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

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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 CuGaSe₂ films, the appearance of the ordered vacancy compounds (OVCs) CuGa₃Se₅ and CuGa₅Se₈ was observed. The dominating A₁ Raman modes were detected at 185, 166 and 159 cm⁻¹, respectively. The PL bands of CuGaSe₂, CuGa₃Se₅ and CuGa₅Se₈ 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 CuGaSe₂ 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 CuGaSe₂ 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 CuGa₃Se₅ and CuGa₅Se₈ have been reported [2,3] in the Cu₂Se–Ga₂Se₃ 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 \((\text{In}²⁺_\text{Cu}^\text{+}) + 2\text{V}_{\text{Cu}}\) 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 CuIn₃Se₅ that precipitates as a secondary phase on the thin film surface of In-rich CuInSe₂ will improve the efficiency of CuInSe₂ 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 properties of CuGaSe₂ [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 CuGa₃Se₅ 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 CuGa₃Se₅. 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...
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 CuGa3Se5. They also combined the analysis of IR and Raman spectra and assigned the corresponding vibrational modes of CuGa3Se5. The most intense peak at 166 cm^{-1} was assigned to the A1 mode. From the X-ray data, it has been established that CuGa3Se5 has a chalcopyrite-related structure that belongs to the space group P42c 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 CuGa5Se8 appears in the literature and there is only one PL study of CuGa5Se8 published. We have investigated the PL properties of CuGa5Se8 [11] and found broad asymmetric bands at 1.788 and 1.765 eV at 10 K in the PL spectra of CuGa5Se8 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 CuGa5Se8 has been reported by Marin et al. [12]. Xu et al. [2] have found seven peaks from room temperature Raman spectra of CuGa5Se8 at 160 cm^{-1} and have suggested that the peak at 160 cm^{-1} is due to the band-to-band transition.

Orlova et al. [13,14] have determined the unit cell parameters of CuGa5Se8 and found that the peak at 160 cm^{-1} is due to the A1 mode. From the X-ray data, it has been established that CuGa3Se5 has a chalcopyrite-related structure that belongs to the space group P42c and has unit cell parameters a = 0.54995 nm and c = 1.09116 nm. It was also found that CuGaSe2 and CuGa3Se5 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 diteriary-butyl-selenide were used as Cu-, Ga- and Se-precursor, respectively. The growth process was derived from the process for CuGaSe2 [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 growth temperature 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 AIBIIIC2⅏ 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:

\[1A_1 + 3B_1 + 3B_2(LO) + 3B_2(TO) + 6E(LO) + 6E(TO).\]

The A1 mode is usually dominating the Raman spectra, because it involves only displacements of the anions with the cations remaining at rest [15]. The B1 modes involve the motion of the cations and the B2 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 CuGa3Se5 and CuGa5Se8 phases in the spectra of CuGa5Se8 and CuGa3Se5 have been reported by Marin et al. [12]. Xu et al. [2] have found seven peaks from room temperature Raman spectra of CuGa5Se8 at 160 cm^{-1} and have suggested that the peak at 160 cm^{-1} is due to the A1 mode of CuGaSe2, CuGa3Se5 and CuGa5Se8, respectively.
CuGaSe₂ films is visible with decreasing [Cu]/[Ga] ratio. The dominating A₁ Raman peaks were detected at 185, 166 and 159 cm⁻¹ for CuGaSe₂, CuGa₃Se₅ and CuGa₅Se₈, 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 A₁ mode ν is given by \( \nu = \sqrt{k/M_{\text{se}}} \), where \( M_{\text{se}} \) 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 CuGa₅Se₈ and CuGa₃Se₅, respectively, it was proposed in Ref. [16] that for the A₁ mode \( k \) is reduced by 25% and 20% for CuGa₅Se₈ and CuGa₃Se₅, respectively, as compared to its value in the normal chalcopyrites. Under this assumption, frequencies \( \nu \approx \sqrt{0.75k/M_{\text{se}}} \approx 0.87\nu \) and \( \nu \approx \sqrt{0.8k/M_{\text{se}}} \approx 0.89\nu \) of this mode, where \( \nu \) is the frequency in the normal chalcopyrites, is to be expected for CuGa₅Se₈ and CuGa₃Se₅, respectively. The frequency of the A₁ mode for CuGaSe₂ at room temperature is 184 cm⁻¹ [17], giving us the frequencies of 164 and 161 cm⁻¹ for the A₁ mode in CuGa₅Se₈ and CuGa₃Se₅, respectively. The recorded A₁ mode frequencies were 185, 166 and 159 cm⁻¹ for CuGaSe₂, CuGa₃Se₅ and CuGa₅Se₈, respectively. The obtained wavenumbers are in very good agreement with the theoretically expected values.

The A₁ mode frequency of GuGaSe₂ 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 CuGa₅Se₈ phase was detected. Apart from the frequency, also the full width at half maximum (FWHM) of the A₁ Raman band of CuGaSe₂ (Fig. 2b) and all other modes is broadening with the increase of Ga content. Similar behavior has been observed in CuIn₀.₅Ga₁.₅Se₈ [18], Cu(In₀.₃Ga₀.₇)₃Se₈ [3] and Cu(In₀.₃Ga₀.₇)₅Se₈ [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 OVCs. The PL results presented below also show the increasing defect concentration with increase in Ga concentration.

The Raman modes of CuGaSe₂, CuGa₃Se₅ and CuGa₅Se₈ 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 VCu reduces the Se p–Cu d interband repulsion in the OVCs, as compared to CuInSe₂. This effect lowers the valence band maximum of CuInSe₂ and CuIn₃Se₅. This phenomenon has been observed also in CuGaSe₂ [20]. Although the defect pair (IIICu₂++) also lowers the conduction band minimum, the first effect predominates, because the p–d repulsion is very strong in the selenides of the OVCs [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 CuGaSe₂, CuGa₃Se₅ and CuGa₅Se₈ 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 ≤ [Cu]/[Ga] ≤ 1.00. The observed PL properties as a function of [Cu]/[Ga] ratio can be summarized as follows:

1. [Cu]/[Ga] = 1: Stoichiometric CuGaSe₂ 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 ≤ [Cu]/[Ga] ≤ 1: The PL spectra of Cu-poor CuGaSe₂ films show single broad emission band with an asymmetric line-shape. 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 ≤ [Cu]/[Ga] ≤ 0.54: New band at around 1.72 eV appears in the PL spectra. This band originates from the CuGa₃Se₅ phase.
bands of CuGaSe₂, CuGa₃Se₅ and CuGa₅Se₈ were detected at 1.615, 1.72 and 1.76 eV, respectively. The broadening of the 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 CuGaSe₂, CuGa₃Se₅ and CuGa₅Se₈ 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.

**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 CuGaSe₂ and CuGa₃Se₅ was observed in the Raman and PL spectra of CuGaSe₂ films with increasing Ga concentration. The Aₑ 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 CuGaSe₂, CuGa₃Se₅ and CuGa₅Se₈ 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.

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**References**


Unfortunately we were unable to grow pure CuGa₃Se₅ films. Similarly to the PL band from Cu-poor CuGaSe₂, 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 CuGaSe₂ 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 CuGa₅Se₈ phase. The corresponding Raman spectra also show the coexistence of CuGaSe₂ and related ordered defect phases CuGa₃Se₅ and CuGa₅Se₈.

4. 0.19<=[Cu]/[Ga]<0.25: The CuGaSe₂ 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 CuGa₅Se₈ that results similarly to the emission of CuGa₃Se₅ films from BT- or Bl-type recombination as was proposed in Ref. [11], where more detailed discussion the PL properties of CuGa₅Se₈ can be found.