical and optical properties after annealing in dry N$_2$ and at 85% RH are also reported.
Experimental Method

The cells used in this study were prepared by co-evaporation of CIGS on a Mo-coated stainless steel substrate, followed by chemical bath deposition of the CdS buffer layer and then the sputtered ITO (SS/Mo/CIGS/CdS/ITO). These structures were fabricated by Global Solar Energy, Inc. and produced in a single run. A series of cells for testing were completed at the University of Florida by depositing an Ag contact layer (300 nm) on the ITO using electron-beam evaporation with a shadow mask. Four cells were scribed, isolated, and characterized on a single larger area of SS/Mo/CIGS/CdS/ITO to establish pre-measurement values of device parameters. The area of each cell was ~0.409 cm².

The rapid thermal annealing (RTA) system consisted of a quartz tube equipped with heating lamps above and below the sample holder (Figure 6-1). Cells were annealed for 5, 10, 15 and 20 min at each temperature (50, 100, 150 and 200 °C). It is noted that the heating time from 25 to 200 °C was ~30s. Flowing dry nitrogen was used as the gas ambient during annealing in one series of studies. In another set of experiments, samples were exposed to a flowing N₂/H₂O gas mixture (85% RH) at 85 °C. The relative humidity was controlled by mixing a water-saturated N₂ flow with a dry N₂ flow, which were maintained at 70 and 12.5 sccm, respectively. The device parameters were again measured after annealing the device.

In a final set of experiments, aluminum foil was wrapped around the outside of the sample boat to block direct exposure to the heater lamp to block direct adsorption. These samples were annealed under dry N₂ flow and the device parameters measured to check for light soaking effects.
Each cell was characterized before and after annealing with J-V and QE measurements. The measurement temperature was controlled at 25 °C during the J-V measurements and the illumination area was maintained at the 1 sun AM 1.5 condition. After the J-V measurement, these samples were annealed under the conditions previously described above and J-V traces were immediately collected. QE measurements were also taken at Oak Ridge National Laboratory one day after the annealing.

Results and Discussion

Four cells were simultaneously annealed at each annealed condition. J-V and QE measurements were taken for each cell before and after annealing. The mean value and standard deviation of difference between the after and before anneal values were computed and the differences were plotted. The mean and standard deviation (σ) values for all the non-annealed cells are \( V_{OC} = 0.6214 \) V (σ=0.014), \( J_{SC} = 35.269 \) mA/cm\(^2\) (σ=2.168), FF == 64.74% (σ=4.45), and \( \eta == 14.02\% \) (σ=1.5). It is noted that there is a relatively large variation in performance from cell to cell and thus statistics on the differences were analyzed.

The measured open circuit voltage (\( V_{OC} \)) difference at each anneal temperature is shown in Figure 6-2 as a function of anneal time. Cells annealed at lower thermal budget showed an increase in \( V_{OC} \). Annealing the device at higher thermal budget, however, significantly reduced the value of \( V_{OC} \). The largest increase in mean value of \( V_{OC} \) (9.26±6.07 mV) occurred after annealing at 50 °C for 300, although similar increases were observed in individual cells at higher anneal temperature and time. Loss in the mean \( V_{OC} \) as a function of annealing temperature at constant anneal time (not shown) reveals a decreasing trend (note Δ\( V_{OC} \) scale differences in Figure 6-2). As
expected, higher temperature promotes a faster degradation process. The results at the two highest temperatures show a decreasing $\Delta V_{oc}$ for the first 3 anneal times followed by a slight improvement when annealed for 900s, suggesting a plateau was reached. Experiments for longer annealing time are needed to better defined the trend.

Figure 6-3 shows the value change of short circuit current density as a function of annealing time at the 4 anneal temperatures. At all measurement temperatures, the mean value of $J_{sc}$ increases when the annealing time was less than 900s, except when annealed at 200 °C for 900s. Previous studies on the influence of temperature on ITO properties indicate that ITO shows better crystallinity, higher carrier concentration and higher roughness due to the rearrangement of atoms after annealing [211]. The larger grain size can decrease the boundary scattering, and thus increase the carrier mobility [212]. Therefore, the improvement in $J_{sc}$ and FF can be explained by improved crystallinity of the ITO decreasing grain boundary resistance, and smoothing of the interface; hence enhanced collection efficiency. At higher temperature the transmittance begins to decrease due higher carrier concentration and associated free carrier adsorption.

The difference between the annealed and control mean values of the fill factor (FF) and efficiency ($\eta$) are plotted in Figure 6-4 and Figure 6-5, respectively. The results point to a decrease in FF with annealing, although a slight increase in the mean value of FF was observed at 3 anneal temperatures for short time (~1% change). The efficiency of each sample was calculated based on the measured $V_{oc}$, $J_{sc}$ and FF. As shown in Figure 6-5, a positive efficiency change upon annealing is observed for both the 300 and 600s anneals at 50 and 100 °C, as well at 150 °C 600s. The maximum
improvement occurred at the lowest thermal budget studied (50 °C for annealing time of 300s). Also, the magnitude of increment of efficiency showed a dependence on the annealing temperature. A high thermal budget clearly lowered the mean cell efficiency.

The results of dark annealing study (Table 6-1) show that the dark annealing are values similar to those observed after the normal annealing condition, and thus the effect of light-soaking is insignificant. Since the annealing time is relatively short in this work, it is unlikely the absorber layer transitioned to the metastable state associated with light-soaking to produce an increased efficiency [213].

When the annealing time exceeds 600s, the electrical properties of the cell begin to deteriorate. Kumar et al. [214] also found significant electrical property decrease when the complete CIS cell was annealed at 164 – 345 °C. It has been suggested that diffusion of Cd⁺² into CIGS and possibly Cu⁺¹ into the CdS buffer layer [215]. The Cd⁺² would act as a donor in the upper layer of the CIGS, potentially leading to type inversion and moving the p-n junction below the metallurgical one. If defects at the CIGS/CdS interface provide a major recombination pathway, the interdiffusion would have a positive impact. Using energy dispersive x-ray spectroscopy, Nakada et al. [207, 208] confirmed that Cd⁺² substitutes on Cu sites at temperature as low as 80 °C. Krishnan et al. recently used in-situ X-ray diffraction (XRD) to study the degradation mechanism of the CIGS device structures from the same source as this study. In both N₂ and forming gas ambient, the collected diffraction patterns revealed formation of the solid solution CuCd₂(GaₓIn₁₋ₓ)Se₄ at ~400 °C [5]. This temperature is much higher than this study, but a significant amount of CuCd₂(GaₓIn₁₋ₓ)Se₄ is needed to be observed by XRD. It is possible that there a trade-off between improvement at low thermal budget by CIGS
type inversion and degradation by CuCd$_2$(Ga$_x$In$_{1-x}$)Se$_4$ formation may contribute to the observed results.

To better understand the effect of annealing on cell performance, quantum efficiency measurements were performed on selected cells. Figure 6-6 shows the quantum efficiency of a cell annealed at 50 °C for 300s. The improvement of QE induced by annealing agrees with the efficiency measurement. The positive effect can be observed in a large range of wavelength (350-1020 nm). The increase in the blue wavelength response can be attributed to the reduction of front surface recombination due to CdS/CIGS mixing at the interface. The most significant benefit appeared in the green responds region (500-950 nm), possibly due to increased transmittance of the ITO layer [212] and a higher electron mobility produced by the better crystallinity of both the ITO and CIGS layers.

The QE curve of a cell annealed at 100 °C for 600s is shown in Figure 6-7. Compared with Figure 6-6, the benefits in the blue responds region have largely disappeared, which may indicate that formation of γ-CuCd$_2$(Ga$_x$In$_{1-x}$)Se$_4$ or CIGS/CdS interface defects that act as a recombination center. The decrease in efficiency in the green region may also be attributed to increasing defect concentration, which decreases the diffusion length of the electrons. As shown in Figure 6-7, the increase of QE in the green region is about half the amount shown in Figure 6-6. This may also be caused by carrier concentration or structural change in the ITO induced by annealing. A previous report showed that higher carrier concentration in ITO layer can lead to lower transmittance [212].
At an annealing temperature of 100 °C and 900s, there is minimal improvement of QE in the green region while the QE is in blue region reduced slightly (Figure 6-8). When the annealing temperature was increased to 150 °C, however, the QE in the green region decreased more than that in the blue region (Figure 6-9). From Figure 6-8 and Figure 6-9, it is seen that RTA on CIGS cells will first decrease the response of the cell to high energy photons and then lower the cell performance by reducing its response in the green region. Since absorption coefficient is larger for high energy photons than low energy photons, it is possible that at low thermal budget, the ITO and absorber layer crystallinity is improved and the CIGS/CdS interface contains fewer defects. Both of these effects will benefit the performance of the cell. When the anneal conditions are more aggressive, it is possible that structural changes take place in ITO layer as well as at the ITO/CdS interface, which will decrease transmittance and electrical performance. Thus, the QE of the sample in green response region decreases significantly.

The electrical properties of samples annealed at 85 °C with relative humidity 85% are shown in Figure 6-10. Compared to the results obtained from dry annealing at 50 and 100 °C, the change of VOC, JSC and efficiency reached a maximum at 300s and decreased thereafter. The fill factor, however, showed the largest decrease (1.8±0.3%) at 300s. The devices started to fail between 300s and 600s, which is a shorter time range than annealing with dry N2 flow. This suggests the acceleration of degradation caused by water vapor.

ITO is typically deposited by RF magnetron sputtering. It has been shown that when ITO is sputtered at temperatures less than 200 °C, CIGS performance increases
because of decrease in ITO resistance. If the temperature exceeds 200 °C, however, the interfacial reaction at CIGS/CdS increases and the device degradation become apparent [216, 217].

The increased conductivity of ITO is due to increased carrier concentration rather than higher mobility. The observed low mobility of ITO compared to bulk In$_2$O$_3$ can be explained in terms of ionized impurities or grain boundaries scattering. Enhanced crystallization of films has been observed for films deposited at higher substrate temperature, which was shown to increase the mobility. Using TEM and electron diffraction Sreenivas et al. observed large stacking faults of ITO films deposited on glass substrates [33]. The high transmission of the ITO is related to the wide band gap of the semiconductor. The absorption edge of ITO films with higher free carrier concentration shifts to shorter wavelengths due to the Moss-Burstein shift.

R.X. Wang et al. [218] showed that air annealing at temperature less than 200 °C increases the transmittance of ITO films because oxygen incorporation and decomposition reactions substantially influence the carrier concentration and chemical states. Furthermore, it was found that the roughness of films does not have a close relationship with their transmittance.

Previous reports indicate the ITO/CdS structure shows much lower sheet resistivity and a wider light transmission range than a single CdS layer. Furthermore, post-annealing of ITO can also change its properties [32, 219]. Annealing in vacuum or reducing atmosphere improves the overall properties of thick ITO. Barlow et al. [32] showed that annealing at low temperature, even at 50 °C for 5 minutes, increases the conductivity of the ITO film from \(~16\) to \(~18\ \Omega^{-1}\text{cm}^{-1}\). This study also showed that the
optical transmission of the ITO films increased after annealing under oxygen-poor condition. These improvements of ITO film properties may contribute to the overall performance of the solar cell. Further characterization (e.g. TEM) of the sample is necessary to understand the structural change mechanism in ITO layer as well as the ITO/CdS interface.

Summary

CIGS devices provided by Global Solar Energy, Inc. were annealed using rapid thermal annealing. The efficiency of the devices was found to increase by 1.8±0.8% after annealed at 50 °C for 300s. When annealed at even higher thermal budget (100 °C for 600s), the efficiency of the devices increased by 2.0±2.3%. This could be attributed to improvement of ITO properties. As the temperature and annealing time was further increased, the performance of the devices declined sharply. This degradation process also could be accelerated by annealing in a humid environment. The results of dark annealing shows that annealing using RTA for no more than 600s will not induce a significant light-soaking effect. Quantum efficiency measurement indicates that the during the annealing process, the front area of the absorber layer degrades at a relatively lower temperature and ITO related degradation takes place under more aggressive annealing conditions.

Further characterizations such as TEM and SIMS depth profile measurement are necessary to better understand the underlying reasons for the changes in device performance induced by annealing.
Table 6-1. Summary of Change of Device Properties after Dark Annealing

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Time (s)</th>
<th>Mean Difference in Value After and Before Annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$V_{OC}$ (V)</td>
</tr>
<tr>
<td>52.8</td>
<td>300</td>
<td>±0.0014</td>
</tr>
<tr>
<td>103.3</td>
<td>600</td>
<td>±0.0128</td>
</tr>
</tbody>
</table>
Figure 6-1. Schematic of the RTA system

Figure 6-2. Change in $V_{OC}$ with annealing time at 4 temperatures. Note $\Delta V_{OC}$ scale varies with anneal temperature.
Figure 6-3. Change in \( J_{sc} \) with annealing time at 4 temperatures.
Figure 6-4. Change of Fill Factor with annealing time at 4 temperatures. Note the change in scale for ΔFF.
Figure 6-5. Change of efficiency with annealing time at 4 temperatures.
Figure 6-6. Quantum Efficiency of sample annealed at 50 °C for 300 s.
Figure 6-7. Quantum Efficiency of sample annealed under 100 °C for 600 seconds.
Figure 6-8. Quantum Efficiency of sample annealed under 100 °C for 900 seconds.
Figure 6-9. Quantum Efficiency of sample annealed under 150 °C for 900 seconds.
Figure 6-10. Electrical properties of samples annealed at 85°C with RH 85%.
CHAPTER 7
ZNO_{1-x}S_x THIN FILM AS ALTERNATIVE BUFFER LAYER MATERIAL USING ATOMIC LAYER DEPOSITION

Literature Review

CIGS thin film cells are an attractive choice for use in photovoltaic applications because of their higher power efficiency and potential lower production cost [203]. The substitution of Ag for Cu in CIGS absorber layers shifts the bandgap energy higher and towards the optimal value (1.4 eV) while decreasing materials cost. With this substitution and higher bandgap energy, an alternative buffer layer material to CdS is needed to retain a favorable band alignment with the absorber. For CdS buffer layer, it has been shown that an electrically resistive i-ZnO layer is beneficial for reducing the shunts effect [18]. However, the extra layer not only reduce the photon transmission but also increasing the manufacturing cost. Therefore, eliminating the i-ZnO layer would simplifying the fabrication process and beneficial for the cost control.

Extensive studies have been done on the alternative Cd-free buffer layer materials [19-24]. Zinc Oxysulfide (ZnO_{1-x}S_x) is a candidate buffer layer material since its electrical and optical properties are tunable by varying the oxygen to sulfur ratio in the film. Furthermore, the wider bandgap of ZnO_{1-x}S_x compared to CdS and the thinner film possible with conformal ALD compared with conventional chemical bath deposited CdS, promises higher transmission especially in high wavelength range. It has been applied on various solar materials as a buffer layer using different deposition technique [22, 25, 26]. Among all these deposition technique, atomic layer deposition shows significant advantage due to its strong capability of thickness, doping concentration and film conformality control. Furthermore, ALD usually requires low deposition temperature
and generate less waste. This would minimize the degradation of the cell performance induced by the thermal diffusion [27].

In this study, the ZnO$_{1-x}$S$_x$ thin film with various H$_2$O:H$_2$S pulse ratio was prepared on Si (111), borosilicate glass and CIGS/Mo/Stainless Steel substrate. The morphological, structural and optical properties of the film were characterized. The complete cell performance was measured and the effect of the thickness of the buffer layer was discussed.

**Experimental Procedures**

The CIGS substrate used in this study was manufactured by Global Solar Energy (GSE) using co-evaporation on Mo/stainless steel sheet. The ZnO$_x$S$_{1-x}$ buffer layer was deposited on Si and Borosilicate Glass for ALD temperature window determination and film characterization, using an atomic layer deposition reactor with reactants diethylzinc (DEZn), H$_2$S, and H$_2$O at 150 °C. The reactant sequence for depositing ZnO$_{1-x}$S$_x$ film was set as ((DEZn-purge-H$_2$O-purge)$x$ (DEZn-purge-H$_2$S-purge)$y$)$n$, where $x$ and $y$ are number of times each Zn-O and Zn-S cycle are respectively executed. The number $n$ indicates the total number of supercycle. To fabricate test cells, the buffer layer was deposited on CIGS substrate and then a layer of aluminum-doped zinc oxide (AZO) was sputtered on the buffer layer, followed by deposition of an Ni/Al contact grid using e-beam evaporation. The buffer layer thickness is precisely controlled by the number of deposition cycles. The deposited films were characterized using XPS, SEM, reflectometer and the complete cell were characterized using solar simulator under AM 1.5 one sun condition.

As shown in the Figure 7-1, The ALD reactor on the left permits up to five gas or liquid reaction precursor or purge flows to be delivered to the deposition chamber. The
top line is devoted to purge gas delivery and the adjacent line is equipped to deliver H$_2$S delivery line. The next three lines, shown from top to bottom, are deployed to deliver diethylzinc (DEZn), biscyclopentadienyl magnesium (MgCp$_2$) and H$_2$O respectively. The flow rate of each line is regulated by a mass flow controller, which downstream of a gas purifier. The ALD deposition cycles are controlled by pneumatic valves located just prior to the entrance of the chamber. The switching of the pneumatic valve is automatically controlled by Labview. The right chamber of the system is designed for ZnO-based TCO material ALD deposition. Thus, connected with a transfer chamber, the whole system can be used for continuous ALD deposition of buffer layer and TCO without exposure to the atmosphere. The heater was made of Inconel 600 alloy and the top heater surface was coated with a protective AlN film.

A 3d-view plot of the substrate carrier is shown in Figure 7-2. Quartz was selected as the material for the substrate carrier due to its high heat capacity and low thermal expansion coefficient between 100 and 200 °C. The bottom part of the carrier covers the entire heating surface and forms a good thermal contact. The substrate will be placed on the top surface. A customized fork can clear the lower diameter section to allow transfer of the carrier from one chamber to the other. The surface temperature will be calibrated before using this substrate carrier.

**Experiment Results and Discussion**

**ALD Process Windows**

The ALD process window was identified by conducting a series of measurements of film growth rate vs. temperature, pulse time for the Zn, O, or S precursors, and purge time to determine conditions that yielded self-limiting reaction [220]. During deposition, the carrier gas flow rate was maintained at 60 sccm and the pressure and bubbler
temperature were controlled at 1 atm and 10 °C, respectively. The base condition for ALD fixed the DEZn and H$_2$O pulse time at 0.2 and 0.1s, respectively with all purge times at 10 s. The base deposition temperature was 130 °C. These settings were then individually varied about the base condition to determine the window for that process variable and base condition. As examples, Figure 7-3 shows the growth rate variation (Å/cycle) for 4 of the process variables (H$_2$O purge time, DEZn and H$_2$S pulse time, and temperature). As shown in Figure 7-3 A, the ZnO growth rate decreased linearly from 2.4 to 2.05 Å/cycle for H$_2$O purge variation in the time range 2 to 20 s, and then was independent of purge time between 20 and 30s (2.05 Å/cycle), which is consistent with ALD growth mode. Figure 7-3 B shows a small ALD window for DEZn pulse time (0.17 to 0.24s) for which the growth rate remained constant. The DEZn pulse time is an important parameter for ALD. With longer DEZn pulse, the growth rate increases and then tends to reach a constant, limited by background adsorbed H$_2$O adsorption during a given cycle. Figure 7-3 D shows the film growth per cycle as the temperature is changed for both growth of ZnO and ZnS. It is observed for ZnO (red symbols) that the growth rate increases linearly from 0.5 to 2.1 Å/cycle with increasing temperature in the range 60 to 120 °C. This behavior is consistent with reaction limited growth conditions, presumably due to partial decomposition of DEZn on the surface. The growth rate reaches a plateau in the temperature range 120 to 200 °C, which is the temperature range for ALD ZnO film deposition.

The data in Figure 7-3C indicates that the H$_2$S saturation window, between 0.09 and 0.12s H$_2$S pulse time, is reached rapidly. When the pulse time is longer than 0.12s, the growth rate increases linearly, which indicates growth is in the continuous chemical
vapor deposition mode. The temperature variation of ZnS growth is provided in Figure 7-3D (blue symbols). The growth rate decreases exponentially in the 60 to 100 °C range. This is likely attributable to the condensation of DEZn on the surface at this relatively low temperature. Based on the data for ZnS deposition in Figure 7-3 D, however, a true plateau is not observed and the growth rate decreases slowly with temperature increase above 120 °C. This is consistent with the observation by Bakke et al. [221] using in-situ generated H₂S. Stuyven et al. [222] attributed this decrease to decreasing number of reactive sites cause by the desorption of ethyl ligands from the film surface at high temperature.

**Film Composition**

X-ray Photoelectron Spectroscopy (XPS) was used to study the composition of the deposited film. Before acquiring an XPS spectrum, the film was sputter with Ar+ to remove the surface contamination. The Ar sputtering gun was attached to the XPS ultra-high vacuum chamber with a base pressure of 7x10⁻⁹ Torr. During sputtering, the Ar gun pressure was set at 20 mTorr and the chamber pressure was increased to 3x10⁻⁷ Torr. The sputtering time (5 min) was determined by previous experience to remove the surface carbon. The XPS scan results of the ALD-deposited ZnO film are shown in Figure 7-4A. The film was deposited at 125 °C with 250 cycles. The spectrum was aligned using Oxygen 1s (532.8 eV) peak as a reference. Before initiating the XPS survey, 10 min Ar+ sputtering was performed to remove the adventitious surface carbon and oxygen. According to the XPS spectrum, no impurities are found in the deposited film within the detection limit of XPS (0.1 atm.%). In other words, no carbon atoms were induced into the ZnO ALD-deposited film from DEZn precursor. Currently, the existence of H atoms in the film possibly induced by H₂O remains unknown due to the limit of
XPS. It is necessary to conduct further characterization (e.g. UPS) to confirm the film is free of hydrogen. Figure 7-4B shows the XPS spectrum of ZnS thin film. It is worth noticing that there are around 5% Oxygen residue in the ZnS. It can be attribute to the oxygen and moisture residue in the deposition chamber as the base pressure of the chamber was kept at 0.17 Torr. Also, due the low deposition thickness per cycle, it is easier for the oxygen incorporation to occur.

The XPS spectra collected for samples with different cycle ratio of ZnO to ZnS are shown in Figure 7-5. It is noted that the Zn, O and S peaks are located at 1022 eV, 533.2 eV and 162.1 eV, respectively. No carbon peak was found within the XPS detection limit, which indicates that during the deposition the surface diethylznic was oxidized cleanly by H\textsubscript{2}O or H\textsubscript{2}S. As shown in Figure 7-5, the sulfur peak intensity decreases with the decreasing of the ratio of ZnS to ZnO cycle and consistently, the oxygen peak becomes stronger with increasing the number of ZnO cycles. The intensity of Zn peaks does not change significantly, which means Zn concentration in the film does not change with the variation of the ratio of ZnO to ZnS cycles.

The actual S/(S+O) value calculated from the XPS spectra are plotted as a function of the pulse ratio in Figure 7-6. The 45° line in this figure represents the condition where the film composition matches the overall exposure composition. Difference from the pulse ratio, the concentration of sulfur in the deposited film deviated negatively from the precursor pulse ratio. When 90% H\textsubscript{2}S pulse was used, the sulfur concentration in the film dropped below 50%. And when H\textsubscript{2}S pulse ratio was below 0.3, the concentration of S in the film is even less than 5%. This negative deviation of sulfur concentration indicates the substitute reaction
\[ \text{ZnO} + \text{H}_2\text{S} \leftrightarrow \text{ZnS} + \text{H}_2\text{O} \]  \hspace{1cm} (7-1)

could take place during the deposition. The Gibbs free energy of the reaction to the right direction was calculated as -78 kJ/mole at room temperature, using Gibbs free energy of formation of ZnO(s), H₂S(g), ZnS(s) and H₂O(g) as -318.32, -33.56, -201.29 and -228.59 kJ/mol. This means the reaction to the right direction is thermodynamically favorable [223]. However, the ALD process is far from equilibrium because for every pulse only one type of precursor or oxidizer was introduced into the reaction, which may enhance the reverse reaction. Higher temperature will increase the reaction rate as excessive H₂S was delivered into the deposition chamber every pulse [26]. Platzer-Björkman et al. reported similar behavior and thus the actual S concentration is highly depend on the deposition process even the parameters were chosen within the ALD window.

Multiplex scan were performed for O, S and Zn peaks only as shown in Figure 7-7. It is noted that the Zn, O and S peaks are located at 1022 eV, 530.4 eV and 162.1 eV, respectively. The sulfur 2p peak can be split into two peaks for 2p3 and 2p1 electron, located at 161.5 eV and 163.1 eV respectively. All these measured binding energy value matches the binding energy value for ZnO and ZnS in XPS binding energy database, which indicates all the O and S atoms are bounded to Zn.

**Morphological and Structural Properties**

In order to test the effect of the precursor pulse time on the surface feature of the deposited thin film. The AFM measurement was conducted on the samples of ZnO thin film using various DEZn and H₂O pulse time. The AFM images were shown in Figure
7-8 and the change of the surface roughness with precursor pulse time was plot in Figure 7-9.

According to the AFM images, the film deposited with ALD windows shows relatively smoother surface and with the increasing precursor pulse time, the “hill and valley” like feature appears and become more visible with higher pulse time. By quantitative analysis, the film deposited within ALD window shows minimum surface roughness at 3.5 nm. The surface roughness increases monotonically with the increasing precursor pulse time and reach 17.8 nm for the sample deposited using 2 s and 3.5 s for DEZn and H₂O pulse time. One important feature of ALD is its “self-limiting” behavior which means during each cycle, only one monolayer of precursor was induced to the substrate surface. This deposition feature will result in relatively less surface roughness.

The topographical SEM images of ZnOₓS₁₋ₓ thin film with different S concentration were shown in Figure 7-10 (H₂S-pulse-rich) and Figure 7-11 (H₂O-pulse-rich). The two films show distinctive surface feature. The grains of the H₂S-pulse-rich ZnOₓS₁₋ₓ thin film shows round shape feature and the grain size slightly increases with the increasing H₂S pulse fraction from ~45 nm to ~80 nm. Even when the H₂S pulse fraction reaches 0.5, the feature remains the same. However, different from the H₂S-pulse-rich ZnOₓS₁₋ₓ thin film, the H₂O-pulse-rich samples show elongated grains on the surface. This results is similar as the feature reported by Sanders et al. [224]. And small incorporation of S does not change the grain feature. All three samples shown in the Figure 7-11 shows similar grain size between 80-110 nm.
In order to analyze the structural information, XRD was conducted on samples with various S concentration ZnO$_x$S$_{1-x}$ thin film and the spectrum was shown in Figure 7-12. As shown in Figure 7-12A, H$_2$O-pulse-rich ZnO$_x$S$_{1-x}$ thin film shows hexagonal Wurtzite ZnO structure. Four major peaks are observed at 31.86°, 34.4873°, 36.3324° and 56.7762°, corresponding to (100), (002), (101) and (110) plane. The intensity of the peaks for (100), (002) and (101) are much higher. These four peaks indicate the thin film is multocrystalline. All the peaks show the shift to the lower angle with the increasing H$_2$S pulse fraction. According to the Bragg's Law:

$$2d \sin \theta = n\lambda$$  \hspace{1cm} (7-2)

where $d$ is the interplanar distance, $\theta$ is the scattering angle, $n$ is a positive integer and $\lambda$ is the wavelength of incident wave. The $d$-spacing value for all these four plane increases as the incorporation of S atoms into the ZnO thin film. On the country, the XRD spectrum of H$_2$S-pulse-rich ZnO$_x$S$_{1-x}$ thin film (Figure 7-12B) shows only one strong peak at 28.65°. This indicates that H$_2$S-pulse-rich ZnO$_x$S$_{1-x}$ thin film has a cubic structure with preferred orientation of (111) direction. As the O composition in the film increasing, the peak shifts to higher angle, which suggests the decreasing of the $d$-spacing. Although there is only one obvious peak shown in the XRD spectrum, the film is multocrystalline based on the surface SEM image. The radii of O$^{2-}$ ion (1.42 Å) is less than that of S$^{2-}$ ion (1.84 Å). Therefore, the incorporation of O into ZnS or S into ZnO thin film will cause the decreasing or increasing of the lattice constant, respectively.

Figure 7-12C shows the XRD spectrum of ZnO$_x$S$_{1-x}$ thin film prepared using H$_2$O:H$_2$S ratio 1:1 and no peak is observed. This indicates that film is amorphous.
The crystallite size was extracted from XRD spectra using Scherrer equation. The crystallite size of H2S-pulse-rich ZnO,S1-x thin film was measured between 40 and 50 nm with relatively small deviation while that of H2O-pulse-rich ZnO,S1-x thin film firstly increases from 28 nm to 80 nm from with the decreasing H2O pulse fraction and then drops back to 50 nm. All the data on the H2O-pulse-rich side shows large deviation due to the different growth direction of the grains in the film.

**Optical Properties**

Transmission of ZnO,S1-x thin film deposited with various H2S pulse fraction was plotted in Figure 7-14. It is worth noting that the thickness of the film was controlled at 50 nm but with slightly variation because the total thickness was controlled by the number of supercycles. And the growth per supercycle was different for films with different H2S pulse ratio. This could be one of the reason for the variation of the transmission for these thin film. The red shift effect can be observed for the incorporation of both S and O. To derive the optical bandgap, further analysis was performed as following.

The adsorption can be calculated using

\[ A = 2 - \log_{10}(\%T) \]  

where A is absorption with arbitrary unit and T is the transmission. The band gap of the samples were exacted from absorption spectrum using Absorption Spectrum Fitting (ASF) method proposed by Ghobadi et al. [225]. The absorption coefficient can be described as a function of wavelength using the equation below,

\[ \alpha(\lambda) = B \cdot (hc)^{m-1} \cdot \frac{1}{\lambda} \left( \frac{1}{\lambda} - \frac{1}{\lambda_g} \right)^m \]  

(7-4)
where $\lambda_g$, $h$, and $c$ are wavelengths corresponding to the optical band gap, Planck's constant, and velocity of light, respectively. $B$ is constant and $m$ is the index which can have different values of $1/2$, $3/2$, $2$, and $3$ [226]. It has been approved that the best fitting can be achieved for $m=1/2$ [225] and using the Beer-Lambert's law, Equation 7-4 becomes

$$Abs(\lambda) = B_1\lambda\left(\frac{1}{\lambda} - \frac{1}{\lambda_g}\right)^m + B_2$$

(7-5)

The bandgap can be calculated using the date obtained by extrapolating the line to $\left(\frac{Abs(\lambda)}{\lambda}\right)^2 = 0$ and the equation as following

$$E_{gap}^{ASF} = \frac{1239.38}{\lambda_g}$$

(7-6)

The derived optical bandgap for both materials was plotted in Figure 7-16. The bandgap of ZnO$_x$S$_{1-x}$ thin film shows linear relation with the sulfur composition. The bandgap of the films using only H$_2$O or H$_2$S as oxidizer was measured as 3.20 and 3.62 eV, respectively. This value is similar to that reported in the literature (3.18 and 3.62 eV for ZnO and ZnS, respectively) [227, 228]. The minimum bandgap can be observed on the film with 1:1 H$_2$O/H$_2$S pulse ratio, corresponding to 0.03 sulfur composition in the film and further increasing the sulfur composition leads to the rise of the bandgap of the film. This trend was also reported in several previous studies [25, 26, 229].

The most important feature of ZnO$_x$S$_{1-x}$ thin film is its tunable properties and by adjusting the S composition in the film, the film bandgap can be adjusted between 2.95 and 3.62 eV. The bandgap can be affected by the lattice structure of the film, the sulfur composition in film as well as the (OH) group residue [25]. However, based on the film composition analysis, no O-H bound was observed. Therefore, the crystallinity and S
composition are the two main reasons varying the bandgap. With small \( \text{H}_2\text{O} \) or \( \text{H}_2\text{S} \) fraction, the crystallite size remains between 30-50 nm but the film turns into amorphous when 1/1 \( \text{H}_2\text{O}/\text{H}_2\text{S} \) pulse ratio was used and the bandgap reaches minimum. Therefore, it is highly possible that for multicrystalline film, \( S \) composition is the main reason leads to the variation of the bandgap and the phase change from multicrystalline to amorphous may further decrease the bandgap.

**ZnO\(_x\)S\(_{1-x}\) Thin Film on CIGS with Stainless Steel Substrate**

Although the mixed ZnO\(_x\)S\(_{1-x}\) film was successfully deposited on Si substrate, the deposition of ZnO\(_x\)S\(_{1-x}\) film on CIGS does not show complete surface coverage and good conformity. As example, Figure 7-17 shows multiple particles with 30 to 50 nm diameter attached on the CIGS surface rather than complete film coverage as was the case when depositing on Si. According to the XPS spectrum shown in Figure 7-18, Zn, O and S are not the only elements detected on the surface. Other elements from underneath layer, such as Cu and In were detected as well. This indicates the incomplete coverage of the ZnO\(_x\)S\(_{1-x}\) film. Of course the surface structure and termination of the substrate influences the ALD window. Also, the thickness uniformity of the film decreases with the increasing of S concentration of the film. The non-uniform thickness pattern suggests that contact resistance between the heater and substrate was not uniform. The samples were provided by GSE and the CIGS was thus grown on a SS substrate. This suggests that a surface temperature difference variation was induced by the poor thermal contact between the heater and the stainless steel substrate as a result of a slight convex curvature. It is further noted that films grown on rigid Si substrates were uniform in thickness across the substrate.
According to the ALD window of ZnO and ZnS film shown in Figure 7-3, when the temperature is lower than the ALD region, the ZnO growth rate decreases and the ZnS deposition rate increases rapidly. The CIGS sample is based on ~0.5 mm thin stainless steel sheet which is flexible. The slight curvature in the sample thus leads to the variable thermal contact between the CIGS sample and the heater under vacuum. Thus a temperature gradient forms from the center to the two sides of the sample, causing poor uniformity of ZnO$_x$S$_{1-x}$ film.

To better initiate the first layer of reaction at the sample surface, the sample was first washed with warm acetone to remove any organic contamination on the surface and then was dipped into hot water maintained at 85 °C for 5 minutes to remove the sodium salts and other soluble contaminations on the CIGS surface. To establish a more uniform temperature profile the substrate heater assembly was modify by inserting a magnetic plate (1/16 inch thickness Neodymium) between the heater surface and the SS substrate of the GSE bare CIGS sample, as schematically shown in Figure 7-19. As shown in Figure 7-20, after the pretreatment, the deposited ZnO$_x$S$_{1-x}$ film shows good coverage and uniformity on CIGS substrate and the absence of the Cu, In peaks in the XPS spectrum (Figure 7-21) confirms the good coverage.

**Complete Cell Performance**

To make complete cell, a layer of ZnO:Al was sputtered on top of the buffer layer using ZnO target containing 1% Al doping. The oxygen flow rate during the sputtering was controlled at 3 sccm in order to control the oxygen vacancy in the TCO to achieve good conductivity. The total sputtered time was controlled at 25 minus and the thickness of TCO layer was measured as 239.5 nm. Finally, a layer of Al/Ni metal contact grip was
deposited on the top of TCO layer using E-beam evaporation. And for all samples, the buffer layer was controlled around 50 nm.

The J-V curve of complete cells shown in Figure 7-22 was measured under AM 1.5 one sun condition using solar simulator. Table 7-1 shows the detailed parameters of the measured curve. The buffer layer of the reference cell was CdS deposited using Chemical Bath Deposition (CBD). The TCO and metal contact grid of the reference cell were deposited using the same methods as the cell with ZnO$_x$S$_{1-x}$ buffer layer.

As shown in Figure 7-23, at H$_2$S-pulse-rich side, the cell using pure ZnS thin film as buffer layer does not show any efficiency and the highest efficiency, 11.58%, was achieved with 0.91 H$_2$S pulse fraction. The efficiency then decreases with increasing S concentration, reaching 0% at 0.5 H$_2$S pulse fraction. At the H$_2$O-pulse-rich side, the highest efficiency was measured as 8.5% with 0.25 H$_2$S pulse fraction. The efficiency of the cells with H$_2$O-pulse-rich buffer layer does not show significant degradation with the decreasing H$_2$S pulse fraction. On the H$_2$O-pulse-rich side, the increasing efficacy can be attribute to the increasing of $V_{OC}$ since the $J_{SC}$ of the cells does not show large variation. The relatively higher $V_{OC}$ may also lead to better Fill Factor since the higher $V_{OC}$ can decrease the ration of rounded area in the J-V curve. Furthermore, from the QE results shown in Figure 7-24A, the cells with 3:1 H$_2$O:H$_2$S pulse fraction buffer shows higher response by 10% than other cells between 700-1000 nm. For the samples with H2S-pulse-rich buffer layer, significant decreasing in $J_{SC}$ down to less than 1 mA/cm$^2$ with the decreasing H$_2$S pulse fraction is observed, which contributes to the large part of the efficiency loss. According to the QE measurement shown in Figure 7-24B, the excessive sulfur composition lead to the decrease over the entire spectrum, especially
between 400 -1000 nm. The reduction in QE between 350-400 nm is relatively smaller. Compared to the cell using CdS as buffer layer, the cell using ZnO$_x$S$_{1-x}$ thin film is 1.62% lower in efficiency. A lower fill factor is primarily responsible for the reduced performance. Beside the aging of the absorber during the sample transportation and treatment, the parasitic resistances induced by recombination at the absorber/buffer layer interface or the conduction bandgap offset may also lowering the efficiency.

A serious of complete cells using ZnO$_x$S$_{1-x}$ buffer layer deposited with different number of supercycles was fabricated in order to find out the optimum buffer layer thickness. The H$_2$O/H$_2$S pulse ratio was controlled at 3/1. The highest efficiency 8.44% was measured on the cells deposited using 39 supercycles and the efficiency decreasing with the increasing number of supercycles. The J-V curve and the detailed parameters are shown in Figure 7-25 and Table 7-2. As shown in Table 7-2, the increase of buffer layer thickness does not affect J$_{SC}$ and fill factor significantly but shows negative effect on the V$_{OC}$. 17% reduction in V$_{OC}$ from 0.47 V to 0.37 V was observed when the number of supercycles increased from 39 to 91. The transmission of the buffer layer deposited using 4 difference number of supercycles is plot in Figure 7-26A and the thickness is shown in Figure 7-26B. According to the results, the thickness of ZnO$_x$S$_{1-x}$ generally shows linear relation with the total number of supercycles, which is a good indication of ALD growth mode.

The cut off edge of the transmission curve does not change with the number of supercycle which means the optical bandgap of the thin film does not change with its thickness and the sulfur composition in the film is consistent as long as the H$_2$O/H$_2$S pulse ratio is fixed. Compared to the film using 39 supercycles (253 cycles), the
transmission of the film deposited with 91 super cycles (396 cycles) shows more than 10% reduction between 500-800 nm. The reduced transmission suggests less photon reach the absorber, which leads to the decrease of electron-hole pair generation and open circuit voltage.

**Summary**

In this study, ZnO$_x$S$_{1-x}$ thin film was prepared using spercycles atomic layer deposition. The S composition shows strong negative deviation from the H$_2$O/H$_2$S pulse ratio, indicating strong exchange reaction of O for S. The H$_2$O/H$_2$S pulse ratio shows strong effect on the morphology and the structure of the thin film. Elongated and round shape grains were observed for H$_2$O-pulse-rich and H$_2$S-pulse-rich film. Both film structure and S composition affect the bandgap properties of the thin film and a bowl shaped relation was mapped out between the bandgap and sulfur composition.

Maximum complete cell efficiency 11.58% was measured with the cell using ZnO$_x$S$_{1-x}$ thin film with 1/10 H$_2$O/H$_2$S pulse ratio. Compared to the cell using CdS, the relatively lower fill factor is primarily responsible for the reduced performance, which may be caused by parasitic resistances induced by recombination at the absorber/buffer layer interface or the conduction bandgap offset. Reducing the buffer layer thickness to 30 nm can further increase the cell efficiency due to the increasing transmission between 500-800 nm.
Table 7-1. Parameter table from J-V curves of devices using buffer layer prepared with various H₂S pulse fraction.

<table>
<thead>
<tr>
<th>H₂S Pulse Fraction</th>
<th>J_sc (mA/cm²)</th>
<th>V_oc (V)</th>
<th>Fill Factor</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>33.097</td>
<td>0.38</td>
<td>49.55</td>
<td>6.24</td>
</tr>
<tr>
<td>0.16667</td>
<td>30.313</td>
<td>0.44</td>
<td>52.91</td>
<td>7.19</td>
</tr>
<tr>
<td>0.25</td>
<td>33.69</td>
<td>0.46</td>
<td>54.67</td>
<td>8.502</td>
</tr>
<tr>
<td>0.5</td>
<td>0.955</td>
<td>0.19</td>
<td>17.11</td>
<td>0.031</td>
</tr>
<tr>
<td>0.75</td>
<td>17.107</td>
<td>0.4698</td>
<td>17.33</td>
<td>1.392</td>
</tr>
<tr>
<td>0.90909</td>
<td>29.36</td>
<td>0.618</td>
<td>63.77</td>
<td>11.58</td>
</tr>
<tr>
<td>0.96774</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 7-2. Parameter table from J-V curves of devices using buffer layer prepared with H₂O/H₂S pulse ratio 3/1.

<table>
<thead>
<tr>
<th>Number of Supercycles</th>
<th>V_oc (V)</th>
<th>J_sc (mA/cm²)</th>
<th>Fill Factor</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>39</td>
<td>0.47149</td>
<td>30.12793</td>
<td>0.594183</td>
<td>8.440376</td>
</tr>
<tr>
<td>69</td>
<td>0.3885667</td>
<td>29.4593</td>
<td>0.617987</td>
<td>7.074036</td>
</tr>
<tr>
<td>78</td>
<td>0.38737</td>
<td>29.17231</td>
<td>0.623583</td>
<td>7.046789</td>
</tr>
<tr>
<td>91</td>
<td>0.37267</td>
<td>28.88534</td>
<td>0.603384</td>
<td>6.495252</td>
</tr>
</tbody>
</table>
Figure 7-1. Schematic setup of ALD system design.
Figure 7-2. 3d-view schematic of the newly designed quartz substrate carrier.
Figure 7-3. ALD window for ZnO and ZnS deposition.
Figure 7-4. XPS spectrum of ZnO and ZnS thin film without doping process.
Figure 7-5. XPS spectra for film with different cycle ratio of ZnS to ZnO. The value of ZnS:ZnO was set at 9:1 (black), 7:1 (red), 5:1 (blue), 3:1 (pink) and 1:1 (green). Note that film deposition began with ZnO.
Figure 7-6. Sulfur concentration on the Group VI sublattice vs. pulse ratio.
Figure 7-7. Multiplex Scan on ZnO$_x$S$_{1-x}$ thin film for O 1s, Zn 2p$^{3/2}$ and S 2p peaks.
Figure 7-8. AFM image of ZnO thin film surface deposited with various DEZn and H$_2$O pulse time. A) DEZn 0.1 s H$_2$O 0.08 s. B) DEZn 0.5 s H$_2$O 0.1 s. C) DEZn 0.8 s H$_2$O 0.5 s. D) DEZn 1.3 s H$_2$O 1 s. E) DEZn 1.5 s H$_2$O 1.8 s. F) DEZn 2 s H$_2$O 3 s.
Figure 7-9. Surface roughness of ZnO thin film vs. DEZn and H₂O pulse time.
Figure 7-10. SEM surface of H$_2$S-pulse-rich ZnO$_x$S$_{1-x}$ samples. H$_2$O/H$_2$S Pulse Ratio: A) 0:1. B) 1:5. C) 1:1.
Figure 7-11. SEM surface of H$_2$O-pulse-rich ZnO$_x$S$_{1-x}$ samples. H$_2$O/H$_2$S Pulse Ratio: A) 1:0 B) 30:1 C) 15:1.
Figure 7-12. XRD spectrum of ZnO$_{x}$S$_{1-x}$ thin film with various H$_2$O/H$_2$S pulse ratios.
Figure 7-13. Crystallite size extracted from XRD FHMW of ZnO$_x$S$_{1-x}$ thin film deposited with various H$_2$O pulse fraction.
Figure 7-14. Transmission of $\text{ZnO}_x\text{S}_{1-x}$ with various $\text{H}_2\text{O}$ pulse fraction.
Figure 7-15. Square of absorption over wavelength of ZnO$_x$S$_{1-x}$ thin film.
Figure 7-16. Bandgap of $\text{ZnO}_x\text{S}_{1-x}$ thin film with various sulfur composition.
Figure 7-17. H$_2$O-pulse-rich ZnO$_x$S$_{1-x}$ thin film on CIGS substrate without pretreatment.

Figure 7-18. XPS spectrum of ZnO$_x$S$_{1-x}$ thin film on CIGS substrate without any treatment.
Figure 7-19. Modified heater assembly showing the insertion of a magnetic plate between the heater surface and CIGS/Mo/SS GSE sample for the ALD reactor chamber.

Figure 7-20. Cross section of CIGS sample with ZnO$_x$S$_{1-x}$ buffer layer deposited using ALD.
Figure 7-21. XPS spectrum of CIGS substrate with ZnO$_x$S$_{1-x}$ buffer layer deposited using ALD.

Figure 7-22. Curve of complete cells using buffer layer of various sulfur concentration.
Figure 7-23. Change of complete CIGS solar cell performance with buffer layer deposited using various H$_2$S pulse ratio. A) Short circuit current density. B) Open circuit voltage. C) Fill factor. D) Efficiency. Red line refers to the value of CIGS reference cell using CdS as buffer layer.
Figure 7-24. QE of complete cell deposited with various H$_2$S pulse fraction.
Figure 7-25. Curve of complete cells using ZnO$_x$S$_{1-x}$ buffer layer with various thickness.
Figure 7-26. Transmission and thickness of ZnO$_x$S$_{1-x}$ thin film using H$_2$O/H$_2$S pulse ratio 3:1 deposited with different number of cycles. A) Transmission. B) Thickness.
CHAPTER 8
ATOMIC LAYER DEPOSITION OF IN-DOPED ZNO THIN FILM

Literature Review

Al-doped ZnO has been the primary TCO used in CIGS thin film-devices [230], although it has been suggested that Ga-doped ZnO has potential advantages [41]. Identifying the optimal tradeoff between transparency and conductivity as well as preventing pin-hole formation are generally accomplished by detailed experiment. ALD has the potential to achieve controlled substitutional dopant incorporation, improve crystallinity, and yield excellent coverage. There has also been interest in developing a Cd-free device and thus a buffer layer based on ZnO has the possibility of replacing the n-CdS buffer layer as well as providing the TCO using a single deposition process. Given the presence of In in the CIGS absorber, the influence of In on the buffer layer is also of interest. Unfortunately, growth of ZnO:In has received little attention and only one report by ALD, which was at a temperature too high for CIGS processing [61]. There has also been considerable interest in developing a variable bandgap buffer layer to better align the band edges to CIGS (e.g. addition of more Ga, Ag, and S). $\text{ZnO}_{1-x}\text{S}_x$ (ZnOS) is a candidate buffer layer material since its electrical and optical properties are tunable. It is critical in depositing both ZnOS and ZnO:In to precisely control the O/S and Zn/In atomic ratio in the film. Atomic layer deposition typically provides precise and effective doping levels as well as vertical placement of the ionized dopants since residence time during deposition can be varied during the deposition of each layer.

In this study, ZnOS and ZnO:In thin films were deposited using ALD with diethylzinc (DEZn), trimethylindium (TMIn), $\text{H}_2\text{S}$ and $\text{H}_2\text{O}$ as precursors. The ALD windows for deposition of ZnO and ZnS thin films were determined and the
microstructural properties of ZnO:In thin film were examined. In addition 2 cells were fabricated by depositing ZnO:Al or ZnO:In using sputtering and continuous super cycle ALD, respectively, on a stacked layer of ZnOS/CIGS/Mo/S.S. to analyze the complete cell performance.

**Experimental Procedures**

In-doped ZnO thin film were deposited on Si (100), Borosilicate Glass and CIGS sample terminated with CdS or ZnOS buffer layer. The CIGS sample terminated with CdS buffer layer were prepared using Co-evaporation and Chemical Bath Deposition method by Global Solar Energy. The CIGS substrate structure were shown in Figure 8-1. Before deposition, all substrates were first cleaned using Electronic Grade trichloroethylene, acetone and methanol. The Si (100) substrate were finally etched with BOE. CIGS substrate and borosilicate glass were rinsed in warm de-ionized water for 4 minutes. All substrates were dried with N₂ before placed in to the reaction chamber.

During the deposition, DEZn, TMIn and water were used as precursors. The film deposition temperatures were set at 150 °C and 200 °C to test the properties of the film deposited under different temperature. The reactant sequence for depositing ZnO:In film was set as (DEZn-purge-H₂O-purge)_x (TMIn-purge-H₂O-purge)_y, where x and y are number of times each Zn-O and In-O cycle are respectively executed. The value of x and y depends on the desired In-doping level in the ZnO:In film. The deposition parameters were optimized in order to keep the deposition as ALD mode. The background pressure was 0.171 Torr and was kept at 0.4 Torr during film growth.

The film thickness was measured suing Filmetrics F20 thin film analyzer. The Zn/In ratio in the bulk films were determined with ICP/AES - Perkin-Elmer Optima 3200 RL. The bounding status of each element were measures with Perkin Elmer 5100 XPS.
System using Mg X-ray source. XRD were performed on samples with 200 nm thickness using Panalytical Xpert Powder system. Shimadzu UV-2401PC spectrophotometer was used for absorption spectroscopy in the wavelength range of 350 nm to 800 nm. The sheet resistance, electron concentration (n) and mobility (μ) were determined by Hall measurements under a magnetic field of 10 kG with Lakeshore 7507. The surface metrology was measured using SPM/AFM Dimension 3100 and FEI Nova NanoSEM 430.

**Experiment Results and Discussion**

**Film Composition**

XPS scan was performed on ZnO:In thin film deposited using \((\text{DEZn-purge-H}_2\text{O-purge})_{40}+(\text{TMIn-purge-H}_2\text{O-purge})_1\) supercycle sequence at 200 °C. The chamber pressure was kept at ~10^{-9} Torr and the detection range was set between 1100 eV to 0 eV. The results of XPS measurement were shown in Figure 8-2.

The carbon 1s peak on the spectrum of the sample surface was due to the contamination such as organics and carbon dioxide from the ambient air. After five-minutes sputtering using Ar^+, no carbon peak was found within the detection limit of XPS (1%), which indicates that all precursors reacted with the oxidizer completely during the deposition. Furthermore, the decomposition of the precursor at the substrate were not observed. The In atomic percentage were analyzed using the following equation:

\[ I_i = N_i \sigma_i \lambda_i K \]  \hspace{1cm} (8-1)

where \(I_i\) is the intensity of the photoelectron peak for a certain element, \(N_i\) is the average atomic concentration of the element in the surface under analysis, \(\sigma_i\) is Scofield factor
and K is the all other factors related to quantitative detection of a signal. The calculation was performed using AugerScan Version 3.22 and the results were plotted in Figure 8-3A.

According to the result, the measured In atomic percent in the film increases with the Ar⁺ sputtering time gradually from 0.6% to 1.6%. One reason is that the DEZn and TMIn were introduced into the reactor separately. Therefore, the deposited film will have a layered structure, which was referred as δ-type doping [231]. In this experiment, the deposition sequence ends with (TMIn-purge-H₂O-purge) cycle and after 5 mins sputtering, the In at top surface were thus removed. Generally, the XPS detection depth limit is between 3-10 nm and 40 cycles of DEZn-purge-H₂O-purge deposition created ZnO layer with 8.8 nm thickness. Therefore, very limited electrons from In atoms can escape the surface of the film. However, with the long sputtering time, the thickness of ZnO top layer decreases, which leads to the stronger signal from the In atoms beneath the ZnO layer. The increasing detected In composition with the sputtering time confirms that the deposited film has a layered structure and therefore, it is necessary to perform other bulk measurement method such as ICP-AES.

In order measure the In/Zn ratio of the film, the samples were fully digested in 5% Nitric Acid for ICP-AES measurement and the measured In atomic composition in the film vs. TMIn pulse fraction was plotted in Figure 8-3B. According to the result, the measured In composition shows 1:1 linear correlation to the TMIn pulse fraction within 0-0.4 TMIn pulse fraction range, which indicates that the deposition was controlled within ALD mode during the film growth. One important feature of ALD is “self-limiting”
behavior and during the deposition, each cycle will deposit one monolayer film on to the substrate. Therefore, the In/Zn ratio in the film is close to the TMIn pulse fraction.

Multiplex XPS scan was performed within 421-428 eV, 527-534 eV and 1021 to 2016 eV range, in order to exam the atom binding status of In, Zn and O atoms. The samples were prepared using DEZn:TMIn=5:1 recipe, in order to increase the signal-noise ratio of In peak. The step size was set as 0.125 eV. The spectrum were aligned using the standard carbon peak at 284.6 eV and were shown in Figure 8-4. It is noted that the Zn, O and In peaks are located at 1022.16 eV, 529.97 eV and 444.71 eV, respectively. The O 1s peak can be spilt into two peaks, located at 529.97 eV and 531.47 eV, standing for Zn-O and In-O bound respectively. All these measured binding energy value matches the binding energy value for Zn-O and In-O in XPS binding energy database, which indicates all the Zn and In atoms are bounded to O in the film. According to the results of quantitative analysis for O peak. The ratio of Zn-O bound to In-O bound is around 4, which is 20% deviation from the cycle ratio 5:1. However, as stated above, the quantitative results from XPS can be inaccurate due to the layered structure of the film and low detection depth of XPS.

**Structural Properties**

The XRD patterns of pure ZnO thin film and In-doped (ZnO:In) on borosilicate glass are shown in Figure 8-5. All samples exhibit three obvious peaks at 31.87°, 36.35° and 53.82° which correspond to reflections from the ZnO (100), (101) and (110) planes. A relatively small peak can be seen at 34.56°, corresponding to the ZnO (002) plane. As the In-doping level increases, the relative intensity of the 36.35°-centered peak increases, while that of the one at 31.87° decreases slowly. This indicates the preferred plane of ZnO:In film changes with the incorporation of In into the ZnO thin film. The XRD
spectra indicates that the In and ZnO mix homogeneously on the Wurtzite lattice and no evidence of In$_2$O$_3$ formation.

The d-spacing value for two major peaks of ZnO (100) and (101) was extracted from the peak position using Bragg's law and plotted in Figure 8-6. The d-spacing for plane (100) increases from 2.805 to 2.818 Å and for (101) the d-spacing value also increases from 2.465 Å to 2.480 Å. The results suggests the lattice parameter of ZnO:In thin film expands for both a and c-axis. This can be explained by the larger In$^{3+}$ ionic radius (0.94 Å) compared to Zn$^{2+}$ (0.74 Å).

For hexagonal crystals, the linear stress components can be calculated using

$$\begin{pmatrix}
\sigma_x \\
\sigma_y \\
\sigma_z
\end{pmatrix} =
\begin{pmatrix}
C_{11} & C_{12} & C_{13} \\
C_{12} & C_{11} & C_{13} \\
C_{13} & C_{13} & C_{33}
\end{pmatrix}
\begin{pmatrix}
e_{xx} \\
e_{yy} \\
e_{zz}
\end{pmatrix}
$$

(8-2)

where $C_{ij}$ are the elastic stiffness constants and $e_{ij}$ is the linear strain in the $i$th direction.

Based on (2), Maniv et al. [233] derived the biaxial strain model as

$$\sigma = \left[ \frac{2C_{13} - C_{33}(C_{11} + C_{12})}{C_{13}} \right] \left( \frac{c - c_0}{c_0} \right)$$

(8-3)

where $c$ is the measured lattice constant and $c_0$ is the lattice constant for pure ZnO, which is 2.80739 Å [ICOD 01-079-0205]. By plug in the values of the stiffness constant for ZnO, $C_{11}$=$C_{33}$=2.1E11 N/m$^2$, $C_{12}$=1.2E11 N/m$^2$, $C_{13}$=1.05E11 N/m$^2$ [233], the equation becomes,

$$\sigma = 4.5 \times 10^{11} \frac{c_0 - c}{c_0}$$

(8-4)
The stress calculated using the biaxial strain model was plotted vs. the TMIn pulse fraction in Figure 8-7A. The undoped ZnO film shows maximum stress, which is mainly due to the lattice mismatch between the substrate and thin film as well as that produced upon cooling. With increasing TMIn pulse fraction, the stress value decreases significantly and reaches a plateau when the TMIn pulse fraction exceeds 0.1. This exponential correlation can be explained by the incorporation of the In$^{3+}$ ions, which occupy the substitutional sites in the hexagonal Wurtzite ZnO lattice. The negative value of the stress indicates the compressive stress type, which can be explained by the lattice expansion due to the relatively larger radius of In$^{3+}$ ion. Singh et al. [40] reported similar results for 1% In-doped ZnO:In sputtered at 700 °C.

The crystallite size was estimated using Scherrer's equation. As shown in Figure 8-7B, the crystallite size increases significantly when the (100) peak shifts from 31.7222° to 31.7452°, corresponding to TMIn pulse fraction of 0.16 and 0.05, respectively. However, the crystallite size remains at the same level for peak position 31.8977° and 31.7425°, corresponding to TMIn pulse fraction of 0 and 0.05, respectively. The decreasing of the crystallite size was caused by the relaxation of the film stress when the TMIn pulse fraction exceeds 0.01.

**Morphological Properties**

The morphology of ZnO:In thin film with various In-doping level was examined using SEM as shown in Figure 8-8A and Figure 8-8B corresponding to DEZn/TMIn ratio 90/1 and 5/1, respectively. The ZnO:In thin film with low In-doping level shows elongated pyramidal grain around 52 nm on the surface, which corresponds to the hexagonal structure of ZnO, while the sample with high doping level shows round grain shape with size more than 200 nm and on the grain surface there are small nucleation
site with 10 nm size. The results confirm the structural and crystallite size information obtained from XRD spectra. According to the crystallite size calculated with XRD spectrum, the grains in low In-doping level ZnO tend to be single crystalline and as the increasing of In-doping level, the grains convert into multi crystalline.

2 μm×2 μm AFM images of ZnO:In with various In-doping level was shown in Figure 8-9 and the change of surface roughness was plotted with TMIn pulse fraction in Figure 8-10. According to the measurement, the roughness of pure ZnO sample was 3.5 nm and increases to 38.3 nm when TMIn pulse fraction reaches 0.33. The roughness shows linear correlation with TMIn pulse fraction with slop of 9.98 nm/0.1 TMIn pulse fraction. According to the SEM and AFM image, the film growth after the deposition of the initiation layer follows Volmer–Weber mode due to the existence of the small nucleation island observed on the surface. Although Baji et al. [234] reported that undoped ZnO thin film shows Volmer–Weber growth mode with Si (100) substrate throughout the film deposition process, the growth mode for the initial layer of ZnO:In remains unclear and need to be further characterized.

**Electrical Properties**

The electrical properties of ZnO:In films at various In-doping levels is displayed in Figure 8-11. These data are consistent with n-type ZnO:In. The minimum resistivity (ρ) value is measured as $1.65 \times 10^{-3}$ Ω·cm when DEZn/TMIn pulse ratio was controlled at 10/1. Further changing the ratio to 5/1 significantly increases the resistivity. When the ratio decreases to less than 60/1, the sample resistivity is constant at $\sim3 \times 10^{-3}$ Ω·cm. The bulk carrier concentration (n) of the sample shows monotonic correlation with the In-doping level and increases significantly when the DEZn/TMIn pulse ratio is less than 30/1, while the carrier mobility (μ) decreases with increasing In-doping level.
Although the incorporation of In leads to the surge of the carrier concentration as shown in Figure 8-11, the substitutional In atoms also provide extra stress to the film, resulting in smaller grains, which can lower carrier mobility due to the grain boundary scattering. In the case of 10/1 DEZn/TMIn pulse ratio, the lower carrier mobility is compensated by higher carrier concentration, leading to the optimum sheet resistance among all samples. Besides the grain boundary scattering, the electron-electron scattering and ionized impurity scattering can also be the reasons for the low carrier mobility, especially for high doping level condition. The significance of these scattering mechanism will be tested with temperature dependent Hall measurement in the future work.

The detailed electrical parameters of ZnO:In using ALD and one of the typical TCO material ZnO:Al using sputtering are listed in Table 8-1. Compared to the ZnO:In, ZnO:Al shows smaller resistivity by one magnitude. The main drawback of ZnO:In thin film is the low carrier mobility. Besides the reason mentioned above, the different deposition technique may place a significant effect on the film properties.

**Complete Cell Performance**

The J-V curve for two completed cells with sputtered ZnO:Al and ZnO:In using ALD were measured. The results are shown in Figure 8-12 and the detailed parameters are listed in Table 8-2. The cell using ZnO:Al as TCO outperforms that with ZnO:In thin film by 4.1%. These two cells show similar open circuit voltage at 0.55 mV but the sample with In-doped ZnO shows lower short circuit current and larger series resistance, leading to relatively lower Fill Factor.

This is largely attributed to the lower mobility (1.68 cm²/Vs) of ALD In-ZnO compared with Al-doped ZnO film (9.82 cm²/Vs). Furthermore, the high carrier
concentration in the ZnO:In thin film may lead to lower transmission due to the plasma oscillation effect of the bulk free electrons. The reduced number of photon reaching the absorber leads to the reduction of electron-hole pair generation and thus shows negative effect on the \( J_{SC} \).

**Summary**

ZnOS and ZnO:In films were prepared using ALD and the ALD deposition windows for ZnOS and ZnO:In were determined. Importantly, no secondary \( \text{In}_2\text{O}_3 \) phase was observed. The minimum resistivity was measured as \( 1.65\times10^{-3} \, \Omega\cdot\text{cm} \) with the main drawback is the low carrier mobility attributed to grain boundary scattering. The completed cells using ZnO:In as TCO show relatively low open circuit current density and high series resistance compared with the cell using sputtered ZnO:Al thin film as TCO.
### Table 8-1. Electrical Properties of ZnO:In (ALD) and ZnO:Al (Sputtering)

<table>
<thead>
<tr>
<th></th>
<th>( \rho ) (ohm·cm)</th>
<th>( n ) (cm(^3))</th>
<th>( \mu ) (cm(^2)/V·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO:Al (sputter)</td>
<td>5.0E-4</td>
<td>1.15E+21</td>
<td>9.82</td>
</tr>
<tr>
<td>ZnO:In (ALD)</td>
<td>1.8E-3</td>
<td>1.95E+21</td>
<td>1.68</td>
</tr>
</tbody>
</table>

### Table 8-2. Properties of Complete Solar Cells.

<table>
<thead>
<tr>
<th>TCO Material</th>
<th>( V_{OC} ) (V)</th>
<th>( J_{SC} ) (mA/cm(^2))</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO:In</td>
<td>0.56</td>
<td>19.63</td>
<td>0.59</td>
<td>6.51579</td>
</tr>
<tr>
<td>ZnO:Al</td>
<td>0.55</td>
<td>29.69</td>
<td>0.65</td>
<td>10.6786</td>
</tr>
</tbody>
</table>
Figure 8-1. The layer structure of CIGS substrate prepared by Global Solar Energy. ZnOS buffer layer were prepared using ALD at UF.

Figure 8-2. XPS spectrum of ZnO:In thin film on Si sputtered with Ar⁺ for various time length.
Figure 8-3. In composition measured with different technique. A) XPS. B) ICP-AES.

Figure 8-4. XPS peak positions of the elements in ZnO:In (pulse ratio Zn:In 5:1) thin film. A) In. B) O. C) Zn.
Figure 8-5. XRD spectra of pure ZnO and ZnO:In with different In levels. The black bars indicate the expected peak position for In$_2$O$_3$.

Figure 8-6. The change of d-spacing of ZnO 100 and 101 direction with increasing In-doping level.
Figure 8-7. Estimated stress and crystallite size of In-doped ZnO film vs. TMIn pulse fraction.

Figure 8-8. Surface SEM image of ZnO:In with different In doping level.
Figure 8-9. 2 μm×2 μm AFM images of ZnO:In thin films on Si (100) substrate with different In-doping Level. DEZn/TMIn ratio: A) Pure ZnO. B) 40. C) 2.
Figure 8-10. The roughness surface evolution with the In-doping level of ZnO:In films as measured on 2 μm×2 μm AFM images.

Figure 8-11. Hall measurements results for ZnO:In thin film.
Figure 8-12. J-V curve for two completed cells.
CHAPTER 9
COMPARISON STUDY OF ZNO:IN AND ZNO:GA THIN FILM FOR PV USING ATOMIC LAYER DEPOSITION

Literature Review

CIGS thin film solar cell has demonstrated high efficiency over 22.3% [107]. The properties of transparent conducting oxides (TCO) can affect the performance of the solar cell because it not only conducts the photocurrent generated from the underlying cell but also, in the meantime, transmits the photon to the absorber layer. Therefore, good transmission and low resistivity are two favorable properties of TCO for photovoltaic application. Stadler et al. [28] did a comprehensive review on various TCO materials including ITO, ZnO:Al etc. These n-type TCOs are important for thin film solar cell production and have been extensively studied [29-33].

Among all these TCO materials, ZnO based material has drawn a lot of attention for PV application due to its wide bandgap of 3.3 eV [34]. Compared with Al-doped ZnO, Ga and In can be a better dopant candidates due to the relatively smaller difference between their ion radius and Zn$^{3+}$ ion radius. Both In (ZnO:In) and Ga-doped ZnO (ZnO:Ga) has been studied using various deposition method such as sputtering [35-42], chemical vapor Deposition [43-46], chemical spray [47-49], pulsed laser deposition [50, 51] and sol-gel method [52-54]. Compared to the deposition technique mentioned above, atomic layer deposition (ALD) shows many advantage such as the ability to finely control the doping level and film thickness, typically lower deposition temperature, good film uniformity and conformality. There are several studies about ZnO:Ga using ALD with various Ga precursor, such as trimethylgallium (TMGa) [55], gallium(III) isopropoxide (GTIP) [56] and triethylgallium (TEGa) [57-59]. However, studies on ZnO:In were much less. Hsia et al. and Kim et al. used trimethylindium (TMIn) [60] with N$_2$O and dimethylamino-dimethylindium (DMLDMIn) [61] with H$_2$O for atomic layer
deposition respectively. Although these studies developed the deposition process, the deposition using CIGS/CdS bilayer substrate has never been conducted before. Furthermore, the high deposition temperature (above 300 °C) leads to the degradation of the solar cell [27].

In this study, we deposited ZnO:In and ZnO:Ga by thermal ALD (Th-ALD) using diethylznic (DEZn), TMIn, TEGa and H₂O as precursors and oxidizer. The supercycle deposition recipe was adopted in this study [235]. The properties of the deposited thin film were characterized and compared. Finally, these two TCOs were deposited directly on CIGS/CdS bilayer substrate. The conduction band offset (CBO) at the ZnO:X/CdS interface and the complete cell performance was measured.

**Experimental Procedures**

ZnO:In and ZnO:Ga thin film were deposited on Si (100), Borosilicate Glass and CIGS sample terminated with CdS using supercycle ALD. The CIGS sample terminated with CdS buffer layer were prepared using Co-evaporation and Chemical Bath Deposition method by Global Solar Energy. The CIGS substrate structure were shown in Figure 9-1. Before deposition, all substrates were pre-cleaned with Electronic Grade trichloroethylene, acetone and methanol. The Si (100) substrate were then etched with buffer oxide etch. CIGS substrate and borosilicate glass were rinsed in warm de-ionized water for 4 minutes in order to further remove the surface contaminates. All substrates were dried with N₂ before placed into the reaction chamber.

During the deposition, DEZn, TMIn, TEGa were used as precursors and water was used as oxidizer. The film deposition temperature was set at 200 °C. The reactant sequence for depositing ZnO:In and ZnO:Ga thin film was set as (DEZn-purge-H₂O-purge)x(TMIn(TEGa)-purge-H₂O-purge)y, where x and y are number of times each Zn-
O and In(Ga)-O cycle are respectively executed. The schematic deposition sequence was shown in Figure 9-2. The value of x and y depends on the desired doping level in the TCO film. The deposition parameters were optimized in order to keep the deposition as ALD mode. The background pressure was 0.171 Torr and was kept at 0.4 Torr during film growth.

The resistivity, electron concentration (n) and mobility (μ) were determined by Hall measurements under a magnetic field of 10 kG with Lakeshore 7507. The film thickness was measured using Filmetrics F20 thin film analyzer. XRD were performed on samples with 200 nm thickness using Panalytical XPert Powder system. Shimadzu UV-2401PC spectrophotometer was used for absorption spectroscopy in the wavelength range of 350 nm to 800 nm. The surface metrology was measured using SPM/AFM Dimension 3100 and FEI Nova NanoSEM 430. The bounding status of each element was measured with Perkin Elmer 5100 XPS System using Mg X-ray source.

Results and Discussion

Electrical Properties

The resistivity of ZnO:In and ZnO:Ga is shown in Figure 9-3. Compared with intrinsic ZnO, doping In and Ga can lower the resistivity of ZnO thin film to the order of $1.65 \times 10^{-3} \ \Omega \cdot \text{cm}$. The minimum resistivity for ZnO:In was found at 0.1 TMIn pulse fraction while for ZnO:Ga, the TEGa precursor pulse fraction 0.05 was used to achieve the lowest resistivity. However, the resistivity tends to rise when the pulse ratio was beyond 0.15 for both films. With 0.17 TMIn and TEGa pulse fraction, the resistivity of the thin film increases to $6.6 \times 10^{-3} \ \Omega \cdot \text{cm}$ and $1.8 \times 10^{-2} \ \Omega \cdot \text{cm}$, respectively, which indicates the induce of Ga into Zn site leads to the stronger increase of resistivity than
that of In at high doping level (>0.1 pulse fraction). The resistivity of the thin film is a function of carrier concentration and Hall mobility [236],

$$\rho = \frac{1}{ne\mu}$$

where $\rho$ is resistivity, $n$ is carrier concentration and $\mu$ is Hall mobility. From the inverse relation between resistivity $\rho$ and the product of carrier concentration $n$ and Hall mobility $\mu$, it is easy to come to the conclusion that for the thin film, the optimum sheet resistance can be reached by adjusting the carrier concentration and mobility. These two parameters were measured using Hall Measurement and the results are shown in Figure 9-4.

The bulk carrier concentration of both materials monotonically increases with the doping level. At low doping level, the bulk carrier concentration of materials shows significant increase by one order of magnitude, up to $2.3 \times 10^{20}$ cm$^3$. When the pulse fraction exceeds 0.05, the carrier concentration of ZnO:Ga stabilizes around $6.6 \times 10^{20}$ cm$^3$, while, for ZnO:In thin film, the carrier concentration ascends up to $2.7 \times 10^{21}$ cm$^3$. The change of carrier concentration indicates that both In and Ga dopants act as extrinsic donors and at high doping level, ZnO:In shows higher bulk carrier concentration than ZnO:Ga. Although higher doping level results in higher carrier concentration, the mobility shows monotonically decreasing behavior with the increasing TMIn(TEGa) pulse fraction, from $15 \text{ m}^2/\text{V} \cdot \text{s}$ (intrinsic ZnO) to $1.1 \text{ m}^2/\text{V} \cdot \text{s}$ when the TMIn(TEGa) pulse ratio exceeds 0.15.

Compared to ZnO:Ga, the bulk carrier concentration of ZnO:In reaches $2.3 \times 10^{20}$ cm$^3$ level using relatively small dopant precursor pulse fraction, but In dopant shows stronger negative effect on the carrier mobility than Ga dopant. As a result, it is
necessary to incorporate more In dopant into intrinsic ZnO thin film in order to archive the minimum resistivity.

**Crystalline Structure**

The XRD patterns of intrinsic ZnO thin film and doped ZnO thin film on borosilicate glass are shown in Figure 9-5. The thickness of all films were kept at 200nm in order to get optimum signal to noise ratio. As shown in Figure 9-5, all samples exhibit two obvious peak at ~31.87° and ~36.35°, which are corresponding to the (100) and (101) plane of ZnO. A relatively small peak is shown at 34.56° corresponding to (002) plane.

The intrinsic ZnO shows a strong preferential direction as (100), but as the doping level increasing, both samples displays a change of the preferential plane since the intensity of (101) peak gradually rises. The XRD spectrum of ZnO:Ga with DEZn/TMGa=5 (i.e. 0.17 TEGa pulse fraction) shows strong peak broadening effect and low peak intensity, indicating the deceasing of the crystallinity. Compared with ZnO:Ga, the peak broadening effect is less significant for ZnO:In, which suggests that Ga shows a stronger effect than In in term of the decreasing of the film crystallinity. In order to confirm the results, GIXRD was performed on samples with 0.1 precursor pulse fraction as shown in Figure 9-6. The results suggest both ZnO:In and ZnO:Ga shows hexagonal wurtzite ZnO structure and no peaks related to In2O3 or Ga2O3 was observed.

The lattice parameters were derived using the following equation:

\[
\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}
\]  

(9-2)

where a and c are the lattice parameters and h,k and l are the miller index of the plane.

The d-spacing can be obtained using the Bragg’s Law:
\[ 2d \sin \theta = n\lambda \]  \hspace{1cm} (9-3)

where \( d \) is the interplanar distance, \( \theta \) is the scattering angle, \( n \) is a positive integer and \( \lambda \) is the wavelength of incident wave. The results were plotted in Figure 9-7. The lattice constant of a-axis for ZnO:In increases to 3.252 nm and remains at the constant value with further increasing doping level. However, for the c-axis the lattice constant slightly rises and then monotonically decreasing with the increasing doping level. Different from the ZnO:In thin film, Ga-doping does not show strong effect on the a-axis lattice parameter but causes significant reduction in the lattice constant of c-axis.

The stress induced by the dopant was analyzed. For hexagonal crystals, the linear stress components can be calculated using [232]:

\[
\begin{bmatrix}
\sigma_x \\
\sigma_y \\
\sigma_z
\end{bmatrix} =
\begin{bmatrix}
C_{11} & C_{12} & C_{13} \\
C_{12} & C_{11} & C_{13} \\
C_{13} & C_{13} & C_{33}
\end{bmatrix}
\begin{bmatrix}
e_{xx} \\
e_{xy} \\
e_{xz}
\end{bmatrix}
\]  \hspace{1cm} (9-4)

where \( C_{ij} \) are the elastic stiffness constants and \( e_{ij} \) is the linear strain in the \( i^{th} \) direction.

Based on Equation 9-4, Maniv et al. [233] derived the biaxial strain model as

\[
\sigma = \left[ \frac{2C_{13} - C_{33}(C_{11} + C_{12})}{C_{13}} \right] \left( \frac{c - c_0}{c_0} \right)
\]  \hspace{1cm} (9-5)

where \( c \) is the measured lattice constant and \( c_0 \) is the lattice constant for pure ZnO, which are 2.80739 Å and 2.46903 Å for plane (100) and (101) respectively [ICOD 01-079-0205]. By plug in the values of the stiffness constant for ZnO, \( C_{11}=C_{33}=2.1 \times 10^{11} \text{ N/m}^2 \), \( C_{12}=1.2 \times 10^{11} \text{ N/m}^2 \), \( C_{13}=1.05 \times 10^{11} \text{ N/m}^2 \) [233], the equation becomes,

\[
\sigma = 4.5 \times 10^{11} \frac{c - c_0}{c_0}
\]  \hspace{1cm} (9-6)
The calculated value was plotted with the precursor pulse fraction in Figure 9-8. For the pure ZnO, the film shows maximum stress due to the lattice mismatch between the substrate and thin film as well as the thermal effect. For In-doped samples, significant negative stress value was found for even low TMIn pulse fraction. However, further increase TMIn pulse fraction doesn’t lead to lower stress. The value was stabilized at -1.01 GPa. Different from the In-doped samples, the ZnO:Ga thin film exhibits positive stress around 0.8 GPa. Based on the calculated stress value, the In dopant results in the compressive stress in the ZnO thin film while the incorporation of Ga leads to the tensile stress in the thin film. Compare to the radius of Zn$^{2+}$ ion (0.74 Å), In$^{3+}$ ion has relatively larger radius (0.94 Å) but the radius of Ga$^{3+}$ is smaller (0.62 Å). The difference in the radius between these ions will causes the distortion of the lattice, leading to compression or tensile stress when the dopant ion is larger or smaller than the Zn ion, respectively. Singh et al. [40] reported that using 1% ZnO:In thin film sputtering at 700 °C shows zero stress and then the value of stress turns to negative with increasing In-doping level. However, for ZnO:Ga, both compressive and tensile was reported using various deposition method (e.g. magnetron sputtering, CVD, etc.) [37, 41, 54]. The negative stress is mainly caused by structural defect [37] and Negi et al. reported that annealing ZnO:Ga film can decrease the defect concentration and cause the film stress shift to positive value [54]. The naturally tensile stress of ZnO:Ga may indicates less lattice defect and the Ga$^{3+}$ ions directly occupy Zn$^{2+}$ position in the deposited film.
The crystallite size and lattice strain were analyzed using the (100) peak, which shows maximum intensity in the XRD spectrum. The crystallite size was calculated using Scherrer’s equation,

\[ D_p = \frac{0.94 \lambda}{\beta \cos \theta} \]  

where \( D_p \) is the average crystallite size, \( \beta \) is line broadening in radians, \( \theta \) is Bragg angle and \( \lambda \) is wavelength of Cu Kα. The results are shown in Figure 9-9. The crystallite size of ZnO:In remains at 44 nm until the precursor pulse fraction reaches 0.1 but Ga-doped samples shows small fluctuation around 40 nm. However, when the precursor pulse fraction is over 0.1, the crystallite size of both samples drops significantly, which may due to the increasing of the thin film microstrain caused by the oversaturated dopant.

**Morphological Properties**

The surface morphology of the deposited thin film was studied using AFM and SEM. The SEM and AFM images of the deposited thin film were shown in Figure 9-10 and Figure 9-11, respectively. With 0.02 precursor pulse fraction, both ZnO:In and ZnO:Ga show grains with pyramidal shape which is corresponding to the hexagonal wurtzite ZnO structure revealed by the XRD spectra. However, the grains of ZnO:In show elongated-shape around 43 nm while the grains of ZnO:Ga show relatively more round-shaped with larger size around 236 nm. When the precursor pulse fraction increases to 0.2, the surface morphology changed significantly. On the surface of ZnO:In, the pyramidal shapes of the grains deteriorate to many round shaped islands around 10-20 nm and these islands agglomerate, leading to large particles measured
around 200-350 nm. For ZnO:Ga, similar effect was observed but the size of the particles is around 794 nm.

The coalesce effect leads to higher surface roughness which was confirmed by AFM measurement (Figure 9-12). The roughness of both thin films shows monotonically increasing relation with the increasing doping level. With the same precursor pulse fraction, ZnO:Ga shows higher roughness than ZnO:In and the difference between the roughness of these two thin films increases with the precursor pulse fraction. Compared to undoped ZnO thin film with roughness around 2.2 nm, the roughness of ZnO:In and ZnO:Ga, with 0.16 precursor pulse fraction, rises to 17 and 45 nm, respectively.

According to the analysis of XRD spectrum, both macrostress and microstrain increases with the precursor pulse fraction. Therefore, with high doping level, it is more likely for lattice relaxation to take place, which results in the smaller crystallite site and the sharp hill-and-valley structure throughout the film surface.

For ZnO:In with 0.02 precursor pulse fraction, the observed particles sizes are identical to the results analyzed using XRD, which indicates that for ZnO:In thin film with low doping level, the grains are more likely to be single crystalline. However, as the In concentration increases, the grains tends to become multi-crystalline as the size of observed grains are serval times of the crystallite size derived from XRD measurement. For ZnO:Ga, even at low doping level, the crystallite tends to agglomerate forming large particles.

**Optical Properties**

Transmission of ZnO:In and ZnO:Ga thin film with various doping level was plotted in Figure 9-13. And the adsorption was calculated using
\[ A = 2 - \log_{10}(\%T) \]  

(9-8)

where \( A \) is absorption with arbitrary unit and \( T \) is the transmission. The band gap of the samples was exacted from absorption spectra using Absorption Spectrum Fitting (ASF) method proposed by Ghobadi et al. [225]. The absorption coefficient can be described as a function of wavelength using the equation below,

\[
\alpha(\lambda) = B(hc)^{m-1} \frac{1}{\lambda} \left( \frac{1}{\lambda_g} - \frac{1}{\lambda} \right)^m
\]

(9-9)

where \( \lambda_g, h, \) and \( c \) are wavelengths corresponding to the optical band gap, Planck’s constant, and velocity of light, respectively. \( B \) is constant and \( m \) is the index which can have different values of 1/2, 3/2, 2, and 3 [226]. It has been approved that the best fitting can be achieved for \( m=1/2 \) [225] and using the Beer-Lambert’s law, Equation 9-9 becomes

\[
Abs(\lambda) = B_1 \lambda \left( \frac{1}{\lambda} - \frac{1}{\lambda_g} \right)^m + B_2
\]

(9-10)

Talking \( m=1/2 \), the linear part of \( \left( \frac{Abs(\lambda)}{\lambda} \right)^2 \) vs. ~1/\( \lambda \) was plotted in Figure 9-14. The bandgap was calculated using the data obtained by extrapolating the line to

\[
\left( \frac{Abs(\lambda)}{\lambda} \right)^2 = 0 \text{ and the equation as following:}
\]

\[
E_{gap}^{ASF} = 1239.38 / \lambda_g
\]

(9-11)

The derived optical bandgap for both materials was plot in Figure 9-15. As shown in Figure 9-13, generally speaking, both films show good transmission in the visible region (400-800 nm) and the ZnO:Ga shows relatively higher transmission than the ZnO:In. Both free carrier concentration and the surface roughness can affect the optical
properties [54, 237, 238]. Higher electron density may lower the transmission of the thin film due to the absorption of light via plasma oscillation of the bulk free electrons and higher surface roughness exhibits the same effect due to the optical scattering. Although ZnO:Ga shows higher surface roughness, the optical transmission is still relatively higher than ZnO:In. Considering the free electron density of ZnO:In is one magnitude higher than that of ZnO:Ga thin film, it is reasonable to assume the free carrier concentration other than the roughness of the thin film, plays a significantly role in changing the optical properties.

At room temperature, the bandgap of undoped ZnO is 3.3 eV [239] and it was reported the band gap of β-Ga$_2$O$_3$ and In$_2$O$_3$ was 4.9 eV [240] and 2.93 eV [241], respectively. With the increasing doping level, the blue and red shift effect can be observed on ZnO:Ga and ZnO:In thin film, respectively. The bandgap shifts to 3.55 eV and 3.14 eV for ZnO:Ga and ZnO:In with 0.17 precursor pulse fraction. The change of the bandgap corresponds to the bandgap difference between the oxides of In/Ga and Zn. For ZnO:Ga, the blue shift of the absorption edge can be attribute to the Burstein–Moss effect which means the lowest states of conduction band are occupied by the free careers induced by Ga dopant and thus more energy is required for valance electrons excitation [29, 41, 242]. Different from the effect on bandgap induced by Ga dopant, In dopant cause red shift of the absorption edge. This is because the when the In atoms gets close enough in the film, the wavefunctions of the electrons bound to the impurity atoms start to overlap, forming new recombination centers with lower emission energy [52, 243, 244]. Furthermore, the change of bonding strength due to size difference between the In$^{3+}$/Ga$^{3+}$ ion and Zn$^{2+}$ could also affect the bandgap.
**Cell Performance**

The top contact Ni/Al bilayer grid was deposited using E-beam evaporator. The measured J-V curve was plotted in Figure 9-16 and the detailed parameters are listed in Table 9-1. The cell with ZnO:Ga as TCO layer outperforms that with ZnO:In. The ideal TCO material for solar cell generally shows wide bandgap and low roughness to allow maximum photon transmission, moderate carrier concentration to control the plasma oscillation of the bulk free electrons and high carrier mobility to maintain high conductivity.

According to the results of Hall measurement, ZnO:Ga shows much higher carrier mobility than ZnO:In when the resistivity reaches minimum. The low carrier mobility can be attributed to grain boundary scattering due to small crystallite size, ionized impurity scattering due to higher dopant concentration and electron–electron scattering due to high electron concentration. Both films with minimum resistivity show similar crystallite size around ~40 nm. Thus, the grain boundary density could be similar for both films. However, ZnO:Ga thin film was deposited using less precursor pulse fraction, leading to relatively lower dopant level. Thus, it is concluded that the high carrier concentration of ZnO:In thin film is the major reason for the relatively lower carrier mobility. And the carrier mobility of both films can be further improved by forming larger crystallite size using higher deposition temperature or post annealing method [27, 54, 238, 245, 246].

Although ZnO:In thin film shows relatively lower surface roughness, due to its relatively high carrier concentration, its optical transmission is still around 8% lower than ZnO:Ga thin film in the visible 400-800 nm region [211]. The reduction in transmission may directly decrease the light generated current, leading to the lower open circuit
voltage and short circuit current. Furthermore, the ZnO:In shows high carrier concentration but low mobility while ZnO:Ga shows opposite properties. The high carrier concentration of ZnO:In, may also raise the fermi level and leads to larger CBO at the heterojunction interface [36, 247]. In order to figure out the band alignment at ZnO:X/CdS interface, the valance band offset (VBO) was firstly measured using XPS. The detailed XPS spectra are shown in Figure 9-17. XPS analysis on bulk CdS, ZnO:Ga, ZnO:In and ZnO:Ga (4 nm)/CdS, ZnO:In (4 nm)/CdS bilayer samples. and the detailed values are shown in Table 9-2. XPS binding energy of ZnO:Ga, ZnO:In, CdS and TCOs/CdS interface. The VBO of the ZnO:X/CdS was determined from the energy separation between the core levels in the ZnO:X/CdS sample and the Valance Band Maximum (VBM) to core level separations in the thick layer ZnO:X and CdS samples, as described by

\[ E_{VBO} = E_{ZnO:X/CdS}^{Zn_2p^3} - E_{Cd_3d^3}^{ZnO:X/CdS} - (E_{ZnO:X/VBM}^{Zn_2p^3} - E_{Cd_3d^3}^{ZnO:X/VBM}) + (E_{CdS/VBM}^{CdS} - E_{CdS/VBM}^{CdS}) \]

(9-12)

where \( E_n \) refers to the binding energy of n in sample i. With the bandgap of ZnO:X was extracted from Figure 9-15, the CBO can be calculated using

\[ E_{CBO} = E_{VBO} + E_g^{CdS} - E_g^{ZnO:X} \]

(9-13)

where \( E_g \) is the bandgap of material i. The detailed band diagram was plot in Figure 9-18. The CBO of ZnO:Ga/CdS shows 0.57 eV less than that of ZnO:In due to its relative small VBO and larger bandgap. Considering the CBO of CdS/CIGS is 0.2-0.3 eV, the CBO between ZnO:In and absorber CIGS layer could be larger than 0.4 eV, which may result in the double diode characteristic for the cell, decreasing the \( J_{sc} \) and Fill Factor [248]. The relatively lower FF factor of the cell with ZnO:In thin film can be
attribute to the relatively low open circuit voltage since the resistivity of the ZnO:In and ZnO:Ga thin film are identical, which eliminate the difference caused by parasitic resistance.

**Summary**

In and Ga were doped into ZnO thin film using atomic layer deposition. The comparable minimum resistivity $1.65 \times 10^{-3} \, \Omega \cdot \text{cm}$ was reached using 0.1 and 0.05 precursor pulse fraction for ZnO:In and ZnO:Ga, respectively. For the samples with minimum resistivity, the ZnO:In shows high carrier concentration but low mobility while ZnO:Ga shows high mobility but relatively lower carrier concentration. Based on the characterization using XRD, AFM and SEM, the relatively lower carrier mobility of ZnO:In can be mainly attributed to ionized impurity scattering and electron–electron scattering.

The efficiency of complete cell using ZnO:In and ZnO:Ga as TCO material was measured as 6.03 and 11.51%. The cell with ZnO:Ga shows better open circuit voltage and short circuit current because the ZnO:Ga shows better transmission property and a more favorable conduction band offset at the ZnO:X/CdS interface.
Table 9-1. Parameters of the complete cell performance

<table>
<thead>
<tr>
<th>TCOs</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>FF</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO:In</td>
<td>0.57</td>
<td>18.11</td>
<td>0.58</td>
<td>6.03</td>
</tr>
<tr>
<td>ZnO:Ga</td>
<td>0.63</td>
<td>28.30</td>
<td>0.64</td>
<td>11.51</td>
</tr>
</tbody>
</table>

Table 9-2. XPS binding energy of ZnO:Ga, ZnO:In, CdS and TCOs/CdS interface

<table>
<thead>
<tr>
<th></th>
<th>ZnO:Ga</th>
<th>ZnO:In</th>
<th>CdS</th>
<th>ZnO:In/CdS</th>
<th>ZnO:Ga/CdS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn 2p$^{3/2}$</td>
<td>1022.95</td>
<td>1022.75</td>
<td>-</td>
<td>1022.45</td>
<td>1022.52</td>
</tr>
<tr>
<td>VBM</td>
<td>2.71</td>
<td>2.83</td>
<td>0.75</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cd 3d$^{5/2}$</td>
<td>-</td>
<td>-</td>
<td>405.15</td>
<td>405.45</td>
<td>405.4</td>
</tr>
</tbody>
</table>

Figure 9-1. Schematic diagram of CIGS solar cell.
Figure 9-2. Schematic diagram of atomic layer deposition cycle sequence.

Figure 9-3. Resistivity change with the In or Ga doping level in ZnO thin film.
Figure 9-4. Electrical properties of In(Ga)-doped ZnO thin film with various doping level.
Figure 9-5. XRD spectrum of doped ZnO with different doping level. A) In-doped ZnO. B) Ga-doped ZnO.
Figure 9-6. GIXRD on doped ZnO thin film with 0.1 TMIn(TEGa) pulse fraction. A) In-doped ZnO. B) Ga-doped ZnO.
Figure 9-7. Lattice Parameters change vs. the precursor pulse fraction. A) A-axis. B) C-axis.
Figure 9-8. Stress of In(Ga)-doped ZnO vs. precursor pulse fraction.
Figure 9-9. Crystallite size and Microstrain of In(Ga)-doped ZnO thin film vs. the precursor pulse fraction. The black square indicates the crystallite size and microstrain of Ga-doped ZnO and the blue round indicates In-doped ZnO.
Figure 9-10. SEM images of doped ZnO with different precursor pulse fraction. A) ZnO:In with 0.02 precursor pulse fraction. B) ZnO:In with 0.2 precursor pulse fraction. C) ZnO:Ga with 0.02 precursor pulse fraction. D) ZnO:Ga with 0.2 precursor pulse fraction.
Figure 9-11. AFM images of doped ZnO with different precursor pulse fraction. A) ZnO:In with 0.02 precursor pulse fraction. B) ZnO:In with 0.2 precursor pulse fraction. C) ZnO:Ga with 0.02 precursor pulse fraction. D) ZnO:Ga with 0.2 precursor pulse fraction.

Figure 9-12. Surface roughness of In and Ga-doped ZnO thin film as a function of precursor pulse fraction.
Figure 9-13. Optical transmission spectra of doped ZnO thin film with various precursor pulse fraction. A) In-doped ZnO. B) Ga-doped ZnO.
Figure 9-14. Tauc’s plot of doped ZnO thin film showing the bandgap change with the doping level. A) In-doped ZnO. B) Ga-doped ZnO.
Figure 9-15. Optical bandgap of In and Ga-doped ZnO thin film.
Figure 9-16. J-V curve of complete cells using In and Ga-doped ZnO thin film as TCO.
Figure 9-17. XPS analysis on bulk CdS, ZnO:Ga, ZnO:In and ZnO:Ga (4 nm)/CdS, ZnO:In (4 nm)/CdS bilayer samples.

CBO 0.23 eV

3.52 eV

VBO 1.28 eV

ZnO:Ga

CdS

CBO 0.8 eV

2.47 eV

3.14 eV

VBO 1.47 eV

ZnO:In

CdS

Figure 9-18. Band diagram of ZnO:Ga/CdS and ZnO:In/CdS using 0.05 and 0.1 TEGa and TMIn pulse fraction, respectively.


CHAPTER 10
CONCLUSION

Thermodynamic Assessment of Ag-Cu-In-Ga-Se System

CALPHAD method was used to conduct critical assessment for Ag-Cu-In-Ga-Se system. For Ag-Cu system, new experimental data were collected and used in the assessment. The solubility of Cu in Ag in FCC phase was evaluated based on not only phase equilibrium data but also the activity of Ag and Cu in the solid phase. The incorporation of the thermodynamics data enables the database more physically founded. The Ag-Se thermodynamic database was established in this work for the first time. The homogeneity range of the intermetallic compound and the liquids was well assessed based on available experimental data. This assessed databased will be of high importance for many other Ag-Se related higher order system as may AgSeX (X=Cu, As, S, Al, Ge, etc.) compounds or alloys show practical use in semiconductor or superionic fields. The higher order ternary systems Ag-Cu-Se, Ag-Ga-Se and Ag-In-Se was assessed based on the binary subsystems and the ternary experimental data. A good agreement has been reached between the calculated and experimental data.

The assessed database for Ag-Cu-In-Ga-Se system was used for the prediction of phase relations during the selenization process. It was found that, the existence of Cu in the unselenized alloy can assist the formation of γ (Ag,Cu)$_9$(In,Ga)$_4$ phase, which will react with Se forming α (Ag,Cu)(In,Ga)Se$_2$ phase even at low Se composition. In the meantime, with the present of Cu, GaSe can be avoided at the beginning stage of selenization. However, one thing worth noticing is that the excessive incorporation of Se can happen for sample with Ag to group I meatal ratio at 0.25, forming defect phase.
Therefore, it is of vital importance to control the incorporation of Se during the selenization process.

**Buffer and TCO Layer Deposition for CIGS Thin Film Solar Cell Using ALD**

ZnO\(_{x}\)S\(_{1-x}\) thin film was prepared using spercycle atomic layer deposition. The S composition shows strong negative deviation from the H\(_2\)O/H\(_2\)S pulse ratio, indicating strong exchange reaction of O for S. The H\(_2\)O/H\(_2\)S pulse ratio shows strong effect on the morphology and the structure of the thin film. Elongated and round shape grains were observed for H\(_2\)O-pulse-rich and H\(_2\)S-pulse-rich film. Both film structure and S composition affect the bandgap properties of the thin film and a bowl shaped relation was mapped out between the bandgap and sulfur composition.

Maximum complete cell efficiency 11.58% was measured with the cell using ZnO\(_{x}\)S\(_{1-x}\) thin film with 1/10 H\(_2\)O/H\(_2\)S pulse ratio. Compared to the cell using CdS, the relatively lower fill factor is primarily responsible for the reduced performance, which may be caused by parasitic resistances induced by recombination at the absorber/buffer layer interface or the conduction bandgap offset. Reducing the buffer layer thickness to 30 nm can further increase the cell efficiency due to the increasing transmission between 500-800 nm.

In and Ga were doped in to ZnO thin film using atomic layer deposition. The comparable minimum resistivity 1.65 x 10\(^{-3}\) Ω·cm was reached using 0.1 and 0.05 precursor pulse fraction for In-doped ZnO and Ga-doped ZnO, respectively. For the samples with minimum resistivity, the In-doped ZnO shows high carrier concentration but low mobility while Ga-doped ZnO shows high mobility but relatively lower carrier concentration. Based on the characterization using XRD, AFM and SEM, the relatively
low carrier mobility of In-doped ZnO can be attributed to ionized impurity scattering and electron–electron scattering.

The efficiency of complete cell using In-doped ZnO and Ga-doped ZnO as TCO material was measured as 6.03% and 11.51%. The cell with Ga-doped ZnO shows better open circuit voltage and short circuit current because the Ga-doped ZnO shows better transmission property due to the relatively lower carrier concentration. Also the large bandgap and moderate carrier concentration may lead to a more favorable band offset at the interface.

**Suggestions for Future Work**

**Thermodynamics Properties and Phase Relation Measurement**

More experiments on the thermodynamic properties for the higher order system can be done in order to further improve the accuracy of the database. For example, as stated in Chapter 3 and Chapter 5, some thermodynamic properties of AgIn₅Se₈ and α-AgCuSe remains unclear and the Gibbs energy of formation of the compounds AgGaSe₂, Ag₉GaSe₆ shows large error. Also, there is no isothermal phase relation data available for Ag-Cu-Se system at low temperature (e.g 500 K). Therefore, more work can be done in terms of thermodynamic properties measurement.

Differential scanning calorimetry (DSC) and electromotive force measurement (EMF) can be used to measure the heat capacity and Gibbs energy of the compounds as a function of temperature. Differential thermal analysis (DTA) and microscopic analysis can be used to determine the phase relation for the ternary system at certain temperature. Furthermore, phonon calculation is a useful and only tool to calculate the Gibbs energy of the defect terminal in the sublattice model used in this work. With these
experimental data, the accuracy of the thermodynamic database can be further improved.

**Deposition Condition, Post Annealing and Deposition Method**

For the buffer layer ZnO$_x$S$_{1-x}$ thin film, the effect of S composition in the buffer layer has been studied. However, the effect of the deposition temperature remains unclear. The major problem for the buffer layer is its band alignment with the absorber. It is possible to find the most favorable band alignment by varying the deposition temperature since it could affect the film electronic and morphological properties. According to the ALD windows mentioned in Figure 7-3, wide temperature range between 125 °C to 150 °C can be try for future work. Similarly, In-doped ZnO and Ga-doped ZnO were studied at 200 °C and the effect of the deposition temperature on the TCO thin film will also be an interesting topic. Furthermore, in this study it has been cleared that the main problem of In-doped ZnO lies in the low free carrier mobility and high free carrier concentration. It is possible to improve the electronic properties as TCO material by annealing the sample with lower In-doping level. This way, the sample may form larger grains and maintain the free carrier concentration at a relatively lower level ($\sim 10^{20} \text{ cm}^{-3}$).

In this study, for both buffer layer and TCO layer materials, the supercycle ALD technique was used, which results in the $\delta$-type layered doping. This feature may lead to longer average free carrier travel path and reduce the mobility. Thus, another deposition technique that introducing H$_2$O-H$_2$S or TMIn/TEGa-DEZn simultaneously is worth trying because it can lead to more homogeneous doping. This may result in different interface between layers and improve the electric properties for the deposited film, which is of vital importance for TCO materials.
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BIOGRAPHICAL SKETCH

Zhi Li was born in 1986 in China. He was admitted to a dual-degree program for his undergraduate education and earned B.S. in chemical engineering from East China University of Science and Technology, China and Diploma (FH) in environmental engineering from Fachhochschule Lübeck, Germany, in August 2009. After his undergraduate degree, he went on to earn his M.S. in chemical engineering from Columbia University and graduated in February 2011. He then joined Proctor & Gamble for internship. After that, he joined the Ph.D. program in chemical engineering at University of Florida and worked for Professor Timothy J. Anderson and he chose photovoltaics as his research topic. Upon graduation, he plans to work for Intel Corporation in Portland, Oregon as a senior process engineer. His main role is to work on the next-generation 10nm tri-gate process.