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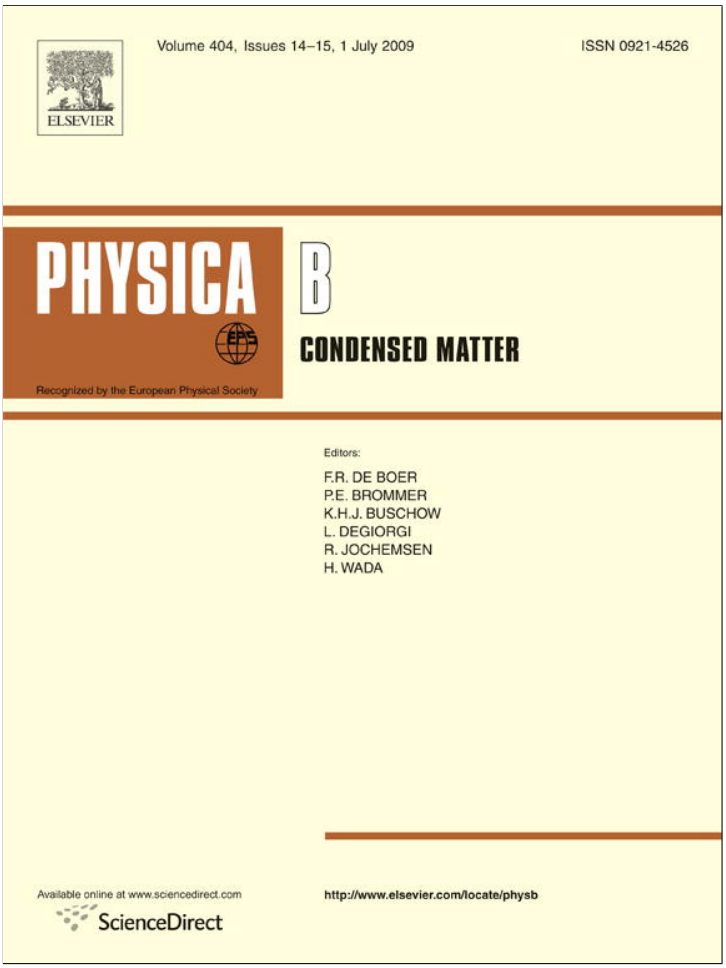

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Compositional dependence of Raman scattering and photoluminescence emission in Cu–Ga–Se films grown by MOCVD

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ABSTRACT

This paper presents Raman scattering and photoluminescence (PL) analysis of polycrystalline Cu–Ga–Se films grown epitaxially on the GaAs substrate. In the compositional dependence of the Raman spectra of the $CuGaSe_2$ films, the appearance of the ordered vacancy compounds (OVCs) $CuGa_3Se_5$ and $CuGa_5Se_8$ was observed. The dominating A_1 Raman modes were detected at 185, 166 and 159 cm^{-1}, respectively. The PL bands of $CuGaSe_2$, $CuGa_3Se_5$ and $CuGa_5Se_8$ at $T = 10$ K were detected at 1.615, 1.72 and 1.76 eV, respectively. The dominating PL emission channel is the band-to-tail (BT) type recombination.

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1. Introduction

The wide bandgap ternary chalcopyrite compound $CuGaSe_2$ is a promising material for optoelectronic devices. In this paper we will present the results of compositional dependent Raman and photoluminescence (PL) studies on ternary chalcopyrite semiconductor $CuGaSe_2$ in an attempt to investigate the effect of the Ga addition on its structural and optical properties. It is known that ternary chalcopyrite compounds tolerate large range of anion to cation off-stoichiometry that leads to the existence of a number of ordered defect compounds (ODCs) [1]. Ga-rich phases $CuGa_3Se_5$ and $CuGa_5Se_8$ have been reported [2,3] in the Cu_2Se–Ga_2Se_3 quasi-binary system. These compounds are called ordered defect compounds since Zhang et al. [1] have explained the existence and stability of such compounds in the related Cu–In–Se system with the presence of $(In_{Cu}^{2+} + 2V_{Cu}^{-1})$ donor–acceptor defect pairs (DADPs) that have very low formation energies. These compounds are also referred to as ordered vacancy compounds (OVCs), because vacancies are expected to orderly occupy particular crystallographic sites in their crystal structure to satisfy the four electrons per site rule [4]. It is expected that the ordered defect compound $CuIn_3Se_5$ that precipitates as a secondary phase on the thin film surface of In-rich $CuInSe_2$ will improve the efficiency of $CuInSe_2$ based solar cells [5]. It is important to understand the effect of the ordered arrays of defects on the electrical and optical properties of opto-electronical devices, when one considers these compounds for photovoltaic applications.

There are several papers published about the Raman and PL properies of $CuGaSe_2$ [6–8]. However, little information can be found in the literature about the PL and Raman properties of OVCs in Cu–Ga–Se system. We have investigated the low-temperature PL properties of $CuGa_3Se_5$ single crystals and found one PL band at 1.76 eV resulting from band-to-tail (BT) type recombination [9], indicating the presence of potential and compositional fluctuations in the crystals. Rincon et al. [2] have investigated photoluminescence, infrared reflectivity and Raman spectra of $CuGa_3Se_5$. They found that the main PL emission at 1.63 eV is due to the donor–acceptor pair (DAP) recombination and estimated the donor and acceptor activation energies 15 and 300 meV, respectively. However, the asymmetric shape and the large blueshift of the PL band with increasing excitation intensity are in contradiction with the DAP recombination theory. We believe

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that the observed emission is related to the recombination involving the band tails as it was found in Ref. [9] for another PL band with similar properties in $CuGa_3Se_5$. They also combined the analysis of IR and Raman spectra and assigned the corresponding vibrational modes of $CuGa_3Se_5$. The most intense peak at 166 cm^{-1} was assigned to the A_1 mode. From the X-ray data, it has been established that $CuGa_3Se_5$ has a chalcopyrite-related structure that belongs to the space group $P\bar{4}2c$ and has unit cell parameters $a = 0.54995(8)$ nm and $c = 1.0946(3)$ nm [10].

To our knowledge, very little work on the optical properties of $CuGa_5Se_8$ appear in the literature and there is only one PL study of $CuGa_5Se_8$ published. We have investigated the PL properties of $CuGa_5Se_8$ [11] and found broad asymmetric bands at 1.788 and 1.765 eV at 10 K in the PL spectra of $CuGa_5Se_8$ single crystal and polycrystalline layer, respectively. The analyses of the PL data suggest that the emission is due to BT- or BI-type (band-to impurity) recombination, indicating the presence of potential fluctuations due to high concentration of charged defects. The temperature dependence of the energy gap in bulk samples of $CuGa_5Se_8$ have been reported by Marin et al. [12]. Xu et al. [2] have found seven peaks from room temperature Raman spectra of $CuGa_5Se_8$, the peak at 160 cm^{-1} being the dominant A_1 mode. Orlova et al. [13,14] have determined the unit cell parameters of $CuGa_5Se_8$ single crystals by using X-ray diffraction method: $a = 0.54682$ nm and $c = 1.09116$ nm. It was also found that $CuGa_5Se_8$ and $CuGa_3Se_5$ have very close values of thermal expansion coefficients and crystal lattice parameters. These properties of OVC compounds are essential for forming heterojunctions and for producing solar cells based on these ternary compounds.

2. Experimental methods

The Cu–Ga–Se thin films were grown in an Aixtron AIX200 MOCVD reactor on GaAs substrates. Cyclopentadienyl-copper, triethyl-gallium and ditertiary-butyl-selenide were used as Cu-, Ga- and Se-precursor, respectively. The growth process was derived from the process for $CuGaSe_2$ [7]. The growth temperature 570 °C was used and the reactor pressure was kept at 50 mbar during the processing time of 4 h. The dependence of the composition ratio on the partial pressure ratio was not linear. The ratio of Cu and Ga elemental compositions [Cu]/[Ga] varied from 1 to 0.19, as was determined by energy dispersive X-ray spectroscopy (EDX). Scanning electron microscopy (SEM) images of the samples showed the surface roughness and polycrystallinity of the Ga-rich films.

The room temperature Raman spectra were recorded by using a Horiba's LabRam HR high resolution spectrometer equipped with a multichannel detection system in the backscattering configuration. In micro-Raman measurements, the incident laser light with the wavelength of 532 nm is focused on the sample within a spot of 10 μm in diameter and the spectral resolution of the spectrometer is about 1.5 cm^{-1}. For PL measurements, the samples were mounted in the He cryostat and cooled down to 10 K. The 514 nm Ar^+ laser line was used for PL excitation.

3. Experimental results and discussion

3.1. Raman results

The chalcopyrite crystal $A^IB^{III}C_2^{VI}$ has eight atoms per primitive cell. Its vibrational spectrum consists of 24 zone-center vibrational modes:

$$1A_1 + 2A_2 + 3B_1 + 4B_2 + 7E,$$

where the E-modes are doubly degenerated. These modes are classified into 3 acoustic (B_2+E) and 21 optical modes ($1A_1$+$2A_2$+$3B_1$+$3B_2$+6E). Except for two silent modes ($2A_2$), there are 22 Raman active modes:

$$1A_1 + 3B_1 + 3B_2(LO) + 3B_2(TO) + 6E(LO) + 6E(TO).$$

A_1 mode is usually dominating the Raman spectra, because it involves only displacements of the anions with the cations remaining at rest [15]. The B_1 modes involve the motion of the cations and the B_2 and E modes correspond to the combined motion of all the atoms. The frequencies of the Raman modes are influenced by the great variety of defects in the chalcopyrite materials and deviation from stoichiometry. Therefore, for fundamental understanding of the structural properties of chalcopyrites, it is important to investigate their vibrational properties.

The compositional dependence of the room temperature Raman spectra of Cu–Ga–Se films is shown in Fig. 1. The appearance of $CuGa_3Se_5$ and $CuGa_5Se_8$ phases in the spectra of

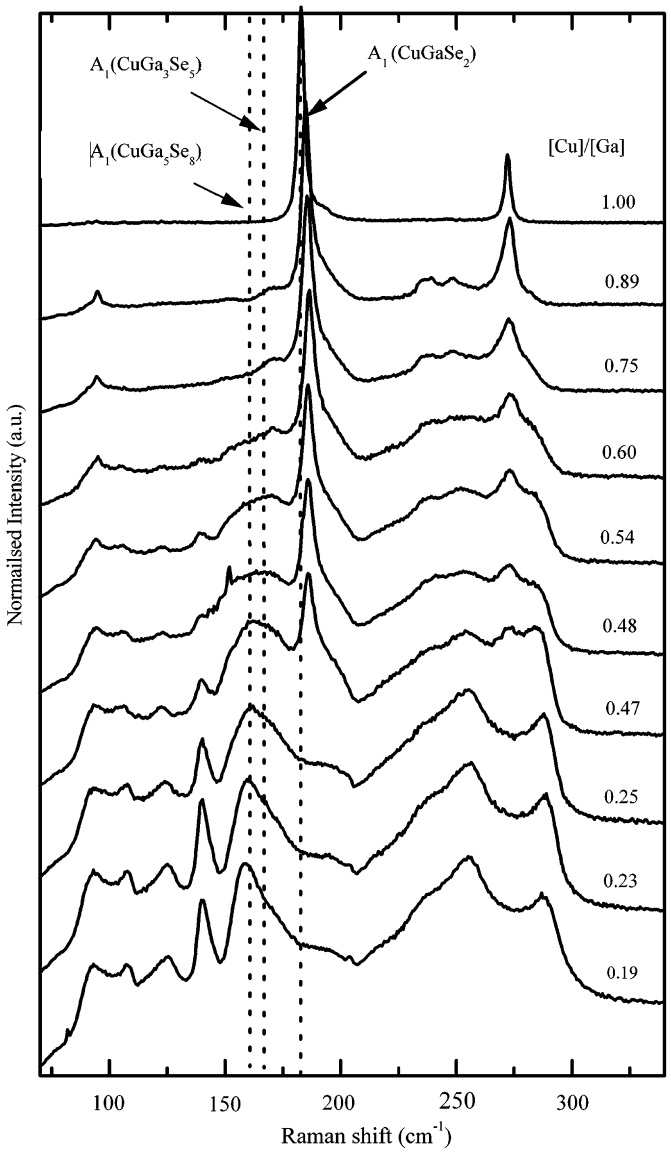

Fig. 1. Room temperature Raman spectra of Cu–Ga–Se films with different [Cu]/[Ga] ratios. The Raman peaks at 185, 166 and 159 cm^{-1} correspond to A_1 mode of $CuGaSe_2$, $CuGa_3Se_5$ and $CuGa_5Se_8$, respectively.

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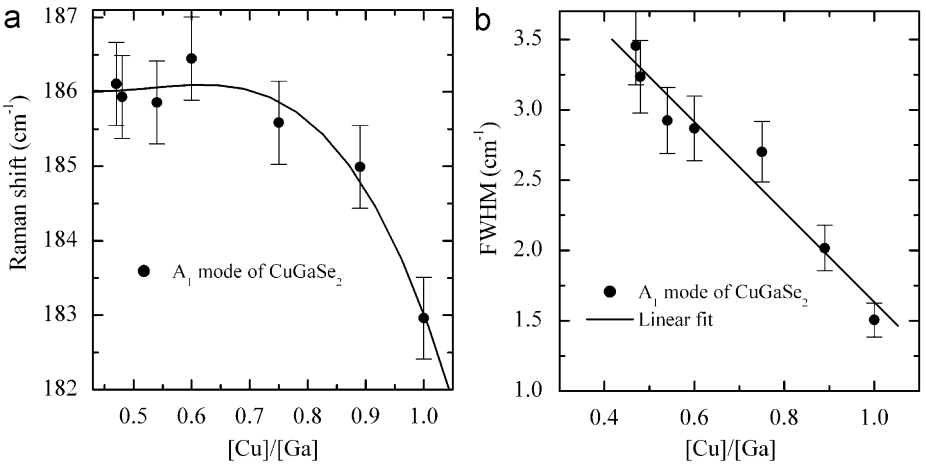

Fig. 2. Compositional dependence of the peak position of the A_1 Raman mode of $CuGaSe_2$ (a) and its FWHM (b).

$CuGaSe_2$ films is visible with decreasing [Cu]/[Ga] ratio. The dominating A_1 Raman peaks were detected at 185, 166 and 159 cm^{-1} for $CuGaSe_2$, $CuGa_3Se_5$ and $CuGa_5Se_8$, respectively. The presence of binary phases in the films was not detected from the spectra.

According to the simplified version of Keating's model [15], the frequency of the A_1 mode v is given by $v \approx \sqrt{k/M_{Se}}$, where M_{Se} is the mass of the Se atom and k being the force constant related to the cation–anion bond-stretching forces. Due to the presence of the vacancy in the OVC the stretching forces are relaxed, thus reducing slightly the corresponding vibrational frequencies compared to chalcopyrites with 1:1:2 stoichiometry. Since in first approximation the vibrational frequencies in chalcopyrites depend mainly on the nearest neighbor atoms interaction [15] and taking also into account that one vacancy exists for each four and five Se atoms in $CuGa_5Se_8$ and $CuGa_3Se_5$, respectively, it was proposed in Ref. [16] that for the A_1 mode k is reduced by 25% and 20% for $CuGa_5Se_8$ and $CuGa_3Se_5$, respectively, as compared to its value in the normal chalcopyrites. Under this assumption, frequencies $v' \approx \sqrt{0.75k/M_{Se}} \approx 0.87v$ and $v' \approx \sqrt{0.8k/M_{Se}} \approx 0.89v$ of this mode, where v is the frequency in the normal chalcopyrites, is to be expected for $CuGa_5Se_8$ and $CuGa_3Se_5$, respectively. The frequency of the A_1 mode for $CuGaSe_2$ at room temperature is 184 cm^{-1} [17], giving us the frequencies of 164 and 161 cm^{-1} for the A_1 mode in $CuGa_3Se_5$ and $CuGa_5Se_8$, respectively. The recorded A_1 mode frequencies were 185, 166 and 159 cm^{-1} for $CuGaSe_2$, $CuGa_3Se_5$ and $CuGa_5Se_8$, respectively. The obtained wavenumbers are in very good agreement with the theoretically expected values.

The A_1 mode frequency of $GuGaSe_2$ shows nonlinear shift to higher wavenumbers with the decrease of Cu content up to [Cu]/[Ga] = 0.47 (Fig. 2a). From the Raman spectra of films with lower [Cu]/[Ga] ratios only the presence of $CuGa_5Se_8$ phase was detected. Apart from the frequency, also the full width at half maximum (FWHM) of the A_1 Raman band of $CuGaSe_2$ (Fig. 2b) and all other modes is broadening with the increase of Ga content. Similar behavior has been observed in $CuIn_{1-x}Ga_xSe_2$ [18], $Cu(In_{1-x}Ga_x)_5Se_8$ [3] and $Cu(In_{1-x}Ga_x)_3Se_5$ [19] films. Differences in the degree of disorder and increasing defect concentration are believed to be responsible for the observed changes in Raman mode width as a function of the [Cu]/[Ga] ratio. Therefore, the broadening of the Raman bands can be an indication of a large defect density in the OVC's. The PL results presented below also show the increasing defect concentration with increase in Ga concentration.

The Raman modes of $CuGaSe_2$, $CuGa_3Se_5$ and $CuGa_5Se_8$ were also discussed in more detail in Refs. [2,11,17].

3.2. Photoluminescence results

According to Zhang et al. [1], the creation of periodic V_{Cu} reduces the Se p–Cu d interband repulsion in the OVC's, as compared to $CuInSe_2$. This effect lowers the valence band maximum of $CuIn_3Se_5$ and $CuIn_5Se_8$. This phenomenon has been observed also in $CuGaSe_2$ [20]. Although the defect pair $(III_{Cu}^{2+}+2V_{\bar{Cu}})$ also lowers the conduction band minimum, the first effect predominates, because the p–d repulsion is very strong in the selenides of the OVC's [21]. Therefore the bandgap of OVC's is wider and the PL emission is observed at higher energies. The available published values of the room temperature bandgap energies of $CuGaSe_2$, $CuGa_3Se_5$ and $CuGa_5Se_8$ thin films and polycrystalline bulk samples are 1.64–1.70 eV [22,23], 1.74–1.87 eV [10,24–28] and 1.78–1.97 eV [12,22,27–29], respectively. The wide range of bandgap energies is, besides different crystallinity of the materials, probably related to the presence of Urbach's tail in the optical absorption spectra, making the precise bandgap determination somewhat complicated.

Fig. 3 shows low-temperature PL spectra of Cu–Ga–Se films with different [Cu]/[Ga] ratios, ranging from $0.19 \leqslant$ [Cu]/[Ga] $\leqslant 1.00$. The observed PL properties as a function of [Cu]/[Ga] ratio can be summarized as follows:

1. [Cu]/[Ga] = 1: Stoichiometric $CuGaSe_2$ film shows PL peak at 1.615 eV. It was proposed in Ref. [6] that PL band at 1.617 eV originates from the band-tail recombination.
2. $0.6 \leqslant$ [Cu]/[Ga] $\leqslant 1$: The PL spectra of Cu-poor $CuGaSe_2$ films show single broad emission band with an asymmetric lineshape. It has an exponential slope on the low-energy side and steeper Gaussian incline on the high-energy side. With increasing Ga content the emission band broadens and shows redshift. This behavior indicates that due to high concentration of native defects resulting from the off-stoichiometry of the films, there are potential fluctuations present in these Cu-poor films as has been observed before. It was proposed in Ref. [7] that this emission results from so-called quasi-DAP transition. The theory of radiative recombination mechanisms in case of Coulomb potential fluctuations can be found in Ref. [30].
3. $0.47 \leqslant$ [Cu]/[Ga] $\leqslant 0.54$: New band at around 1.72 eV appears in the PL spectra. This band originates from the $CuGa_3Se_5$ phase.

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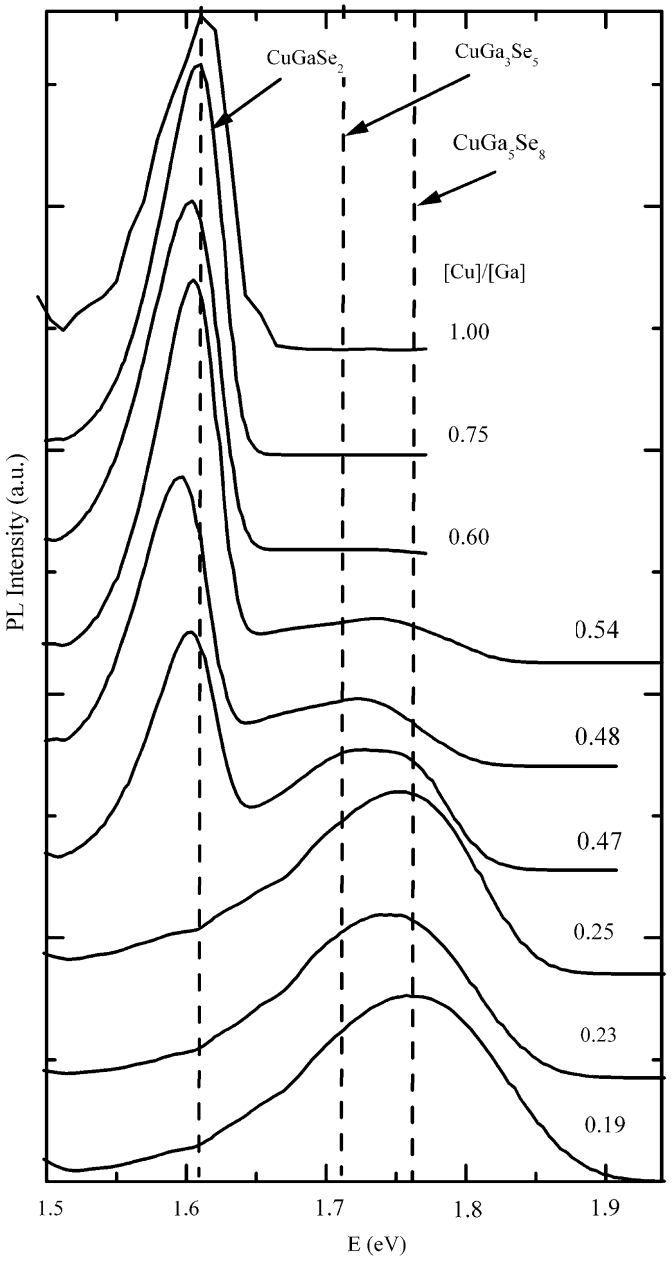

Fig. 3. Compositional dependence of PL spectra of Cu–Ga–Se films at 10 K. The PL bands of $CuGaSe_2$, $CuGa_3Se_5$ and $CuGa_5Se_8$ were detected at 1.615, 1.72 and 1.76 eV, respectively. Predicted peak positions for different phases are indicated by dashed lines.

Unfortunately we were unable to grow pure $CuGa_3Se_5$ films. Similarly to the PL band from Cu-poor $CuGaSe_2$, the band at 1.72 eV results from radiative recombination governed by the recombination of carriers localized in spatially separated potential wells originating from Coulomb potential fluctuations. The PL properties of $CuGa_3Se_5$ are discussed in more detail in Ref. [9], where it is proposed that this emission results from the BT -type recombination. The film with $[Cu]/[Ga] = 0.47$ shows a shoulder around 1.76 eV that originates from the $CuGa_5Se_8$ phase. The corresponding Raman spectra also show the coexistence of $CuGaSe_2$ and related ordered defect phases $CuGa_3Se_5$ and $CuGa_5Se_8$.

4. $0.19 \leqslant [Cu]/[Ga] \leqslant 0.25$: The $CuGaSe_2$ phase is no longer present in the samples as can also be seen from the Raman spectra of the films with these compositions. The Ga-rich films show only broad asymmetric emission from $CuGa_5Se_8$ that results similarly to the emission of $CuGa_3Se_5$ films from BT- or BI-type recombination as was proposed in Ref. [11], where more detailed discussion the PL properties of $CuGa_5Se_8$ can be found.

4. Conclusions

In conclusion, the compositional dependence of the Raman and PL properties of polycrystalline Cu–Ga–Se films was studied. The appearance of the OVCs $CuGa_3Se_5$ and $CuGa_5Se_8$ was observed in the Raman and PL spectra of $CuGaSe_2$ films with increasing Ga concentration. The A_1 Raman modes were detected at 185, 166 and 159 cm^{-1}, respectively. The broadening of the Raman modes with increasing Ga concentration was detected and it was assigned to the increasing defect concentration in the films. The PL bands of $CuGaSe_2$, $CuGa_3Se_5$ and $CuGa_5Se_8$ were detected at 1.615, 1.72 and 1.76 eV, respectively, at 10 K. The photoluminescence analysis showed the presence of potential fluctuations in the Cu–Ga–Se films.

Acknowledgments

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