Mechanism of Sulfur Incorporation into Solution Processed CuIn(Se,S)2 Films

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ABSTRACT: We have investigated the incorporation of sulfur into CuIn(Se,S)2 thin films from different bonding environments in hydrazine-based precursor solutions. Sulfur is present in the form of \((N_2H_5)_2S\), \([Cu_6S_4]^{2-}\), and \([In_2(Se,S)_4]^{2-}\) complexes in mixed CuIn(Se,S)2 precursor solutions. On the basis of compositional information from the precursor solutions and annealed films, we find that the incorporation efficiency of sulfur from \((N_2H_5)_2S\) into the final film is extremely low as a result of the high volatility of this compound and its weak interaction with other species while in solution. Using the same methodology, we additionally report that approximately 80% of the sulfur from \([In_2(Se,S)_4]^{2-}\) is incorporated into the final material, compared to approximately 40% of the sulfur from \([Cu_6S_4]^{2-}\) complexes. This difference in sulfur incorporation efficiency may be due to the relatively weak Cu–S bonds in the \([Cu_6S_4]^{2-}\) structure, which are somewhat unstable compared to the In–S bonds in the \([In_2(Se,S)_4]^{2-}\) complex. This method makes it possible to precisely control the sulfur content in CuIn(Se,S)2 films by adjusting the S/Se ratio of the \([In_2(Se,S)_4]^{2-}\) ions in the final precursor solution. These results will enable the precise adjustment and optimization of the energy band gap in solution-processed CuIn(Se,S)2 absorber layers for the future fabrication of improved photovoltaic devices.

KEYWORDS: solar cells, CuIn(Se, S)2, band gap, hydrazine, molecular precursors

INTRODUCTION

CuInSe2 and its alloys have been extensively investigated as some of the most promising absorber materials for thin film photovoltaic device applications, owing to a high optical absorption coefficient, structural tolerance to large changes in material stoichiometry, and a tunable electronic band gap.1 Band gap optimization is typically achieved by partially replacing indium or selenium with gallium or sulfur, respectively. Cu(In,Ga)Se2 thin film solar cells with efficiencies of roughly 20% have been reported through the use of the vacuum processing techniques in the deposition of the absorber layer.2 However, these techniques introduce challenging issues for the low-cost production of large area modules as a result of the processing complexities associated with vacuum-based device fabrication.3,4 Thus, non-vacuum deposition techniques have been extensively pursued for more than a decade in an attempt to overcome these issues.5–8

Hydrazine solution processing has demonstrated CuInSe2-based thin film solar cells with efficiencies of up to 13.6% despite the early developmental stage of this technique.9 While this approach can readily be used to incorporate gallium into the deposited films,10–12 hydrazine-processed CuIn(Se,S)2 layers are almost completely devoid of sulfur, often despite the addition of excess sulfur to the precursor solutions. W. Liu et al. have reported hydrazine solution-processed CuIn(Se,S)2 films with sulfur content up to approximately 15 atomic %,13 but the detailed mechanism of sulfur incorporation into the films during the formation of the chalcopyrite phase from liquid precursors remains largely undetermined. Precise control over the sulfur content of CuIn(Se,S)2 and Cu(In,Ga)(Se,S)2 thin films is essential in order to facilitate the optimization of the energy band gap and to produce any desired band gap grading. Thus, a deeper understanding of the incorporation mechanism of dissolved sulfur into deposited CuIn(Se,S)2 absorber layers represents a significant asset to the further improvement of hydrazine-processed device performance. In this report, we investigate the mechanism of sulfur incorporation into hydrazine solution-processed CuIn(Se,S)2 films prepared using precursor solutions containing the complexes \((N_2H_5)_2S\), \([Cu_6S_4]^{2-}\), and \([In_2(Se,S)_4]^{2-}\).

EXPERIMENTAL SECTION

The solutions employed in this investigation consisted of elemental sulfur, Cu,S precursor, In2(Se,S)3 precursor, and the combined CuIn-(Se,S)2 precursor mixture, all dissolved in anhydrous hydrazine. Caution: hydrazine is highly toxic and should be handled with appropriate protective equipment to prevent contact with both the liquid and the vapor. The elemental sulfur solution was prepared by dissolving the desired amount of sulfur in anhydrous hydrazine. Protective equipment to prevent contact with both the liquid and the vapor are almost completely devoid of sulfur, often despite the addition of excess sulfur to the precursor solutions. W. Liu et al. have reported hydrazine solution-processed CuIn(Se,S)2 films with sulfur content up to approximately 15 atomic %,13 but the detailed mechanism of sulfur incorporation into the films during the formation of the chalcopyrite phase from liquid precursors remains largely undetermined. Precise control over the sulfur content of CuIn(Se,S)2 and Cu(In,Ga)(Se,S)2 thin films is essential in order to facilitate the optimization of the energy band gap and to produce any desired band gap grading. Thus, a deeper understanding of the incorporation mechanism of dissolved sulfur into deposited CuIn(Se,S)2 absorber layers represents a significant asset to the further improvement of hydrazine-processed device performance. In this report, we investigate the mechanism of sulfur incorporation into hydrazine solution-processed CuIn(Se,S)2 films prepared using precursor solutions containing the complexes \((N_2H_5)_2S\), \([Cu_6S_4]^{2-}\), and \([In_2(Se,S)_4]^{2-}\).

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quantity of elemental sulfur powder in hydrazine. To prepare the Cu$_2$S precursor solution, Cu$_2$S powder was combined with elemental sulfur in hydrazine, with the Cu$_2$S/S molar ratio adjusted to 3 in all cases. To prepare the In$_2$(Se,S)$_3$ precursor solutions, In$_2$Se$_3$ was combined with elemental selenium and elemental sulfur in hydrazine, with the total amount of chalcogen (combined S and Se) set equal to that of In$_2$Se$_3$. Each solution was stirred for more than one week at room temperature. To prepare the final CuIn(Se,S)$_2$ precursor solutions, the Cu$_2$S precursor solution was combined with the In$_2$(Se,S)$_3$ precursor solution. Additionally, extra sulfur solution was added to adjust the S/(S + Se) ratio to the same value in each of the final CuIn(Se,S)$_2$ solutions. All solution preparation and film deposition took place inside an N$_2$-filled drybox with water and oxygen levels each below 1 ppm. The CuIn(Se,S)$_2$ solutions were then spun onto SiO$_2$-coated silicon substrates, followed by a thermal annealing step at 350 °C for 30 min to form a polycrystalline film. These films were then characterized using Raman spectroscopy, X-ray diffraction (XRD), and energy dispersive X-ray (EDX) spectroscopy. Films with thicknesses of approximately 1 μm were prepared on Mo-coated glass substrates for photoluminescence (PL) measurements by repeating the spin coating and annealing process six to eight times.

Raman spectroscopy was performed on the precursor solutions and CuIn(Se,S)$_2$ thin films in a confocal backscattering configuration at room temperature using a Renishaw InVia model with a 514.5 nm argon laser as a light source. Prior to measurement, each solution was sealed by placing vacuum grease between a cavity slide and a thin cover slide while inside an N$_2$-filled drybox to reduce the possibility of chemical changes in solution due to exposure to oxygen and moisture. The laser power was adjusted to 10 mW and 1 mW when measuring solutions and thin films, respectively. The laser beam size was approximately 10 and 1 μm for precursor solutions and films, respectively. XRD characterization was performed on the annealed films using a PANalytical XPert Pro X-ray diffractometer with a Cu Kα radiation source beam. The compositions of the thin films were obtained using EDX spectroscopy within an FEI Quanta 600 scanning electron microscope at an acceleration voltage of 5 kV. Each EDX spectrum was obtained from an area of 100 μm × 100 μm on the sample surface. FeS$_2$, copper, selenium, and InAs were used as standards for the analysis of the sulfur, copper, selenium, and indium content of the films during EDX measurements. Room temperature PL spectra were obtained to estimate the band gap of the CuIn(Se,S)$_2$ films using a Horiba Fluorolog-3 spectrometer with a 660 nm semiconductor laser as the excitation source. The PL signal from the samples was detected by a Hamamatsu H10330A photomultiplier tube cooled to −60 °C during operation.

## RESULTS AND DISCUSSIONS

Knowledge of the specific sulfur-containing molecular species present in hydrazine precursor solutions is essential to investigate the effectiveness of sulfur incorporation into hydrazine-processed CuIn(Se,S)$_2$ films. It has been reported that elemental sulfur dissolves in hydrazine to form the (N$_2$H$_5$)$_2$S compound, and Cu$_2$S dissolves in hydrazine in the presence of additional sulfur to form [Cu$_6$S$_4$]$_{2-}$ complexes. Figure 1 shows typical Raman spectra of (a) the elemental sulfur solution and (b) the Cu$_2$S precursor solution with a Cu$_2$S/S ratio of 3. The distinct peak located at 2560 cm$^{-1}$ can be assigned to an S-H stretching vibrational mode of (N$_2$H$_5$)$_2$S, and the peak located at 335 cm$^{-1}$ can be assigned to a Cu-S stretching mode of the [Cu$_6$S$_4$]$_{2-}$ ions. More detailed analysis can be found elsewhere.
The $\text{In}_2\text{Se}_3^{-2}$ complexes can be formed by mixing equal amounts of $\text{In}_2\text{Se}_3$ and elemental selenium in hydrazine. In our precursor solutions, we make use of $[\text{In}_2\text{Se}_{1.0}\text{S}_{1.0}]^{2-}$, or more simply $[\text{In}_2\text{SeS}]^{4-}$, ions by partially or fully replacing elemental chalcogen (Se and S) and $\text{In}_2\text{Se}_3$ as a function of the amount of precursor solution containing an equal amount of elemental precursor solutions, each with an $S/(\text{Se} + S)$ ratio of 0.6.

Figure 1d. Furthermore, the peaks corresponding to $S$ (secondary peak), were substantially enhanced by increasing chalcogen (Se and S) and $\text{In}_2\text{Se}_3$ as a function of the amount of precursor solution containing an equal amount of elemental precursor solutions, each with an $S/(\text{Se} + S)$ ratio of 0.6.

Figure 2. Raman spectra of three different types of CuIn(Se,S)$_2$ precursor solutions, each with an $S/(\text{Se} + S)$ ratio of 0.6.

The $[\text{In}_2\text{Se}_3]^{2-}$ complexes can be formed by mixing equal amounts of $\text{In}_2\text{Se}_3$ and elemental selenium in hydrazine. In our precursor solutions, we make use of $[\text{In}_2\text{Se}_{1.0}\text{S}_{1.0}]^{2-}$, or more simply $[\text{In}_2\text{SeS}]^{4-}$, ions by partially or fully replacing elemental selenium with elemental sulfur when dissolving the initial material. Figure 1c shows the Raman spectra of $\text{In}_2(\text{Se,S})_3$ precursor solution containing an equal amount of elemental selenium with elemental sulfur when dissolving the initial material. It clearly exhibits a strong peak in the range 192–200 cm$^{-1}$, which can result from the formation of $(\text{N}_2\text{H}_5)_2\text{S}$ molecules, which can be deconvoluted into two peaks, located at 315 cm$^{-1}$ (main peak) and 335 cm$^{-1}$ (secondary peak), were substantially enhanced by increasing the sulfur content in the precursor solutions, as shown in Figure 1d. Furthermore, the peaks corresponding to $S$--H bonds, which can result from the formation of $(\text{N}_2\text{H}_5)_2\text{S}$ molecules, was not detected because all the sulfur atoms in the $\text{In}_2\text{Se}_3$ solution are consumed to form $[\text{In}_2(\text{Se,S})_4]^{2-}$, which is no longer capable of exhibiting an $S$--H vibration. Therefore, the dominant indium--selenium--sulfur phase present in hydrazine solutions must be $[\text{In}_2(\text{Se,S})_4]^{2-}$, which is formed through the following the overall chemical equation:

$$2\text{In}_2\text{Se}_3 + 2x\text{Se} + (2 - x)\text{S} + 2\text{N}_2\text{H}_4 \rightarrow 2[\text{In}_2\text{Se}_{3.0}\text{S}_{1.0}]^{2-} + 4\text{N}_2\text{H}_4^+ + \text{N}_2(g)$$

The stoichiometry of the $[\text{In}_2\text{Se}_{3.0}\text{S}_{1.0}]^{2-}$ complex can be easily adjusted by varying the elemental sulfur and selenium initially added to the solutions.

To investigate of sulfur incorporation efficiency from each molecular species into final CuIn(Se,S)$_2$ films, three specific $[\text{In}_2(\text{Se,S})_4]^{2-}$ complexes, $[\text{In}_2\text{Se}_4]^{2-}$, $[\text{In}_2\text{Se}_3\text{S}_{0.5}]^{2-}$, and $[\text{In}_2\text{Se}_3\text{S}_{1.0}]^{2-}$, were prepared. The Cu$_2$S precursor solutions were mixed with each of the three $\text{In}_2(\text{Se,S})_3$ solutions to prepare three distinct CuIn(Se,S)$_2$ solutions. Type I CuIn(Se,S)$_2$ precursor solution was prepared by combining $[\text{Cu}_2\text{S}]^{2-}$ with $[\text{In}_2\text{Se}_4]^{2-}$; Type II CuIn(Se,S)$_2$ precursor solution was prepared by combining $[\text{Cu}_2\text{S}]^{2-}$ with $[\text{In}_2\text{Se}_3\text{S}_{0.5}]^{2-}$; and Type III CuIn(Se,S)$_2$ precursor solution was prepared by combining $[\text{Cu}_2\text{S}]^{2-}$ with $[\text{In}_2\text{Se}_3\text{S}_{1.0}]^{2-}$. Appropriate amounts of CuIn(Se,S)$_2$ solution were then added to adjust the $S/(\text{Se} + \text{S})$ ratio in the final CuIn(Se,S)$_2$ precursor solutions to the constant value of 0.6.

Figure 2 shows the Raman spectra obtained from each Type of CuIn(Se,S)$_2$ solution with $S/(\text{Se} + \text{S})$ ratios set to 0.6. The peak intensity is normalized using the hydrazine peak intensity. After their initial mixing, solutions were stirred for 1 h before Raman characterization. The intensity of In--$S$ originating from the $[\text{In}_2(\text{Se,S})_4]^{2-}$ species gradually increases from Type I through Type III, while both the S--H bond intensity originating from $(\text{N}_2\text{H}_5)_2\text{S}$ and the In--$S$ bond intensity originating from $[\text{In}_2(\text{Se,S})_4]^{2-}$ are gradually reduced. The increase of a peak located at 335 cm$^{-1}$ is also originated from the increase of the secondary peak of the In--$S$ bond in $[\text{In}_2(\text{Se,S})_4]^{2-}$. In other words, a larger fraction of sulfur atoms are bonded to indium atoms in the form of $[\text{In}_2(\text{Se,S})_4]^{2-}$ and fewer sulfur atoms are bonded to hydrogen atoms in the form of $(\text{N}_2\text{H}_5)_2\text{S}$, in the progression of Type I, Type II, and Type III.

CuIn(Se,S)$_2$ films were prepared by spin-casting each of the CuIn(Se,S)$_2$ solutions, followed by a thermal annealing step at 350 °C. Figure 3 shows the dependence of the diffraction angle 2θ of the (112) peak of the CuIn(Se,S)$_2$ films on the $S/(\text{Se} + \text{S})$ ratios in the precursor solutions. The sulfur to selenium ratio for each type of solution was controlled by varying the amount of $(\text{N}_2\text{H}_5)_2\text{S}$ added to the mixed $[\text{Cu}_2\text{S}]^{2-}$ and $[\text{In}_2(\text{Se,S})_4]^{2-}$ solutions. Increased sulfur incorporation in the CuIn(Se,S)$_2$ phase would cause its lattice parameter to shift to lower values, resulting in larger 2θ values. In this case, however, the 2θ$_{112}$ values of the CuIn(Se,S)$_2$ films were almost identical regardless of the $S/(\text{Se} + \text{S})$ ratio for each type of CuIn(Se,S)$_2$ precursor solution, as shown in Figure 3a. This indicates that the sulfur incorporation efficiency from the $(\text{N}_2\text{H}_5)_2\text{S}$ molecular species is negligible, even at relatively high concentrations within the CuIn(Se,S)$_2$ precursor solution.
Additionally, it has been shown that interaction between molecular species in hydrazine precursor solutions can affect their Raman shift peak intensities. However, the peak intensity of the S–H bond originating from (N$_2$H$_5$)$_2$S shows negligible change when the elemental sulfur solution is mixed with either or both of the Cu$_6$S and In$_2$(Se,S)$_3$ precursor solutions, indicating that sulfur from precursor solutions with different values of the sulfur content based on these Raman spectra are increased intensity from Type I to Type III. These effects indicate that the sulfur content introduced into the annealed Cu(In$_2$S)$_2$ films progressively increases in direct correlation with the sulfur content of the Cu(In$_2$S)$_2$ precursor.

The compositional data discussed above allows us to quantitatively estimate the efficiency of sulfur incorporation into the annealed Cu(In$_2$S)$_2$ films prepared from solutions containing [Cu$_6$S]$_4^{2-}$ and [In$_2$(Se,S)$_3$]$_3^{2-}$. We propose the following chemical reaction for the formation of the Cu(In$_2$S)$_2$ phase from [Cu$_6$S]$_4^{2-}$ and [In$_2$(Se,S)$_3$]$_3^{2-}$ molecular precursors:

$$[\text{Cu}_6\text{S}]_4^{2-} + 3[\text{In}_2(\text{Se,S})_3]_3^{2-}$$

$$+ 8\text{N}_2\text{H}_4 \rightarrow 6\text{CuInSe}_2 + 3\text{H}_2\text{Se} + (4(1 - \varepsilon) + 3(1 - \chi)(1 - \zeta))\text{S} + 8\text{N}_2\text{H}_4 + 4\text{H}_2$$

where $\eta$ is the incorporation efficiency of sulfur from the [Cu$_6$S]$_4^{2-}$ into the films and $\varepsilon$ and $\chi$ are the incorporation efficiencies of sulfur from the [Cu$_6$S]$_4^{2-}$ and [In$_2$(Se,S)$_3$]$_3^{2-}$ species, respectively. In this analysis, we have set the incorporation efficiency of copper and indium from their respective molecular precursors into the Cu(In$_2$S)$_2$ phase to be unity. The left-hand side of the above equation represents the molecular species [Cu$_6$S]$_4^{2-}$ and [In$_2$(Se,S)$_3$]$_3^{2-}$ present in the Cu(In$_2$S)$_2$ precursor solution. Although (N$_2$H$_5$)$_2$S molecules are clearly present in the final precursor solution, we have not included them in the proposed chemical reaction because this species negligibly incorporates into the final films. We include [N$_2$H$_4$]$^-$ ions on the reactant side to maintain charge neutrality within the mixed solution. The first term on the right-hand side the equation is the Cu(In$_2$S)$_2$ phase whose composition will be determined by the incorporation efficiency of chalcogen (S and Se) from the [Cu$_6$S]$_4^{2-}$ and [In$_2$(Se,S)$_3$]$_3^{2-}$ species, and the latter terms represent loss of excess chalcogen, hydrazine, and hydrogen during the coating and thermal annealing processes.

In the proposed chemical equation, we assume that sulfur and selenium evaporate in the form of elemental vapor for the simplicity of the proposed reaction. Even if the chalcogen specie that do not play an important role in the solid phase were to volatilize in other forms such as H$_2$S and H$_2$Se, it would not change the calculated values for the incorporation efficiencies of each precursor molecule into the final film.

With a quantitative model in place, EDX spectroscopy was employed to more precisely determine the composition of the Cu(In$_2$S)$_2$ films from different solutions, and the results are listed in Table 1. The sulfur compositions calculated from the XRD and Raman spectra were used as accuracy standards, serving to double and triple check the measured EDX values, which showed good agreement at each film composition. The incorporation efficiencies of selenium from [Cu$_6$S]$_4^{2-}$ into the solid phase can be estimated at each x value because $[\text{In}_2(\text{Se,S})_3]_3^{2-}$ is the only molecule containing selenium atoms in the mixed precursor solutions. However, two molecular precursors, [Cu$_6$S]$_4^{2-}$ and [In$_2$(Se,S)$_3$]$_3^{2-}$, contain sulfur atoms, so that a combination of EDX data at two different x values is necessary to obtain incorporation efficiencies of sulfur from [Cu$_6$S]$_4^{2-}$ and [In$_2$(Se,S)$_3$]$_3^{2-}$ into the films. Approximately 40% of the sulfur atoms in [Cu$_6$S]$_4^{2-}$ are estimated to be incorporated into the annealed films, while approximately 80% of sulfur and 90% of selenium atoms from [In$_2$(Se,S)$_3$]$_3^{2-}$ are quite close to the values deduced using the (112) peak position obtained from XRD measurements. In addition, the sulfur vibrational mode in CuIn(S,Se)$_2$, located at 291 cm$^{-1}$ shows increased intensity from Type I to Type III. These effects indicate that the sulfur content introduced into the annealed Cu(In$_2$S)$_2$ films progressively increases in direct correlation with the sulfur content of the Cu(In$_2$S)$_2$ precursor.
Table 1. EDX Results for the Composition of Annealed CuIn(Se,S)2 Films Prepared Using Three Different Types of CuIn(Se,S)2 Precursor Solution, Each with an S/(Se+S) Ratio of 0.6

<table>
<thead>
<tr>
<th>type</th>
<th>CuIn(Se,S)2 precursor</th>
<th>[Cu] atomic %</th>
<th>[In] atomic %</th>
<th>[Se] atomic %</th>
<th>[S] atomic %</th>
<th>stoichiometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>[Cu6S4]2−, (N2H5)2S, [In2Se3]2−</td>
<td>25.21</td>
<td>24.89</td>
<td>43.39</td>
<td>6.51</td>
<td>CuInSe1.53S0.47</td>
</tr>
<tr>
<td>II</td>
<td>[Cu6S4]2−, (N2H5)2S, [In2Se3]2−</td>
<td>24.8</td>
<td>25.22</td>
<td>38.19</td>
<td>11.79</td>
<td>CuInSe1.53S0.47</td>
</tr>
<tr>
<td>III</td>
<td>[Cu6S4]2−, (N2H5)2S, [In2Se3]2−</td>
<td>2.47</td>
<td>25.24</td>
<td>33.71</td>
<td>16.34</td>
<td>CuInSe1.53S0.47</td>
</tr>
</tbody>
</table>

Table 2. Incorporation Efficiency of Sulfur in [Cu6S4]2− and [In2(Se,S)4]2− and Selenium in [In2(Se,S)4]2− into Annealed CuIn(Se,S)2 Films

<table>
<thead>
<tr>
<th></th>
<th>x = 0.0</th>
<th>x = 0.5</th>
<th>x = 1.0</th>
<th>ave</th>
<th>std</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se</td>
<td>η (%)</td>
<td>90</td>
<td>87</td>
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<tr>
<td>S</td>
<td>η (%)</td>
<td>38</td>
<td>39</td>
<td>39</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>ϵ (%)</td>
<td>73</td>
<td>84</td>
<td>79</td>
<td>5.5</td>
</tr>
</tbody>
</table>

η is calculated based on the equation (3 + x)η/2 = y in CuInSeS2. η and ε are calculated based on the equation (2/3)ε + (1 − x)η/2 = z in CuInSeS2. y and z values at different x values are obtained from Table 1.

estimated to be incorporated into the films, as is tabulated in Table 2. The higher incorporation efficiency of selenium can be ascribed to the lower volatility of selenium compared to sulfur. It should be also noted that an error range of about 1 atomic %, which is a typical value for EDX measurements, will change the values of incorporation efficiency by around 10% in the above calculation.

The observed effects of molecular species on the incorporation efficiency of sulfur into CuIn(Se,S)2 films can be rationalized in the following manner. The chalcogen (Se + S) to metal (Cu + In) ratio is 1.33:1 in the mixed [Cu6S4]2− and [In2(Se,S)4]2− precursor solution while the ratio in the films is 1:1. Therefore, sulfur from [Cu6S4]2− competes with sulfur and selenium from [In2(Se,S)4]2− to incorporate into the films. It has been demonstrated through thermogravimetric analysis that [Cu6S4]2− is relatively unstable during heat treatment compared with [In2Se3]2−. [Cu6S4]2− ions present in a hydrazine solution convert to Cu6S4 sheets by thermogravimetric analysis that [Cu6S4]2− is relatively unstable during heat treatment compared with [In2Se3]2−. [Cu6S4]2− ions present in a hydrazine solution convert to Cu6S4 sheets by thermogravimetric analysis that [Cu6S4]2− is relatively unstable during heat treatment compared with [In2Se3]2−.

Through the compositional analysis of films formed using different precursor compositions and ratios, we have determined that sulfur in the (N2H5)2S precursor is too volatile to effectively incorporate into the growing CuIn(Se,S)2 phase. Sulfur from the [Cu6S4]2− complex is forced to compete with chalcogen from [In2(Se,S)4]2− to incorporate into the films because the chalcogen content in the molecular precursor solution is necessarily larger than that in the films. Approximately 40% of the sulfur atoms from [Cu6S4]2− appear to incorporate into the annealed films while approximately 80% of the sulfur and 90% of the

![Figure 5. Photoluminescence spectra of CuIn(Se,S)2 films prepared using the three different types of CuIn(Se,S)2 precursor solution.](image)

### CONCLUSIONS

In summary, we have developed a simple and reliable description of sulfur and selenium incorporation from their soluble precursor compounds into CuIn(Se,S)2 films. Sulfur values of over 16.3 atomic %, which corresponds to roughly a 33% displacement of selenium by sulfur in the CuIn(Se,S)2 phase, have been demonstrated, and they have produced a corresponding band gap of up to 1.14 eV. This value agrees well with the average band gap of roughly 1.15 eV typically employed in high efficiency Cu(In,Ga)Se2 devices. The facile adjustment of the absorber band gap within a range quite close to its ideal value makes the use of [In2Se4-xSx]2− precursors highly relevant to the fabrication of high performance CuIn(Se,S)2 photovoltaic devices.

Through the compositional analysis of films formed using different precursor compositions and ratios, we have determined that sulfur in the (N2H5)2S precursor is too volatile to effectively incorporate into the growing CuIn(Se,S)2 phase. Sulfur from the [Cu6S4]2− complex is forced to compete with chalcogen from [In2(Se,S)4]2− to incorporate into the films because the chalcogen content in the molecular precursor solution is necessarily larger than that in the films. Approximately 40% of the sulfur atoms from [Cu6S4]2− appear to incorporate into the annealed films while approximately 80% of the sulfur and 90% of the
selenium atoms from the \([\text{In}_2(\text{Se,S})_4]^{2-}\) precursor are successfully incorporated. The higher volatility of the sulfur atoms in \([\text{Cu}_6\text{S}_4]^{2-}\) compared to that of those in \([\text{In}_2(\text{Se,S})_4]^{2-}\) can possibly be ascribed to the lower thermal stability of the \([\text{Cu}_6\text{S}_4]^{2-}\) complex, as compared with \([\text{In}_2(\text{Se,S})_4]^{2-}\). Controlling the composition of the \([\text{In}_2\text{Se}_3\text{S}_1]^{2-}\) precursor in the mixed CuIn(Se,S) \(_2\) precursor solution offers a reliable mechanism through which to control the sulfur content of the resulting semiconductor material, which, in turn, can enable the precise adjustment of the band gap of hydrazine processed CuIn(Se,S) \(_2\) thin films.

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**NOTE ADDED AFTER ASAP PUBLICATION**

This article was published ASAP on October 17, 2011, with an error in eq 3. The corrected version was published ASAP on October 19, 2011.