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$CuIn_{1-x}Al_xS_2$ thin films prepared by sulfurization of metallic precursors

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ABSTRACT

$CuIn_{1-x}Al_xS_2$ thin films ($x = 0$, 0.09, 0.27, 0.46, 0.64, 0.82 and 1) with thicknesses of approximately 1 μm were formed by the sulfurization of DC sputtered Cu–In–Al precursors. All samples were sulfurized in a graphite container for 90 min at 650 °C in a 150 kPa Ar + S atmosphere. Final films were studied via X-ray diffraction (XRD), scanning electron microscopy (SEM) and micro-Raman spectroscopy. It was found that all samples were polycrystalline in nature and their lattice parameters varied slightly nonlinearly from $\{a = 5.49\,\text{Å}, c = 11.02\,\text{Å}\}$ for $CuInS_2$ to $\{a = 5.30\,\text{Å}, c = 10.36\,\text{Å}\}$ for $CuAlS_2$. No unwanted phases such as $Cu_{2-x}S$ or others were observed. Raman were recorded at a room temperature and the most intensive and dominant A_1 phonon frequency varied nonlinearly from 294 cm^{-1} ($CuInS_2$) to 314 cm^{-1} ($CuAlS_2$).

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1. Introduction

Chalcopyrite ternary semiconductors have often been employed as absorber layers in high-efficiency thin film solar cells [1–3] because of their physical properties such as band gap, crystallinity, absorption coefficient and hardness. During the last 20 years many research groups have worked on increasing the efficiency of $A^{I}B^{III}C_2^{VI}$ chalcopyrite photovoltaic modules from 14.1% (world record for $CuInSe_2$) [4] by substitutions for In and Se with other elements from the same groups of periodic table. They created photovoltaic modules based on an absorber layer of $CuIn(S,Se)_2$ [5], $Cu(In,Al)Se_2$ [6], $Cu(In,Al)S_2$ [7], $CuGaSe_2$ [8], $Cu(In,Ga)S_2$ [9] and many other combinations. Currently the greatest energy conversion efficiency of 19.9% has been achieved with a $CuIn_{0.7}Ga_{0.3}Se_2$ absorber layer that has a band gap of 1.2 eV [10]. Although the fact that the band gap tunability of $CuIn_{1-x}Ga_xSe_2$ (CIGS) system is in the range 1.04 eV ($CuInSe_2$) to 1.69 eV ($CuGaSe_2$)—see Fig. 1, further increasing of E_g towards to optimum value of 1.37 eV [11] leads to losses in fill factor and open circuit voltage, and a decrease in the junction quality factor [12,13]. Moreover gallium is a rare and expensive element and selenium is a toxic material [14], so we have investigated the effects of replacing indium with aluminum and selenium with sulfur in order to study the growth process and some properties of the ternary chalcopyrite $CuIn_{1-x}Al_xS_2$ (CIAF).

CIAF thin films or nanocrystals have been prepared using a several methods such as sulfurization of sputtered metallic precursors by sulfur vapors in hermetically sealed ampules [15], sulfurization of precursors in H_2S flow [7], thermal evaporation of elemental Cu–In–Al–S mixture [16] or spray pyrolysis technique [17]. Unfortunately according to our knowledge, no scientific study describing formation of binary sulfide compounds CuS, Cu_2S, In_2S_3 and Al_2S_3 serving as educts for formation of the final compound $CuIn_{1-x}Al_xS_2$ have been published yet. All previously reported sulfurization or evaporation techniques utilizing elemental sulfur for synthesis of $CuIn_{1-x}Al_xS_2$ [15,16] or $CuAlS_2$ thin films [18–20] operate with sulfurization temperatures 570–1000 °C and reaction time in the range 5 h to 14 days. This paper describes a preparation of CIAF thin films by the sulfurization of DC sputtered metallic precursors Cu–In–Al in an argon/sulfur atmosphere during 90 min under a pressure of 150 kPa and temperature 650 °C. Final $CuIn_{1-x}Al_xS_2$ thin films were studied as a function of composition and sulfurization conditions in an attempt to investigate the effect of the aluminum addition on the structural and optical properties measured by Raman spectroscopy and X-ray diffraction (XRD). To the best of our knowledge no scientific studies presenting Raman spectroscopy of CIAF materials have been published.

2. Experimental details

$CuIn_{1-x}Al_xS_2$ thin films were deposited onto soda lime glass (SLG) by a two-step process consisting of DC magnetron sputtering of composite Cu–In–Al metallic

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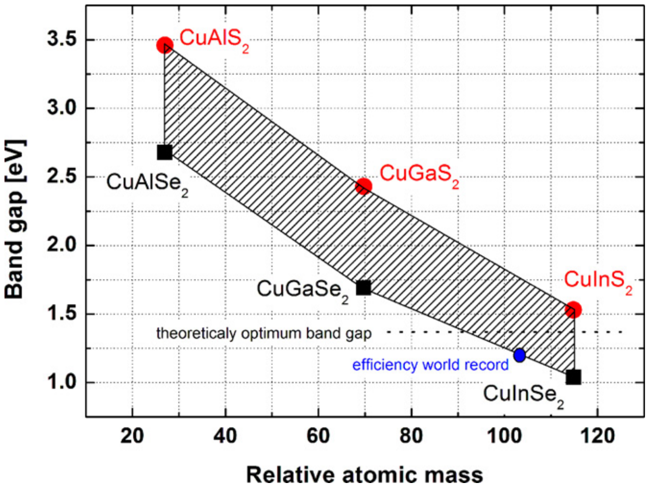

Fig. 1. Band gaps of chalcopyrites $A^{I}B^{III}C_2^{VI}$ (C = S, Se), (B = Al, Ga, In) as a function of atomic mass of B.

precursors, followed by sulfurization in an Ar and S atmosphere. All precursor layers were sputtered from composite targets with fixed stoichiometric ratio of $Cu_{0.5}In_{0.5}$ or $Cu_{0.45}In_{0.55-y}Al_y$ (y = 0.05, 0.15, 0.25, 0.35, 0.45, 0.55). This limited copper deficiency, Cu/(In + Al) = 0.82, was used in order to minimize the formation of $Cu_{2-x}S$ phases during the sulfurization process. Prior to deposition the chamber was evacuated to a base pressure of 1×10^{-4} Pa with a turbo molecular pump. The distance between target and substrate was 7 cm and it was the same for all samples. High purity (99.998%) Ar was used as the working gas. The argon flow rate was set to 40 sccm and the total deposition time was approximately 20 min. A deposition rate of 20 nm/min produced thin films with thicknesses near 400 nm before sulfurization (after sulfurization the thickness approximately doubled). A set of 7 samples with initial ratio x = Al/(In + Al) = 0.00, 0.09, 0.27, 0.46, 0.64, 0.82 and 1.00 was prepared.

All samples were sulfurized in a quartz halogen lamp heating system using sublimed sulfur powder (CAS 7704-34-9) as a sulfur source. The sulfur was placed in a graphite container along with the substrate. The container was loaded into a quartz tube, which was evacuated by a rotary mechanical pump to a base pressure of less than 1 Pa and then filled with 1.5 atm of pure Argon. The higher than atmospheric pressure was chosen to slow down fast diffusion of sulfur particles out of graphite container during the heating process. A thermocouple was embedded in the container and served as the process temperature monitor. A computer was used to control the temperature profile during the experiment. The sulfurization temperature was set to 650 °C. The temperature profile during sulfurization was the following: a one step ramp and soak process with a 10 min ramp directly to the final temperature of 650 °C followed by an 80 min soak and controlled cool down to return the container to room temperature. The total reaction time was 90 min.

The final samples were studied by X-ray diffraction and Raman spectroscopy. Surface morphology of the films was observed using scanning electron microscopy (SEM).

3. Results and discussion

3.1. X-ray diffraction

X-ray diffraction patterns were recorded on an XRD diffractometer (Rigaku D/Max-B, Cu $K_\alpha \sim 1.544$ Å) and XRD patterns of final CIAF samples are shown in Fig. 2. All spectra are normalized to the same intensity of the main reflection. Because of deteriorating crystallinity for higher value of parameter x the relative level of noise in presented spectra is growing. The fact that all films are polycrystalline in nature with chalcopyrite crystal structure is clearly identified by the characteristic (1 1 2), (0 0 4)/(2 0 0), (2 0 4)/(2 2 0) and (1 1 6)/(3 1 2) reflections of the tetragonal structure. All layers have preferred (1 1 2) orientation and no peaks corresponding to metallic phase or binary sulfide/oxide phase were observed. Because of poor crystallinity the noise level for $x > 0.5$ reaches almost 20% of the intensity of the main reflection (1 1 2). This ratio is approximately the same like relation between intensity of (2 0 4)/(2 2 0) vs. (1 1 2) peak in case of $x = 0$. For this reason the weak peaks such as (0 0 4)/(2 0 0) or (2 0 4)/(2 2 0) are not seen in the spectra corresponding to higher values of composition parameter x.

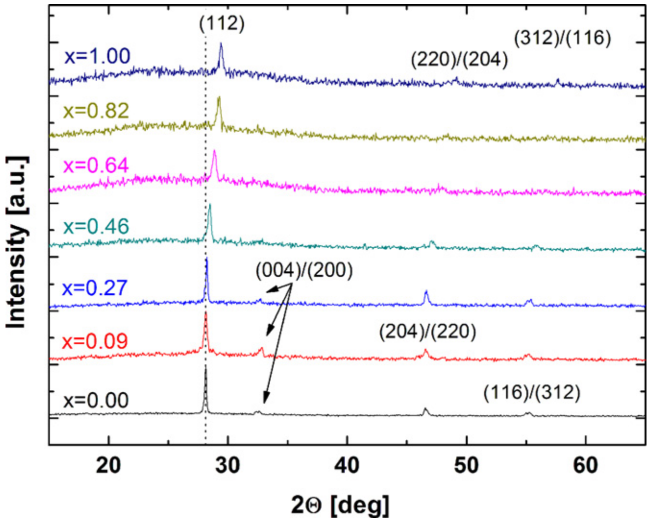

Fig. 2. XRD spectra of $CuIn_{1-x}Al_xS_2$ thin films with various x ratio.

An expected significant shift of all peaks to higher 2θ positions is observed with increasing Al ratio due to a decrease in d-spacings and unit cell dimensions. Detailed examples of this shift are presented in Fig. 3, where the normalized fits of (1 1 2) reflections are shown. From the graph it can be seen that the shift in the (1 1 2) peak is very small or immeasurable until the composition parameter x reaches a value of at least 0.25. The dependence of lattice spacing d(1 1 2) on Al content is shown in Fig. 4. The value of d-spacing is decreasing as expected, from 3.17 Å ($CuInS_2$) to 3.04 Å ($CuAlS_2$), but its variation is nonlinear. A similar dependence of lattice parameters, a and c, of the tetragonal structure, that were calculated from peak positions corresponding to reflections (1 1 2), (2 0 4) and (3 1 2) was seen. Their values varied also nonlinearly from {a = 5.49 Å, c = 11.02 Å} for $CuInS_2$ to {a = 5.30 Å, c = 10.36 Å} for $CuAlS_2$. The same nonlinear behavior was observed in previous work focused on thin films of a similar chalcopyrite, $CuIn_{1-x}Al_xSe_2$ [21–24]. Reddy at al. [22] explained this nonlinearity as a consequence of fact that Al is not completely incorporated substitutionally and it is segregated as Al_2O_3 at the surface for

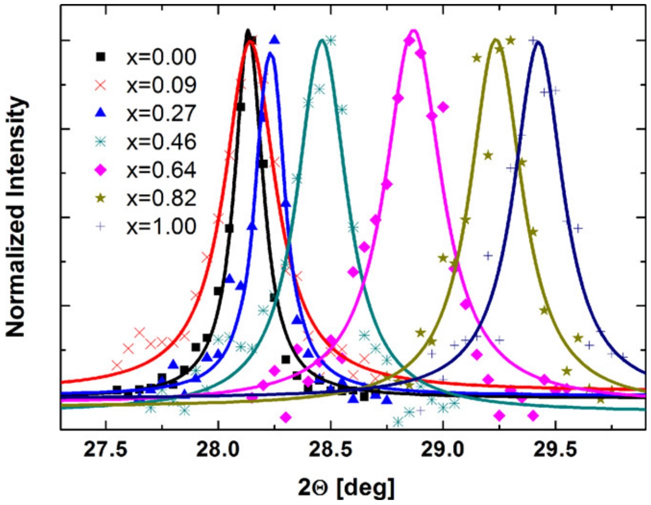

Fig. 3. Detail of previous picture. Experimental data (the points) and their Lorentzian fit (the lines) of (1 1 2) XRD peaks of $CuIn_{1-x}Al_xS_2$ thin films with various x ratio.

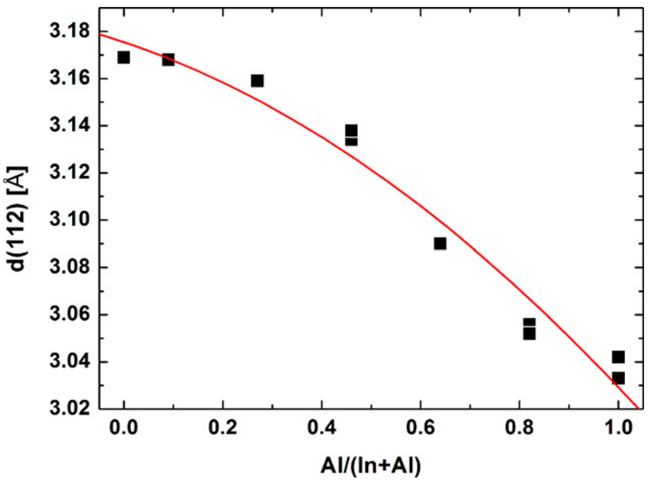

Fig. 4. *D*-spacing *d*(1 1 2) as a function of Al concentration.

the lower values of *x*. These observations were confirmed by XPS measurements. However, only one study, known to us, of lattice parameters of $CuIn_{1-x}Al_xS_2$ as a function of Al concentration by Bhandari et al. [15] reported linear behavior in accordance with Vegard's law.

The value of the tetragonal distortion $(2-c/a)$ which is very important parameter in $A^{I}B^{III}C_2^{VI}$ chalcopyrite is strongly affected by the existence of the two basic chemical bonds A–C and B–C with unequal lengths. The changes in Al concentration affect the length of both bonds and therefore the tetragonal ratio, c/a, is also changed. Previously reported values of tetragonal distortion [15,25–28] are in good agreement with our results −0.007 for $CuInS_2$ and 0.045 for $CuAlS_2$. The fact that deviation of this parameter from zero significantly grows with increasing Al ratio could be indicative of tension in a crystal structure and therefore on the crystallite size (*S*).

3.2. Scanning electron microscopy

The SEM images of four selected samples with $x = 0.00$, 0.09, 0.27 and 1.00 are presented in Fig. 5a–d, respectively. The scale of all pictures is the same so that it is easer to visibly see that the films with lower values of *x* are coarse grained and at higher values of *x* are fine grained (compare namely Fig. 5c and d). This indicates that the increase in aluminum content in the films decreases the grain size which is in accordance with conclusions of the previous paragraph which described the XRD results.

3.3. Raman spectroscopy

A Raman spectroscope (Horiba/Jobin Yvon Lab RAM HR800) with a He–Ne laser ($\lambda = 632.81$ nm) was used to measure the Raman scattering. To the best of our knowledge there are no publications on the Raman scattering from $CuIn_{1-x}Al_xS_2$ films. Thus, the present work is a first investigation on the compositional dependence of the Raman spectra of $CuIn_{1-x}Al_xS_2$.

The Raman spectra of CIAF thin films with a resolution 0.3 cm^{-1} were recorded at room temperature and the results are presented in Fig. 6. The most intense line within 291–314 cm^{-1} range could be assigned to the A_1 mode which is the strongest mode generally observed in the Raman spectra of $A^{I}B^{III}C_2^{VI}$ chalcopyrite compounds. This mode results from the motion of the C^{VI} atom with the A^{I} and B^{III} atoms remaining at rest and its frequency is

$$\omega = \sqrt{\frac{k}{M_C}}, \tag{1}$$

where *k* is the force constant and M_C is the mass of the C^{VI} atom [29]. Other weaker modes for example B_2(TO) and B_2(LO) with theoretical positions between 320 and 350 cm^{-1} for $CuInS_2$ and 440 and 500 cm^{-1} for $CuAlS_2$ [30] are visible only for films with very low concentrations of Al.

As can be seen in Fig. 6 and as demonstrated in graphical form in Fig. 7, where the Raman frequency were obtained by fitting

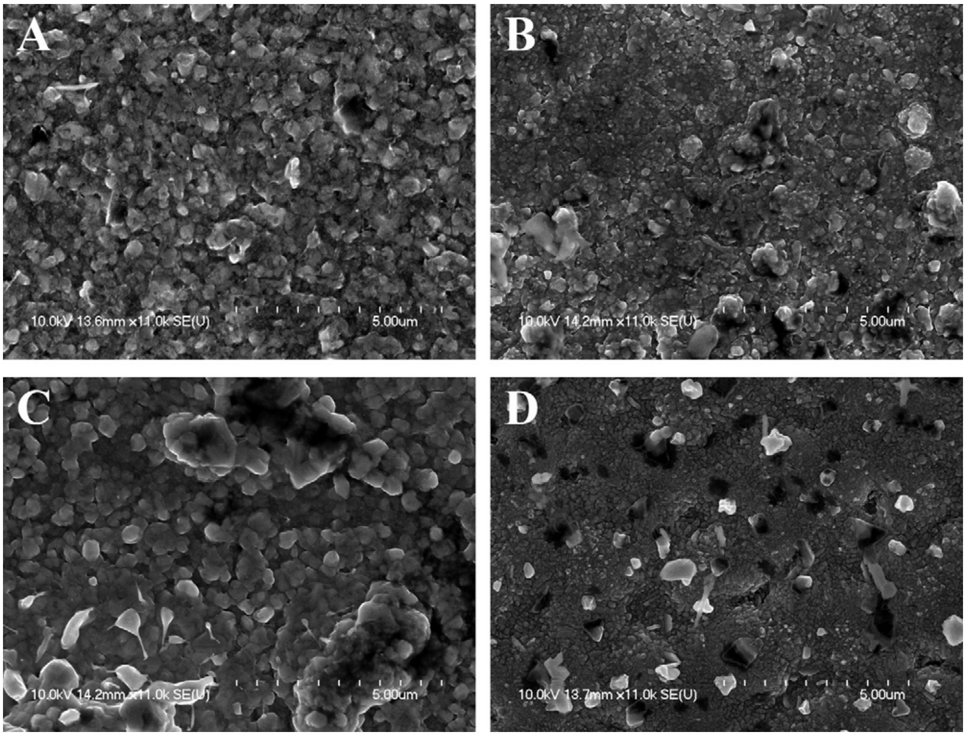

Fig. 5. Scanning electron micrographs of $CuIn_{1-x}Al_xS_2$ thin films for different values of *x*: (a) $x = 0.00$, (b) $x = 0.09$, (c) $x = 0.27$, and (d) $x = 1.00$.

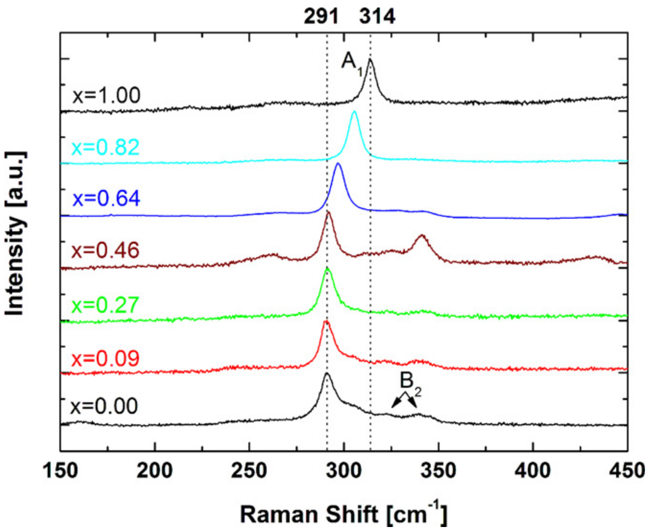

Fig. 6. Raman spectra of $CuIn_{1-x}Al_xS_2$ samples.

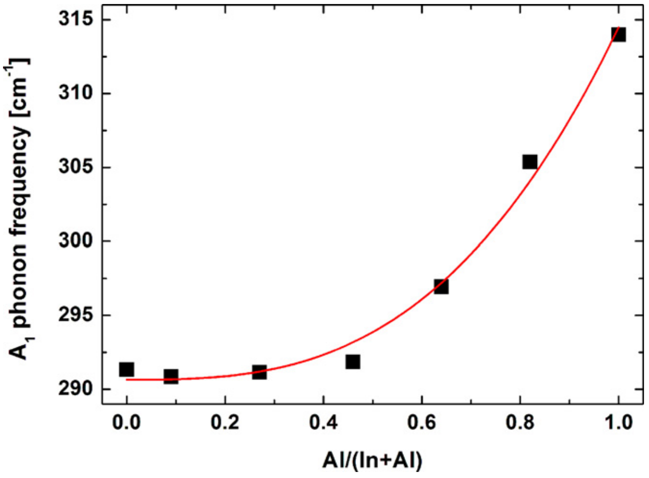

Fig. 7. A_1 phonon frequency as a function of Al ratio.

the signal with Lorentzians, the A_1 mod frequency increases significantly with the increase of Al/(In + Al) content from 291 cm^{-1} (A_1-mode frequency of $CuInS_2$) to 314 cm^{-1} (A_1-mode frequency of $CuAlS_2$). These values are in good agreement with previously reported data for $CuInS_2$ and $CuAlS_2$ chalcopyrites [28,30,31], but the shift in phonon frequency for $x < 0.5$ is negligibly small. Nonlinearity in this shift is even more visible than similar effect in crystal lattice parameters previously described. Because the frequency of A_1 mode is given by Eq. (1) and because the mass of the C^{VI} atom in all $CuIn_{1-x}Al_xS_2$ crystals remains the same, the force constant k must be slightly changed during gradual substitution of aluminum for indium. In a previous paper [24], where the dependence of A_1 mod frequency of similar chalcopyrite $CuIn_{1-x}Al_xSe_2$ was studied, it was shown that A_1 mod frequency is also nonlinear in Al/(In + Al) ratio but seems to be nearly linearly dependent on the lattice parameters. That result could just be coincidental, but this is definitely not true in the case of the CIAF thin films. The dependence between (1 1 2) d-spacing and A_1 mod frequency is demonstrated in Fig. 8 and it is evident that is not linearly dependent. A possible explanation can be found by considering the differences in the depth of penetration of the X-ray beam and the He–Ne laser beam into the measured film. While the X-ray beam was able to easily penetrate through whole CIAF layer with a thickness of 800 nm and therefore collect an average signal from the entire profile, the Raman laser was focused on the surface of studied material and therefore provided information only about top layer of CIAF thin films. If the explanation about segregation of unincorporated Al as Al_2O_3 at the surface for the lower values of x given by Reddy at al. in [22] is true, the Raman results reflect the absence of aluminum in the chalcopyrite crystals in the surface area more clearly and the strong nonlinearity depicted in Figs. 7 and 8 is an expected result.

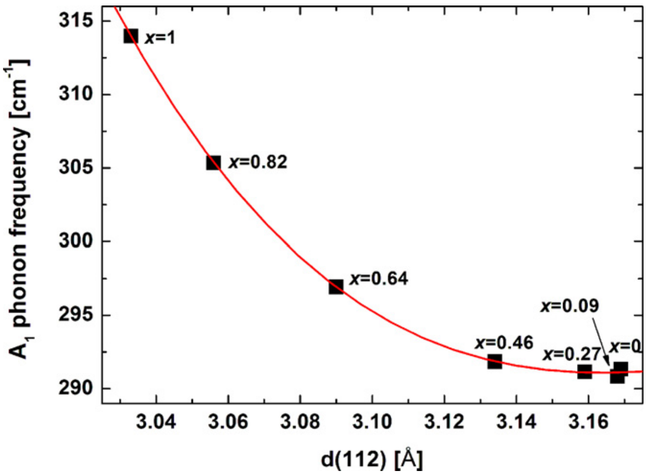

Fig. 8. A_1 phonon frequency as a function of d-spacing (1 1 2).

4. Conclusion

$CuIn_{1-x}Al_xS_2$ thin films with a greatly varying composition range were deposited on soda-lime glass by DC magnetron sputtering of metallic precursors followed by high pressure sulfurization in an Ar + S atmosphere. Analysis by XRD confirmed that all layers are crystalline with the chalcopyrite structure and the lattice constants vary slightly nonlinearly with composition parameter x. Raman scattering disclosed that the A_1 mode frequency increases from 291 cm^{-1} ($CuInS_2$) to 314 cm^{-1} ($CuAlS_2$) and its dependence on Al/(In + Al) ratio is also nonlinear.

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