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Identification of the Molecular Precursors for Hydrazine Solution Processed $CuIn(Se,S)_2$ Films and Their Interactions

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We investigate the molecular species present in hydrazine $CuIn(Se,S)_2$ precursor solutions, their interactions, and phase formation in solution processed $CuIn(Se,S)_2$ thin films through Raman spectroscopy. The reaction between Cu_2S and sulfur yields $[Cu_6S_4]^{2-}$ ions, while $[In_2Se_4]^{2-}$ ions are formed by the reaction of In_2Se_3 with selenium within their respective solutions. Once combined to prepare a $CuIn(Se,S)_2$ precursor solution, these two species appear to be bridged via newly formed In−S bonds. The creation of the In−S bonds in the $CuIn(Se,S)_2$ precursor solution provides strong evidence for the mixing of copper, indium, sulfur, and selenium at a molecular level even prior to deposition. From this configuration, relatively little atomic diffusion is required to reach the chalcopyrite structure, which enables the formation of highly uniform polycrystalline $CuIn(Se,S)_2$ films at relatively low temperatures.

Introduction

The use of high vacuum deposition techniques in the preparation of $CuInSe_2$ and related chalcopyrites has allowed researchers to fabricate laboratory-scale thin film solar cells with efficiencies approaching 20%.[1] However, vacuum processing presents a number of challenging issues that must be addressed before the production of low cost and large area photovoltaic modules can be fully realized.[2,3] Nonvacuum deposition techniques offer an important alternative to many of these shortcomings and have thus been extensively pursued for more than a decade.[4,5]

Recently, hydrazine solution processing has been developed as a simple and high-throughput process for the preparation of chalcopyrite thin films for solar cell applications.[6−11] Though this process is still in the early stages of development, $CuInSe_2$-based thin film solar cells with efficiencies of up to 12.8% have been demonstrated.[10] In this approach, Cu_2S and In_2Se_3 precursor solutions are prepared separately and then combined to form a $CuInSe_2$ precursor solution with adjustable stoichiometry. The precursor solution is then spun onto the desired substrate and forms a high quality $CuIn(S,Se)_2$ film after a thermal annealing step. This approach can also readily be used to incorporate gallium into the final films.[6,7]

In order to further enhance the efficiency of hydrazine solution processed chalcopyrite thin film solar cells, it will be necessary to understand the structure of the involved precursor species and their interactions within the hydrazine solutions. Previously, hydrazine precursor research has been based on information obtained from the study of solid specimens prepared by the drying of the corresponding precursor solutions.[12−14] However, in order to gain a better understanding of the deposition and film formation processes, it is essential to identify the molecular species as they are present in the liquid-phase hydrazine precursor solutions.

In this study, we investigate the molecular structures present in solutions containing Cu_2S, In_2Se_3, or mixtures of the two through Raman spectroscopy. This characterization technique offers the unique opportunity to simultaneously probe the vibrational modes of a variety of solvated species and has previously been proven a valuable

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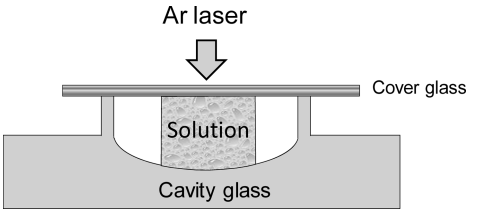

Figure 1. Schematic diagram for the encapsulation system used to protect the hydrazine specimens during Raman spectrum acquisition.

tool in the study of hydrazine-based systems.[15] We also examine the formation of the $CuIn(Se,S)_2$ phase after annealing the solution-processed precursor films.

Experimental Section

Sulfur and selenium solutions were prepared by dissolving elemental sulfur (Aldrich, 99.998%) and elemental selenium (Alfa Aesar, 99.999%) into hydrazine (Aldrich, anhydrous, 98%). In order to prepare Cu_2S solutions with controlled S/Cu_2S ratios, 1 mmol of Cu_2S (American Elements, 99.999%) was combined with an appropriate amount of elemental sulfur in 4 mL of hydrazine. To prepare In_2Se_3 solutions with similarly controlled Se/In_2Se_3 ratios, 1 mmol of In_2Se_3 (American Elements, 99.999%) was combined with appropriate amounts of elemental selenium in 4 mL of hydrazine. The $CuIn(Se,S)_2$ precursor solutions were prepared by combining a Cu_2S solution with an S/Cu_2S ratio of 0.33 with an In_2Se_3 solution of Se/In_2Se_3 ratio 1 in equal proportions. Solution preparation was done inside a N_2 filled drybox with the oxygen and moisture levels both below 1 ppm. All solutions were stirred for more than 1 week at room temperature. *Caution: hydrazine is highly toxic and should be handled with appropriate protecting equipment to prevent contact with either the vapors or liquid.* In order to form $CuIn(Se,S)_2$ thin films, the precursor solution was spun onto Mo-coated glass substrates at 3000 rpm for 50 s, followed by thermal treatment at temperatures ranging from 120 to 370 °C for 30 min.

Raman analysis was performed on the hydrazine precursor solutions and $CuIn(Se,S)_2$ thin films in a backscattering configuration with a confocal configuration at room temperature with unpolarized light using a Renishaw inVia Raman system equipped with a 514.5 nm Ar laser. Laser power was adjusted to 12.5 and 1.25 mW for precursor solutions and thin films, respectively. The laser beam size was approximately 1 and 10 μm for precursor solutions and films, respectively. The intensities of the peaks due to hydrazine in the precursor solutions were normalized to one another in order to facilitate comparison between the spectra. All curve fitting was done using Wire 3.2 software as provided by the supplier. Prior to measurement, each solution was sealed by placing vacuum grease between a cavity slide and a thin cover glass while inside an N_2 filled drybox in order to reduce the possibility of chemical changes due to oxygen and moisture. A diagram of the encapsulation schematic is shown in Figure 1.

Results and Discussion

Cu_2S precursor solutions were prepared by mixing Cu_2S and elemental sulfur in hydrazine. Additionally, sulfur solutions were prepared separately, so that the bonding environment of each reactant could be analyzed individually. The Raman spectrum of a 0.5 M sulfur solution exhibits a distinct band located at 2560 cm^{-1} as shown in Figure 2a, which can be assigned to an S−H stretching vibrational mode.[16] Conspicuously absent from the spectrum is the S−S stretching mode, which typically appears in the range 380−540 cm^{-1}, despite the fact that this mode typically produces a strong Raman signal.[17] Therefore, it is reasonable to assume that sulfur atoms are mainly bonded to hydrogen atoms in the form of H_2S or $(N_2H_5)_2S$ molecules. Previous studies of the S−H stretching mode of H_2S have shown its position to typically fall at values 20−30 cm^{-1} larger than the observed peak of 2560 cm^{-1} shown in Figure 2a.[18] Thus, it is most probable that the elemental sulfur in solution has formed $(N_2H_5)_2S$ molecules according to the following chemical reaction:[19]

$$2S + 5N_2H_4 \rightarrow N_2 + 2(N_2H_5)_2S \quad (1)$$

Figure 2b shows the Raman spectrum of a 0.25 M Cu_2S precursor solution in which the S/Cu_2S molar ratio has been adjusted to 2. Two distinct peaks are visible at 335 and 2560 cm^{-1}, respectively. The peak located at 335 cm^{-1} can be assigned to a Cu−S stretching mode,[20] while the peak at 2560 cm^{-1} is once again the S−H stretching mode of $(N_2H_5)_2S$ molecules formed by the elemental sulfur present in the solution. Numerical analysis shows the integrated intensity of the S−H peak in the 0.25 M Cu_2S solution spectrum to be slightly smaller than that produced by the 0.5 M sulfur solution. Since the amount of elemental sulfur added into these two solutions was originally the same, the slightly reduced S−H signal indicates that some of the elemental sulfur present has reacted with Cu_2S to form a Cu_xS_y complex which is no longer capable of exhibiting an S−H vibrational mode.

In order to identify the composition of the Cu_xS_y complex, we investigate the intensities of the S−H vibrational peak in Cu_2S precursor solutions containing a variety of S/Cu_2S molecular ratios. Figure 2c shows the intensities of the Cu−S and S−H peaks as a function of the S/Cu_2S molecular ratio. The concentration of Cu_2S was fixed to be 0.25 M, while the concentration of elemental sulfur was varied in order to adjust the S/Cu_2S ratio in the solutions. The intensity of the Cu−S peak remained constant versus the S/Cu_2S ratio, indicating that the Cu_2S powder was fully dissolved in each sample. In contrast, the intensity of the S−H peak increased linearly with the S/Cu_2S ratio and can be traced back to its x-intercept at an S/Cu_2S value of approximately 0.33. Since the x-intercept represents the point at which all added sulfur has been consumed by the Cu_xS_y complex formation

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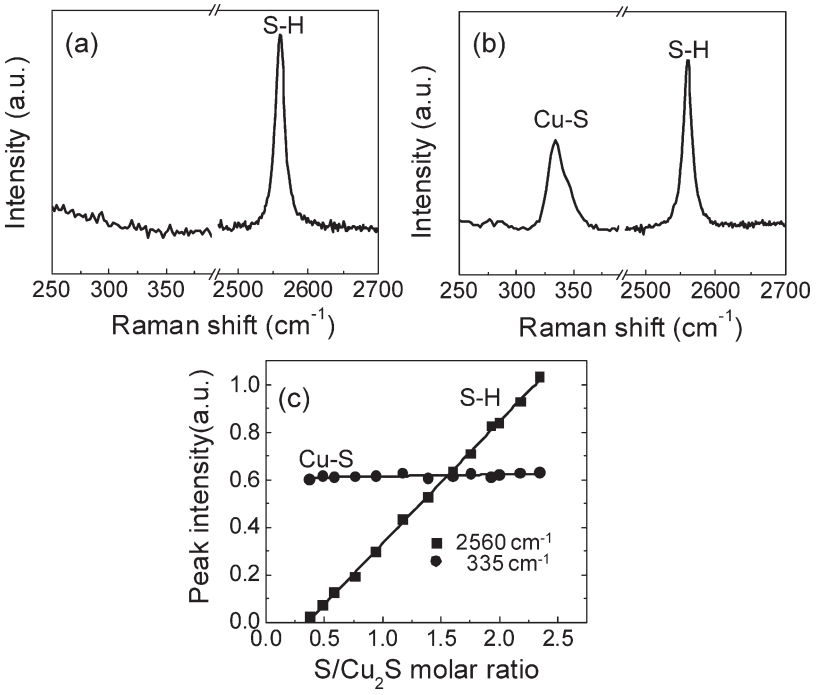

Figure 2. Raman spectra of (a) the 0.5 M sulfur solution and (b) the 0.25 M Cu_2S precursor solution having an S/Cu_2S ratio of 2. (c) The integrated intensities of the peaks located at 335 (●) and at 2560 cm^{-1} (■) as a function of S/Cu_2S ratio obtained from the 0.25 M Cu_2S precursor solutions.

reaction, it can be concluded that the S/Cu_2S ratio of the complex is 0.33. At S/Cu_2S values smaller than 0.33, we observed black precipitates in the solution, which were assumed to be undissolved Cu_2S. From this information, we propose that $[Cu_6S_4]^{2-}$ ions are formed by the following overall chemical reaction in hydrazine:

$$6Cu_2S + 2S + 5N_2H_4 \rightarrow 2[Cu_6S_4]^{2-} + 4N_2H_5^+ + N_2(gas) \quad (2)$$

It has been previously reported that the Cu_6S_4 anion is relatively stable and is less reactive than other Cu_xS_y complexes.[21] Additionally, the evaporation of Cu_2S precursor solutions has been shown to produce the compound $N_4H_9Cu_7S_4$, which is composed of extended Cu_7S_4 sheets separated by a mixture of hydrazinium and hydrazine molecules.[13] Therefore, we assume that $[Cu_6S_4]^{2-}$ ions present in a hydrazine solution convert into Cu_7S_4 sheets by losing sulfur during the drying process.

Following an analogous procedure, we have also analyzed In_2Se_3 precursor solutions prepared by dissolving In_2Se_3 and elemental selenium in hydrazine. Figure 3a shows the Raman spectrum of a 0.1 M selenium solution. The most intense peak, located at 260 cm^{-1}, can be attributed to symmetric Se−Se stretching in the Se_8 cyclic species while the peak at 235 cm^{-1} most likely represents Se−Se vibration in polymeric selenium chains.[22,23] Thus, it appears that elemental selenium dissolves in hydrazine to form polyselenide molecules such as Se_8 rings and polymeric chains. The observed dark green color of the elemental selenium solution supports this conclusion, since polyselenide molecules have previously been shown to produce solutions of similar colors.[24]

Figure 3b shows the Raman spectrum of a 0.25 M In_2Se_3 precursor solution containing an equal molar amount of elemental selenium and In_2Se_3. The Raman spectrum of the solution exhibits a strong peak at 192 cm^{-1} that can be attributed to the In−Se stretching mode.[25] The additional bands at 175 and 240 cm^{-1} can be assigned to secondary vibrational modes also observed in indium selenide complexes.[26−28] The Se−Se stretching modes were not detected, despite the significant of amount of elemental selenium that was added to the solution. This indicates that all of the elemental selenium added into the solution had been consumed during the formation of an indium selenide complex.

Figure 3c shows the Raman spectra of several Se-rich solutions, prepared with Se/In_2Se_3 ratios ranging between 1 and 1.3. As shown in the figure, the Se-rich solutions show an additional peak at 260 cm^{-1} that corresponds to the previously absent Se−Se stretching mode. The peaks resulting from the indium selenide complex, however, show negligible changes as the relative selenium concentration is increased. This indicates that all selenium atoms above a threshold Se/In_2Se_3 ratio remain free to form polyselenide molecules, while a set amount of selenium

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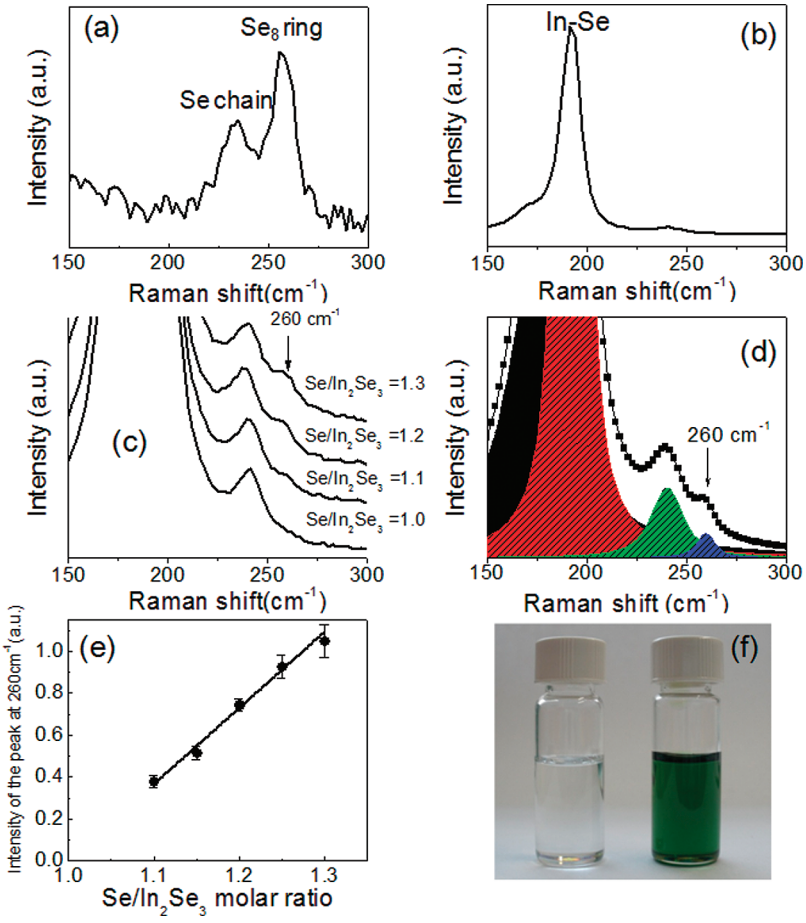

Figure 3. Raman spectra of (a) the 0.1 M selenium solution, (b) the 0.25 M In_2Se_3 precursor solution with an Se/In_2Se_3 ratio of 1, and (c) several Se-rich 0.25 M In_2Se_3 precursor solutions with various Se/In_2Se_3 ratios. (d) Deconvolution of the peaks obtained from the In_2Se_3 precursor solution with an Se/In_2Se_3 ratio of 1.3. (e) The integrated intensity of the peak located at 260 cm^{-1} as a function of the Se/In_2Se_3 ratio in the Se-rich 0.25 M Se/In_2Se_3 precursor solutions. (f) A picture of the Se/In_2Se_3 precursor solutions containing an equal molar amount of elemental selenium and In_2Se_3 (left) and with an Se/In_2Se_3 ratio of 1.1 (right).

preferentially reacts with In_2Se_3 to form indium selenide complexes. We have obtained the intensity of the Se−Se peak located at 260 cm^{-1} through the deconvolution of the complete Raman spectrum, which is shown in Figure 3d. The integrated peak intensity has been plotted as a function of Se/In_2Se_3 ratio, which is shown in Figure 3e. The signal increases linearly with the Se/In_2Se_3 ratio and can be traced back to its x-intercept at an Se/In_2Se_3 ratio of approximately unity. Since the x-intercept represents the point at which all dissolved selenium has been consumed by the complex formation reaction, it can be concluded that the Se/In_2Se_3 ratio of the complex is 1. Therefore, the dominant indium−selenium phase present in hydrazine solutions must be $[In_2Se_4]^{2-}$, which is formed through the following overall chemical equation:

$$2In_2Se_3 + 2Se + 5N_2H_4 \rightarrow 2[In_2Se_4]^{2-} + 4N_2H_5^{+} + N_2(gas) \quad (3)$$

This conclusion is supported by the color of the In_2Se_3 precursor solutions, which are transparent when the amount of elemental selenium present in solution is equal to or less than the amount of In_2Se_3 present. Further increases in selenium concentration cause the color of the solution to turn dark green, indicating the presence of increasing amounts of polyselenide species (Figure 3f).

In order to examine the interactions between the complex ions $[Cu_6S_4]^{2-}$ and $[In_2Se_4]^{2-}$ in the combined $CuIn(Se,S)_2$ precursor solution, Cu_2S and In_2Se_3 solutions were prepared with S/Cu_2S and Se/In_2Se_3 ratios chosen to effectively eliminate the presence of $(N_2H_5)_2S$ and polyselenide molecules. The Cu_2S solution was formed by dissolving 1 mmol of Cu_2S and 0.33 mmol of elemental sulfur in 4 mL of hydrazine and the In_2Se_3 solution by combining 1 mmol of In_2Se_3 with 1 mmol of elemental selenium in 4 mL of hydrazine. A $CuIn(Se,S)_2$ precursor solution was prepared by combining the two solutions in equal proportions. In addition, in order to facilitate the direct comparison of scattering signal upon mixing, the unmixed Cu_2S and In_2Se_3 solutions were diluted by a factor of 2 with pure hydrazine since the combined precursor solution was necessarily diluted by 2 times when the two solutions were mixed.

Figure 4 shows the Raman spectra of the diluted Cu_2S and In_2Se_3 solutions as well as the $CuIn(Se,S)_2$ precursor solution. Immediately noticeable is the presence of a peak located at 315 cm^{-1} in the $CuIn(Se,S)_2$ precursor solution,

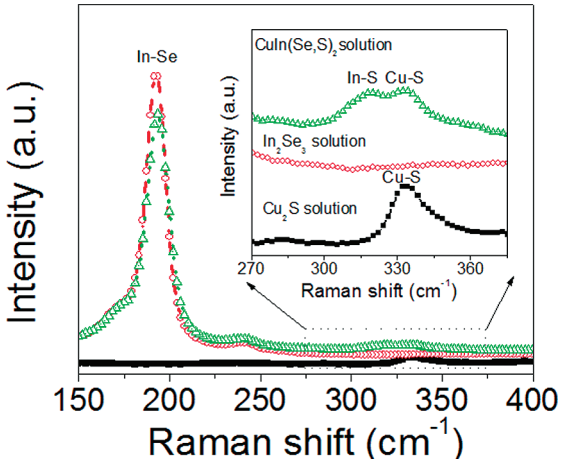

Figure 4. Raman spectra of the 0.125 M Cu_2S solution in which the S/Cu_2S ratio is 0.33, the 0.125 M In_2Se_3 solution in which the Se/In_2Se_3 ratio is unity, and the $CuIn(Se,S)_2$ precursor solution prepared by mixing a 0.25 M Cu_2S solution and 0.25 M In_2Se_3 solution in equal proportion.

which did not exist in the spectra of either of the individual solutions. In addition, the intensities of the In−Se and Cu−S peaks have decreased in the combined solution by approximately 15% and 25%, respectively.

According to one of the most widely used empirical relationships between bond length and force constant[29,30] and using information about typical Cu−S and In−S bond lengths in complex molecules,[13,20,31] the Cu−S and In−S force constants can be estimated to be approximately equal. The frequency of an In−S stretching mode is not readily available in the literature, but using the known Cu−S vibration frequency and approximating the two force constants as equal, we can use the harmonic oscillator approximation for isolated binary vibrational modes to estimate In−S vibration frequency:[32]

$$\nu(\mathrm{In-S}) = \nu(\mathrm{Cu-S})\sqrt{\frac{M_{\mathrm{Cu}}(M_{\mathrm{In}}+M_{\mathrm{S}})}{M_{\mathrm{In}}(M_{\mathrm{Cu}}+M_{\mathrm{S}})}} \qquad (4)$$

This expression produces a value for ν(In−S) of roughly 310 cm^{-1} which is very close to the value of the new Raman peak produced by the $CuIn(Se,S)_2$ precursor solution as shown in the inset of Figure 4. We therefore propose the new scattering signal to result from an In−S vibrational mode. This vibration mode could be the result of anion exchange between the complex ions $[Cu_6S_4]^{2-}$ and $[In_2Se_4]^{2-}$ which would necessarily generate additional peaks corresponding to the Cu−Se, Se−Se, or S−H vibrational modes, which would be expected at approximately 275, 260, and 2560 cm^{-1}, respectively.[33,18,22] However, the creation of any other peaks besides the In−S vibration mode was not detected in the combined $CuIn(Se,S)_2$ precursor solution. This suggests that the

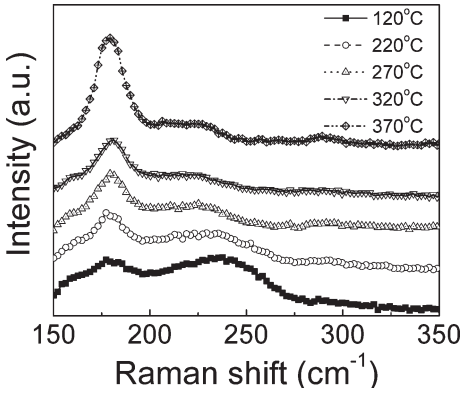

Figure 5. Raman spectra of several hydrazine-processed $CuIn(Se,S)_2$ thin films subject to thermal annealing at temperatures ranging from 120 to 370 °C for 30 min on a hot plate in an N_2-filled drybox.

$[Cu_6S_4]^{2-}$ ions attach to the $[In_2Se_4]^{2-}$ ions via In−S bonding in the $CuIn(Se,S)_2$ precursor solution. Interaction between the two precursor species may also be responsible for the decrease of signal intensity for the In−Se and Cu−S stretching mode upon the mixing of the Cu_2S and In_2Se_3 solution. It should be also noted that the In−S peak resulting from the interaction between the two species is very weak compared to the In−Se peak from $[In_2Se_4]^{2-}$ and that the intensity of the Cu−S peak from $[Cu_6S_4]^{2-}$ is inherently very low. Thus, it might be possible that a prospective Cu−Se peak resulting from the interaction between the two species would not be detectable over the background of the spectra. The presence of a vanishingly weak Cu−Se peak would offer the possibilities that there may be some degree of interaction between the two precursors via Cu−Se bond formation similar to the previously discussed In−S bonding or that a small amount of anion (S^{2-} or Se^{2-}) exchange may be occurring. These possibilities should not be ruled out until further experiments can prove or disprove their validity.

The creation of In−S bonds in the $CuIn(Se,S)_2$ precursor solution provides strong evidence for the mixing of copper, indium, sulfur, and selenium at a molecular level even prior to deposition. From this configuration, relatively little atomic diffusion is required to reach the chalcopyrite structure, which may make it possible to form the $CuIn(S,Se)_2$ phase at fairly low temperatures. In order to explore the formation of the $CuIn(Se,S)_2$ phase in deposited films, the $CuIn(Se,S)_2$ precursor solution was spun onto Mo-coated soda-lime glass substrates and annealed at a range of temperatures prior to characterization. Figure 5 shows the Raman spectra of several $CuIn(Se,S)_2$ thin films annealed at various temperatures.

The peak resulting from the oscillatory motion of selenium atoms with respect to their neighboring copper and indium atoms in chalcopyrite $CuInSe_2$ is typically reported at 174 cm^{-1}.[34,35] The corresponding peak in our spectra is slightly shifted in energy and is located at 178 cm^{-1}, which is due to the introduction of sulfur into

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selenium sites.[36] The $CuIn(Se,S)_2$ appears to form at as low as 120 °C. Further increase of the annealing temperature decreases the full width half-maximum of the peak at 178 cm^{-1}, indicating improvement in the grain size and crystal quality of the film. The spectra show no evidence of the formation of binary phases such as CuS, Cu_2S, CuSe, Cu_2Se, and In_2Se_3 which have been shown to be detrimental to photovoltaic device performance.[37] Compositional inhomogeneities in the precursor film can cause the formation of these binary phases at temperatures around 300 °C.[38] The low temperature formation of $CuIn(Se,S)_2$ films free of binary phases likely results from the thorough mixing of each elemental constituent on a molecular level.

Conclusions

In summary, elemental sulfur and selenium dissolved in hydrazine have been shown to form $(N_2H_5)_2S$ molecules and polyselenide molecules such as Se_8 rings and polymeric selenium chains, respectively. It has also been determined that the reaction between Cu_2S and sulfur yields $[Cu_6S_4]^{2-}$ ions, while $[In_2Se_4]^{2-}$ ions are formed by the reaction of In_2Se_3 with selenium in hydrazine. Mixing of the Cu_2S precursor and In_2Se_3 precursor solutions leads to the formation of In−S bonds, which likely bridge the two anions. This evidence suggests that all the components of the $CuIn(S,Se)_2$ phase are necessarily mixed on a molecular level, which in turn enables the formation of highly uniform polycrystalline $CuIn(Se,S)_2$ films at relatively low temperatures. Hydrazine solution processing therefore has tremendous potential for application to flexible solar cells, displays, and other electronics owing to the ability of this method to achieve high quality semiconductor films at low fabrication temperatures.

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