

Optoelectrical properties for CuGaSe₂ layers grown by hot wall epitaxy

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CuGaSe₂ (CGS) layers were grown by the hot wall epitaxy method. The optimum temperatures of the substrate and source for the growth turned out to be 450 and 610 °C, respectively. The CGS layers were epitaxially grown along the <110> direction and retained the initial mole fraction during the layer growth. Based on an absorption measurement, the band-gap variation of CGS was well interpreted by Varshni's equation. But, the band-gap energies at low temperatures were large values unlike that of other CGS. From a low-temperature photoluminescence experiment, sharp and intensive free- and bound-exciton peaks were observed. By analyzing these emissions, a band diagram of the observed optical transitions was obtained.

Key words: A1. Characterization, A3. Hot wall epitaxy, B2. Semiconducting ternary compounds.

Introduction

The I-III-VI₂ compounds are known to be ternary analogues of the II-VI compounds. These compounds crystallize with the chalcopyrite structure, which is closely related to the zinc structure [1]. These materials have received considerable attention in recent years because of their applications in photovoltaic devices [2, 3]. They can be used as environmental-friendly materials for the Cd-free buffer layer as an absorbant of solar cells [4, 5]. Among these compounds, copper gallium selenide (CuGaSe₂, CGS) has an energy gap of 1.68 eV at room temperature and it is expected to be a promising material for red-light-emitting devices. Currently, solar cells based on CGS have achieved efficiencies of 9.5% and 9.7% as absorber of thin film and single crystal shapes, respectively [6, 7]. Despite this technological progress, many of the fundamental properties of CGS are still not fully understood. But, the physical properties strongly relate to native defects due to deviations of the stoichiometry. Therefore, a reduction of the stoichiometry deviations during crystal growth is required. As such, CGS layers have been grown by many different techniques such as metalorganic chemical vapor deposition (MOCVD), metalorganic vapor phase epitaxy (MOVPE), physical vapor deposition (PVD), RF sputtering, and flash evaporation [8-12]. In fact, hot wall epitaxy (HWE), which has been used to grow a high-purity ZnSe epitaxial layer at low temperatures [13], is one of the better methods for CGS growth. Thus, HWE has been especially designed to grow epilayers under the condition of near thermodynamic equilibrium [14]. But, CGS growth by the HWE method has rarely been reported before now.

In this paper, the CGS layers, which could be used as

the absorbant of a solar cell, were grown on a GaAs substrate by the HWE method. The grown CGS layers were investigated for their structural and optical characterization by means of X-ray diffraction (XRD), photoluminescence (PL), and absorption spectroscopy. From these results, a discussion of the structural and optical properties of the CGS layers is given.

Experimental Procedures

Prior to the layer growth, polycrystalline CGS was formed as follows. A quartz tube was sequentially cleaned with trichlorethylene, acetone, methanol, and deionized water. The starting materials were 6 N purity shot-types of Cu, Ga, and Se. After the materials were weighed to the mole fraction of each element, they were sealed in the quartz tube while maintaining a vacuum atmosphere.

The sealed ampoule was placed in a synthesis furnace and was continually rotated at a rate of 1 revolution per minute. In order to avoid an explosion of the ampoule due to the Se vapor pressure, the temperature of the ampoule was gradually increased to 1180 °C, and was then maintained for 48 hours. To grow the CGS layer, a polycrystalline CGS ingot was used for the HWE source. The CGS layers were grown on semi-insulating GaAs (100) by the HWE method using the grown CGS ingot as a source material. Figure 1 presents a schematic diagram of the HWE apparatus used for the CGS growth. Prior to growing the CGS layers, the GaAs substrate was cleaned ultrasonically for 1 minute in successive baths of trichloroethylene, acetone, methanol and 2-propanol, and then etched for 1 minute in a solution of H₂SO₄ : H₂O₂ : H₂O (5 : 1 : 1). The substrate was degreased in organic solvents and rinsed with deionized water (18.2 MW). After the substrate was dried off, it was immediately loaded onto the substrate holder in Fig. 1 and was annealed at 580 °C for 20 minutes to remove the residual oxide on the

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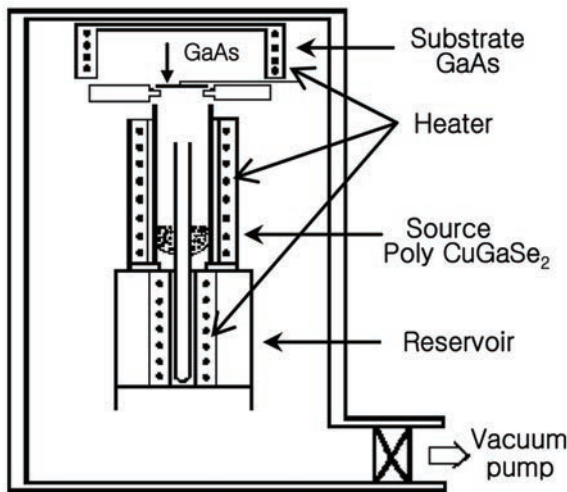


Fig. 1. Schematic diagram of the HWE apparatus used for the CGS growth.

surface of the substrate. To obtain the optimum growth conditions, the grown CGS layers were estimated through PL and XRD measurements. The PL measurement of the sample was performed at 10 K in a low temperature cryostat during the excitement by a He-Ne laser (632.8 nm, 50 mW). The thickness, growth orientation, and stoichiometric composition of the CGS layers were measured by using an α -step profilometer, XRD, and an energy dispersive X-ray spectrometer (EDS), respectively. Optical absorption was used to measure the band-gap energy using an UV-VIS-NIR spectrophotometer for a wavelength range of 670 to 750 nm with the temperature varying from 10 to 293 K.

Results and Discussion

Growth and structural properties

After the heat treatment of the substrate surface, the CGS layers were grown by varying the substrate temperature from 410 to 470 °C, while the source temperature was fixed at 610 °C. At this stage, the crystal quality of the grown CGS layers was evaluated by measuring the PL spectra at 10 K and, the FWHM value of XRD was also considered. Exciton emissions were used to predict the crystal-quality criterion of the grown layer because the exciton could only be observed in a less defective crystal at a low temperature. Here, the emissions of free excitons (E_{FX}) and bound excitons (E_{BX}) were used for the optimum growth conditions. The grown layers were considered

Table 1. Comparison of the PL intensities and the XRD as a function of substrate temperature (arbitrary units)

Substrate Temperature (°C)	Intensities of PL at 10 K		XRD (one theta)
	E_{FX}	E_{BX}	FWHM (arcsec)
410	5.75	7.36	1827
430	10.72	16.84	1163
450	26.19	37.36	457
470	21.35	30.90	651

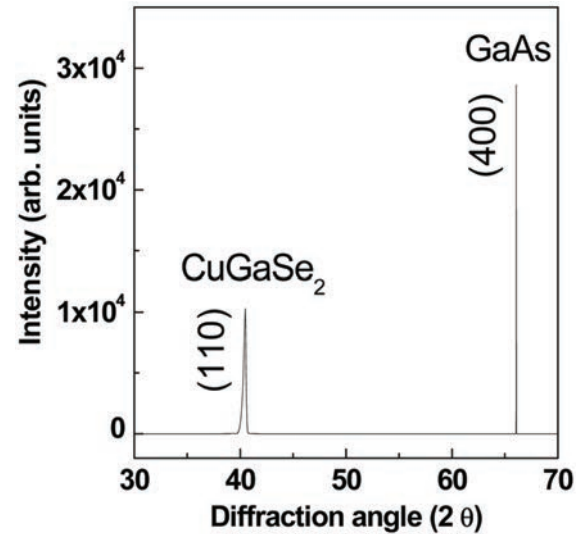


Fig. 2. XRD ω -2 θ scans of the CGS layer grown under optimized conditions.

to have good crystal quality when the measured PL spectra showed that the intensities of E_{FX} and E_{BX} tend to increase. As shown in Table 1, the E_{FX} and the E_{BX} peaks in the layer, which were grown while the substrate temperature was kept at 450 °C, had a higher intensity than all the other samples. By contrast, the narrowest FWHM, which indicated high crystal quality, obtained from the XRD experiment was observed in the CGS layer grown at 450 °C as well. This observation indicates that the CGS layer grown at 450 °C has a very high quality because the exciton emission can be observed only under the condition of a long-range Coulomb coupling between the electron and the hole. Therefore, the optimum temperature of the substrate was found to be 450 °C while the source temperature was 610 °C. At this stage, the thickness and the growth rate of the layer were 2.5 μm and 0.83 $\mu\text{m/h}$, respectively. Figure 2 presents the XRD ω -2 θ scans of the CGS layers grown at the source and substrate temperatures of 610 and 450 °C, respectively. Thus, the curve obtained corresponds to the diffraction peaks of the CGS (110) and GaAs (004). This means that the orientation of the layer grown on the GaAs (100) substrate is converted to the (110) plane. This phenomenon was also observed in a CdTe epilayer grown on the GaAs (100). Faurie et al. [15] reported that the orientation of the CdTe epilayer was related to the pre-annealing process used to remove the residual oxide on the surface of the substrate. They concluded that the growth of the CdTe (100) or (111) planes on the GaAs (100) was possible by controlling the different annealing temperatures and times of the substrate. On the other hand, the observation of only one peak of the CGS (110) indicates that the CGS layer was grown epitaxially along the $\langle 110 \rangle$ direction onto the GaAs (100) substrate. This orientation is suggested to be beneficial for a CGS layer to be fabricated for solar energy conversion. Also, the CGS (110) peak is located at two theta of 40.489° and its FWHM value is 0.205°. This

Table 2. Composition ratios of each element on the synthesized polycrystalline and the CGS layer analyzed by EDS measurements (atomic %)

Elements	Synthesized polycrystalline		Grown layer	
	Before synthesis	After synthesis	Before growth	After growth
Cu	37.610	36.882	36.882	37.426
Ga	40.034	40.799	40.034	40.591
Se	22.356	22.319	22.319	21.983

FWHM value is similar to that of CGS grown from MOCVD by Orsal et al. [16]. Therefore, it should be noted that the layers grown by the HWE method are high quality crystalline. The mean crystallite size of the layer can be extracted from

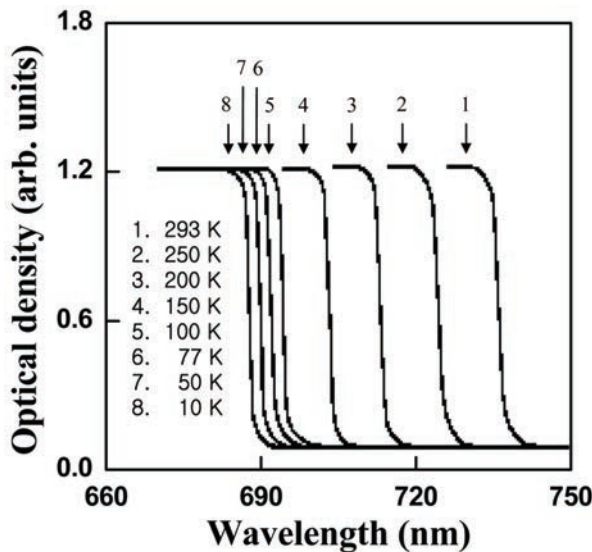
$$D = 0.94\lambda / (B \cos \theta) \quad (1)$$

where λ , θ , and B are the X-ray wavelength (0.15405 nm), the Bragg diffraction angle, and the FWHM value on the (110) peak in radians, respectively [17]. From the Eq. (1), the mean crystallite size was estimated to be about 81 nm.

Table 2 presents the composition ratios of each element during the growth process of the CGS layer, analyzed by EDS measurements. As shown in Table 2, the component ratios of the initial mole fraction were continuously maintained during the layer growth. Consequently, this suggests that the grown CGS layer was formed stoichiometrically.

Optical properties

Figure 3 shows the optical absorption spectra obtained in the temperature range from 10 K to 293 K. To identify the band-gap energy for the CGS layer, we carefully examined the relationship between the optical absorption coefficient (α) and the incident photon energy ($h\nu$) from the optical absorption measurements in Fig. 3. The


Fig. 3. Optical absorption spectra according to the variation of the measurement temperature.

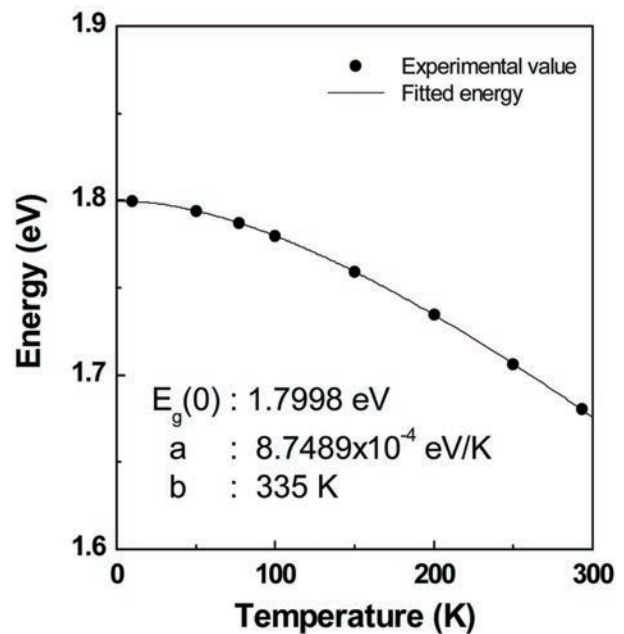
relationship for a direct band gap between $h\nu$ and a is given by:

$$(\alpha h\nu)^2 \sim (h\nu - E_g) \quad (2)$$

According to Eq. (2), $(\alpha h\nu)^2$ linearly depends upon the photon energy. From the plots of $(\alpha h\nu)^2$ versus photon energy for different temperatures, the band gaps may be determined by extrapolating the linear portions of the respective curves to $(\alpha h\nu)^2 = 0$. Figure 4 displays the band-gap variation of the CGS layer as a function of temperature. The temperature dependence of the band-gap energy in our experiment is well fitted numerically by the following formula [18, 19]:

$$E_g(T) = E_g(0) - aT^2 / (T + b) \quad (3)$$

where a is a constant and b is approximately the Debye temperature. Also, $E_g(0)$ is the band-gap energy at 0 K, which is estimated to be 1.7998 eV. When a and b are taken to be 8.7489×10^{-4} eV/K and 335 K, respectively, the curve plotted by Eq. (3) closely fits the experimental values. Our result on the Debye temperature is also in close agreement with the reported value of 394 K [20]. Thus, the band-gap energy of the CGS obtained at 293 K


Fig. 4. Band-gap variation of the CGS layer as a function of temperature.

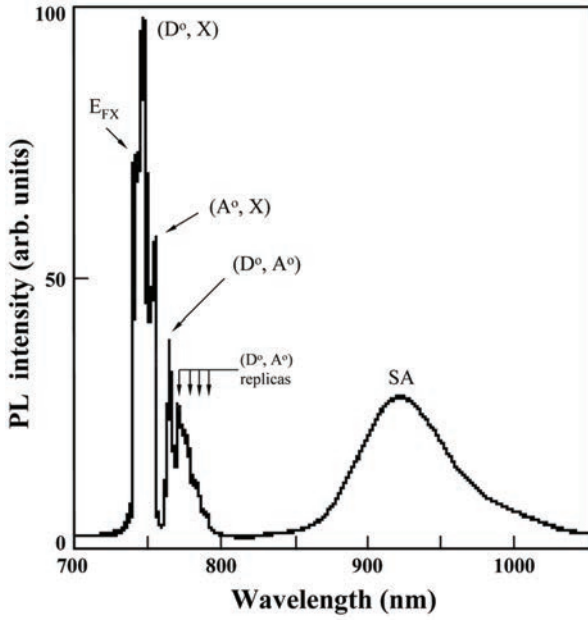


Fig. 5. PL spectrum of the CGS layer measured at 10 K.

is estimated to be 1.6802 eV.

Figure 5 shows a typical PL spectrum of the CGS layer measured at 10 K. As shown in Fig. 5, an intense and sharp peak was observed at 747.2 nm (1.6593 eV). This peak is associated with the neutral donor bound exciton, (D^0, X), caused by the recombination from free exciton to neutral donor. Also, the E_{FX} at 741.6 nm (1.6718 eV) appears on the shoulder towards the short-wavelength region of the (D^0, X) emission. From the E_{FX} emission, the binding energy, E_{FX}^b , is obtained from:

$$E_{FX}^b = E_g(10) - E(E_{FX}) \quad (4)$$

where $E_g(10)$ is the band-gap energy at 10 K. The value of $E_g(10)$ was calculated to be 1.7995 eV using Eq. (3) and the E_{FX}^b is obtained to be 0.1277 eV. The E_{FX}^b value is about ten times larger than the reported one [21]. This is caused by the absence of a considerable concentration of defects and lattice strain at low temperatures. Therefore, we suggest that the increase of E_g at the low temperature is due to the activation of high photon-energy transitions as a result of the high quality crystallinity in the layer. Indeed, it means that the crystalline quality of the grown CGS layer is better than that of other CGSs. Also, the shoulder peak towards the long-wavelength region of the (D^0, X) emission appears at 755.5 nm (1.6411 eV). This peak is suggested to be the neutral acceptor bound exciton, (A^0, X). This bound exciton has been known to be related to the recombination of a free exciton to a neutral acceptor. The binding energy (E_{BX}^b) of the E_{BX} emission is obtained from:

$$E_{FX}^b = E(E_{FX}) - E(D^0, X) \text{ or } E(A^0, X) \quad (5)$$

Therefore, the E_{BX}^b values of the (D^0, X) and the (A^0, X) emissions are calculated to be 12.5 and 30.7 meV, respectively. In addition, the neutral donor-acceptor pair,

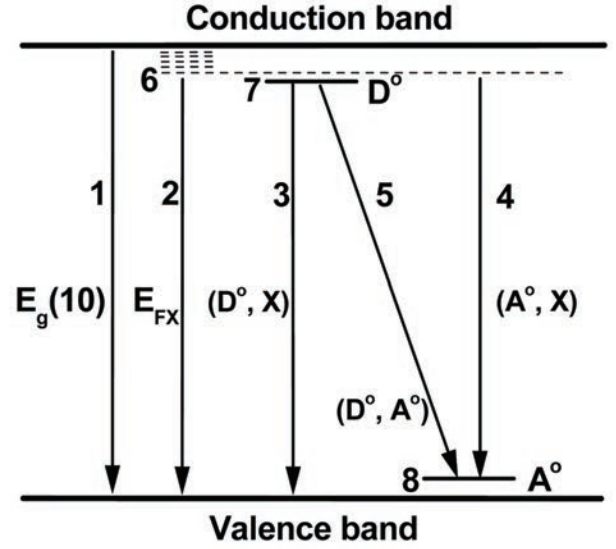


Fig. 6. Band diagram of the optical transitions on the CGS layer measured at 10 K. 1. Band-gap energy of CGS at 10 K: 1.7995 eV. 2. Free exciton energy: 1.6718 eV. 3. Neutral donor bound exciton energy: 1.6593 eV. 4. Neutral acceptor bound exciton energy: 1.6411 eV. 5. Neutral donor-acceptor pair energy: 1.6231 eV. 6. Binding energy of free exciton: 0.1277 eV. 7. Neutral donor levels: 0.1402 eV. 8. Neutral acceptor levels: 0.0307 eV.

(D^0, A^0), emission was observed at 763.9 nm (1.6231 eV). The (D^0, A^0) emission occurred due to the interaction between the neutral donor and the neutral acceptor states in the energy band gap. Thus, the replica peaks of the (D^0, A^0) emission are observed at 770.2 (1.6098 eV), 776.6 (1.5965 eV), 783.1 (1.5833 eV), and 789.5 nm (1.5704 eV). These peaks are considered to be associated with the longitudinal optical (LO) phonon replicas of the (D^0, A^0) emission, because the energy difference between these peaks is equal to a multiple of the LO phonon energy of B_2 -modes such as 13.3 (1LO), 26.6 (2LO), 39.8 (3LO), and 52.7 meV (4LO) [22]. The relatively low and broad peak caused by the self-activated (SA) emission was observed at 919.6 nm (1.3483 eV) in the longer-wavelength region. This emission strongly relates to the native defects formed in the CGS layer. Therefore, based on these PL results, we schemed out a band diagram of the recombination process on the CGS layer. Figure 6 plots the band diagram of the observed optical transitions including the band-gap energy of 10 K. In this band diagram, the $E_g(10)$ is the band-to-band transition corresponding to the band-gap energy. Also, the (D^0, A^0) emission is due to the recombination transition between the neutral donor and the neutral acceptor states in the band-gap energy.

Conclusions

CGS layers, which are now attracting interest as solar-cell materials, were grown by the HWE method. From the results of the PL and XRD measurements, the optimum growth temperatures of the substrate and the source turned out to be 450 and 610 °C, respectively. Also, the

CGS layers were confirmed to be epitaxially grown along the <110> direction onto GaAs (100) substrate. Thus, from the EDS measurements, the grown CGS layers were consistent with stoichiometry maintaining the initial mole fraction during the layer growth. The band-gap variation of CGS extracted from the absorption measurement was well fitted by $E_g(T) = 1.7998 - 8.7489 \times 10^{-4} T^2 / (T + 335)$. But, the band-gap energy at a low temperature is slightly larger than that of other CGSs. This fact means that the crystalline quality of the grown CGS layer is better than that of CGS grown by other methods. From the low-temperature PL measurements, the E_{FX} , the (D^0, X) , and the (A^0, X) emissions, which can be observed at the high-quality crystalline nature, appeared at 1.6718, 1.6593, and 1.6411 eV, respectively. Also, the (D^0, A^0) and its LO phonon replica emissions, which are due to the interaction between the neutral donor and the neutral acceptor states, were observed in the wavelength region between 770.2 and 789.5 nm. Based on these PL results, a band diagram of the observed optical transitions was obtained.

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