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Raman Scattering Studies of CuInS₂ Films Grown by RF Ion Plating

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CuInS₂ films were grown by rf ion plating and their crystallinity was characterized by Raman spectroscopy. Six Raman peaks were observed, most of which were assigned to the phonon modes of CuInS₂, except for a peak at 307 cm⁻¹ that was clearly observed in the films with a poor crystalline quality. The peak at 307 cm⁻¹ was assigned to the totally symmetric mode by polarized Raman measurement. This peak was related to some kind of a localized mode with a smaller mean atomic weight of cations.

KEYWORDS: CuInS₂, Raman spectroscopy, characterization, mean atomic weight of cations, rf ion plating, crystallinity

The chalcopyrite semiconductor CuInS₂ is one of the most attractive candidates for photovoltaic devices, because of the closest match of its band gap (1.53 eV) to the solar spectrum.¹⁾ A number of techniques for fabrication of CuInS₂ films have been proposed. Recently we have developed a new fabrication technique using rf ion plating, capable of the preparation of films with high-productivity.²⁾ For the ternary analogue CuInSe₂, the formation of an ordered vacancy compound, CuIn₃Se₅, is important for the good heterojunction.³⁾

In our previous report, the films were characterized only by X-ray diffraction (XRD).²⁾ In order to obtain further information on the composition and structure of the films, we performed Raman scattering measurements using a back-scattering configuration.

CuInS₂ films were grown by rf ion plating on Mo-coated soda-lime glass substrates at 400°C. The rf power for ionization was 200 W. The Cu and In compositions were controlled by varying the electron beam power of the Cu₂S and In₂S₃ sources. The substrate bias conditions were (1) positively biased with +50 V (hereafter called P), (2) grounded (G), (3) floating (F) and (4) negatively biased with -50 V (N). The resulting film thickness was about 2 μm. All films were covered with Cu-S compounds, they were etched by a 10% KCN solution to remove the copper sulfides. Next, the films were characterized by XRD, scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX) and from the results, it is observed that the F film showed the best crystalline quality. Details of the growth technique and characterization of these films have been reported previously.²⁾

To perform Raman measurements, we used a JOBIN YVON T6400 spectrometer in which the incident light of the Ar⁺ laser (514.5 nm, 40 mW) was focused on the surface about 1 mm in diameter and the scattered beam was dispersed using a triple monochromator combined with a CCD photon-counting apparatus. The polarized Raman spectra of horizontal-horizontal (HH) and vertical-horizontal (VH) configurations were performed using a λ/2 plate and a polarizer. All measurements were carried out at room temperature in air.

Figure 1 shows Raman spectra of these films. Six peaks were observed at 240 cm⁻¹, 266 cm⁻¹, 292 cm⁻¹, 307 cm⁻¹, 320 cm⁻¹, and 340 cm⁻¹, except for the peak at 307 cm⁻¹, these peaks at 240 cm⁻¹, 266 cm⁻¹, 292 cm⁻¹, 320 cm⁻¹, and 340 cm⁻¹ were previously assigned to E, B₂, A₁, E, and B₂ modes of CuInS₂, respectively.³⁾ Another peak with a relatively stronger intensity was observed at 307 cm⁻¹. To our knowledge, no such Raman peak has been reported previ-

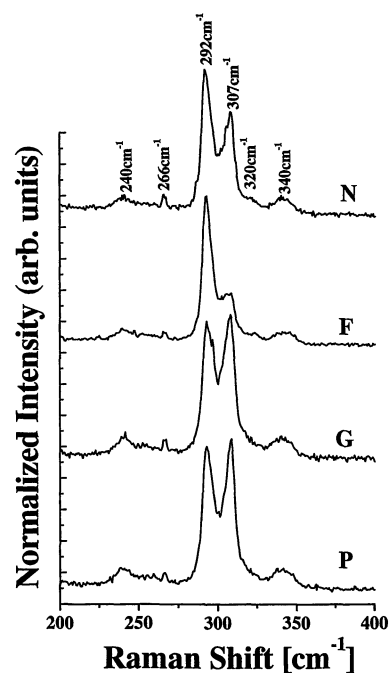


Fig. 1. Raman spectra of KCN-treated N, F, G, and P films.

ously. It was observed that the relative peak intensity of the peak at 307 cm⁻¹ varied with the substrate bias and was weaker in the F and N films than in the G and P films.

To determine the characteristics of the peak at 307 cm⁻¹, polarized Raman measurements were performed for the G film (Fig. 2). The intensity of each spectrum was normalized to that of the peak at 292 cm⁻¹.

It has been established⁴⁾ that the intensity ratios of the VH and HH configurations are different between the totally symmetric and the non totally symmetric modes. As shown in Fig. 2, the normalized intensities for the 240 cm⁻¹, 266 cm⁻¹, 320 cm⁻¹, and 340 cm⁻¹ peaks shows clear differences between the two polarizations. On the other hand, the normalized peak intensity for the 307 cm⁻¹ peak was the same as the A₁ mode of CuInS₂ in the HH and VH configurations. This suggests that the 307 cm⁻¹ peak (hereafter referred to as A₁') and the 292 cm⁻¹ peak (A₁) share the same symmetry, in which the latter is totally symmetric.³⁾ Therefore, the newly observed peak can also be assigned to the totally symmetric mode.

We previously reported similar results of the Raman scat-

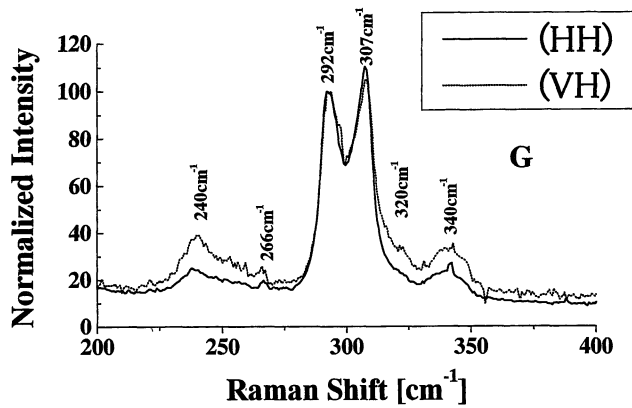


Fig. 2. Polarized Raman spectra of G film in HH and VH configurations.

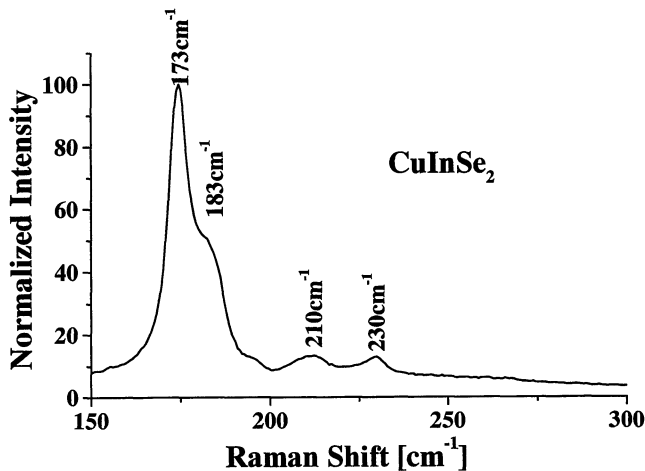


Fig. 3. Raman spectrum of CuInSe₂.

tering measurements for CuInSe₂ films.⁵⁾ In these films, a strong peak appears at 183 cm⁻¹, alongside the A₁ mode at 173 cm⁻¹, when the film had a Cu-poor surface composition (Fig. 3). This peak was also assigned to the totally symmetric mode. Yamanaka *et al.* also reported a similar peak during their selenization process of Cu/In alloy, in which the intensity of the 185 cm⁻¹ peak decreased as the annealing temperature was decreased, however, they did not offer a clear explanation for this.⁶⁾

Bodnar *et al.*⁷⁾ suggested that the A₁ mode frequency of I–III–VI₂ group compounds is inversely proportional to the square root of the anion atomic weight. We calculated the frequency ratios of the A₁ and A₁' modes by assuming that the A₁' mode originated from a modified chalcopyrite structure. The calculated frequency ratios (Table I, fourth row) for the two modes were 1.69 and 1.68 for CuInS₂ and CuInSe₂, respectively. This result shows that the A₁' modes of CuInS₂ and CuInSe₂ share a common origin.

On the other hand, Matsushita *et al.*⁸⁾ reported that the frequencies of the A₁ mode depend on the mean atomic weights of the cations and proposed the following equation for the same anion elements,

$$(m_A + m_B/m_X + m_Y)^{1/2} = \nu_{A_1}(XYC_2)/\nu_{A_1}(ABC_2),$$

where m_A, m_B, m_X and m_Y are atomic weights of the cations.

Using this relationship where XYC₂ is the A₁ mode configuration and ABC₂ is the A₁' mode configuration, we calcu-

Table I. Raman peaks and Frequency ratios.

	A ₁	A ₁ '	A ₁ /A ₁ '
CuInS ₂	292 cm ⁻¹	307 cm ⁻¹	0.951
CuInSe ₂	173 cm ⁻¹	183 cm ⁻¹	0.945
CuInS ₂ /CuInSe ₂	1.69	1.68	

lated the frequency ratios for CuInS₂ and CuInSe₂ to be 0.951 and 0.945, respectively (Table I, fourth column). These values suggest that the A₁' mode has a lower mean atomic weight of cations (similar to the Cu-poor configurations) compared to the A₁ mode of stoichiometric compounds. If the mean atomic weight of cations of A₁' was Cu-deficient, the value would be about 30% deficient. In the case of selenides, it is widely believed that in the Cu-poor phase, CuIn₃Se₅ is often formed on the surface of CuInSe₂. However, this compound is not responsible for the A₁' mode that we observed, since the Raman peak of the CuIn₃Se₅ single-crystal film on GaAs was observed at lower frequency, 152 cm⁻¹.⁹⁾ In addition, no other lines that cannot be attributed to stoichiometric chalcopyrites were observed in our experiments. Therefore we tentatively suggest that the A₁' mode is not caused by an extraneous crystalline phase but by some sort of localized phonon mode involving some defective structure in the chalcopyrite phase. A similar phenomena have been reported in GeSe₂ and GeS₂,¹⁰⁾ in which a strong Raman peak called the “companion A₁ Raman line” appears alongside the A₁ mode. The origin of such a mode has been associated with a large cluster. Further investigations regarding the characteristics of the 307 cm⁻¹ Raman peak are necessary.

In conclusion, a) we first observed the 307 cm⁻¹ Raman line in CuInS₂, b) the Raman peak intensity for the 307 cm⁻¹ peak was the smallest in the F film which showed the best crystalline quality, c) the peak at 307 cm⁻¹ belongs to the totally symmetric mode, d) the frequency ratios of A₁ and A₁' suggest that the peak at 307 cm⁻¹ (CuInS₂) and the peak at 183 cm⁻¹ (CuInSe₂) share the same origin, and e) the frequency ratios of A₁ and A₁' for CuInS₂ and CuInSe₂ were smaller than 1.0. These results suggest that the newly observed Raman peak at 307 cm⁻¹ can be related to a localized phonon mode with a smaller mean atomic weight of cations.

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