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Growth and optoelectrical properties of $CdIn_2S_4$ epilayers by hot wall epitaxy

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High quality $CdIn_2S_4$ epilayers on GaAs(100) substrates were first grown using a hot wall epitaxy (HWE) method. The $CdIn_2S_4$ epilayer was found to grow in the <110> direction. The optimum growth temperatures of the substrate and the source turned out to be 420 and 630 °C, respectively. From the measurements of the temperature dependence of the Hall mobility, the scattering in the high temperature range was mainly related to the acoustic mode of lattice vibrations and the scattering in the low temperature range was most pronounced due to an impurity effect. The temperature dependence of the energy band gap on the $CdIn_2S_4$/GaAs epilayer obtained from the optical absorption measurement was found to be $E_g(T) = 2.7116$ eV - $(7.65 \times 10^{-4}$ eV/K$)T^2/(425 + T)$.

Key words: $CdIn_2S_4$ epilayer, hot wall epitaxy, semiconducting ternary compound, Hall mobility, acoustic mode, impurity effect, energy band gap.

Introduction

Cadmium indium sulfide ($CdIn_2S_4$) is a semiconducting ternary chalcogenide of the type A^{II}-B_2^{III}-C_4^{IV}. The band gap of $CdIn_2S_4$ at room temperature is 2.62 eV with a direct transition. $CdIn_2S_4$ is one of the materials to have the potential capability for applications as photoconductors, solar cells, and light emitting diodes (LED) [1-4]. In order to realize these applications, it is of primary importance to grow high quality epilayers and characterize their fundamental properties. Such studies were carried out on bulk crystals that were grown by chemical transport and the Bridgman method over the past few years [2, 5-10]. Also, thin films of $CdIn_2S_4$ deposited using vacuum evaporation [11-13] have been achieved. However, the fundamental physical properties of the $CdIn_2S_4$ epilayers have rarely been investigated since it is hard to obtain high quality films. The growth of high quality $CdIn_2S_4$ epilayers is very difficult due to the stoichiometric deviation generated during the growth or the additional thermal treatment. It is been known that this stoichiometric deviation is strongly related to the native defects and self-compensation of the $CdIn_2S_4$. The stoichiometric deviation mainly occurrs when the partial vapor pressure of the sulfed is higher than that of the cadmium during the growth. Therefore, a low-temperature crystal growth method is required to suppress the stoichiometric deviation. The hot wall epitaxy (HWE) method [14], which has been used to grow high-purity ZnSe epilayers at low-temperatures [15], is one of the low-temperature crystal growth technologies. Thus, HWE has been especially designed to grow epilayers under the conditions of near thermodynamics equilibrium [16].

In this paper, we first tried to grow $CdIn_2S_4$/GaAs epilayers using HWE. The crystal quality of the grown $CdIn_2S_4$/GaAs epilayers was investigated by means of photoluminescence (PL) and the double crystal X-ray diffraction (DCXD) techniques. Also, electric and optical measurements on the grown $CdIn_2S_4$/GaAs epilayers have been carried out at temperatures ranging from 10 to 293 K. From these results, we will discuss the energy band gap as a function of temperature.

Experimental Procedures

Prior to the epilayer growth, polycrystalline $CdIn_2S_4$ was formed as follows. The starting materials were 6N purity shot-types of Cd, In, and S. After the materials were weighed in stoichiometric proportions, they were sealed in a quartz tube to maintain a vacuum atmosphere. Figure 1 shows the horizontal furnace used for the $CdIn_2S_4$ polycrystalline synthesis. The sealed ampoule was placed in the synthesis furnace and was continually rotated at a rate of 1 revolution per minute. In order to avoid the explosion of the ampoule due to the sulfur vapor pressure, the temperature of the ampoule was increased gradually to 1120, which was then maintained for 48 h. To grow the $CdIn_2S_4$ epilayer, a polycrystalline $CdIn_2S_4$ ingot was used for the HWE source. The $CdIn_2S_4$ epilayers were grown on semi-insulating GaAs (100) by the HWE method using the grown $CdIn_2S_4$ ingot as source materials. Figure 2 presents the HWE apparatus used for the $CdIn_2S_4$/GaAs growth. Prior to growing the $CdIn_2S_4$/GaAs epilayers, the GaAs substrate

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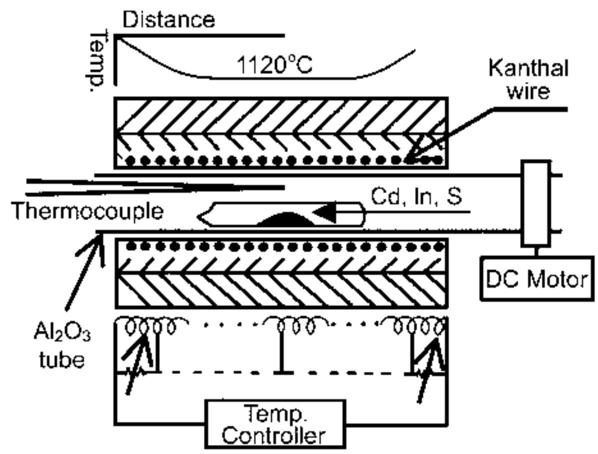

Fig. 1. Horizontal furnace for synthesizing $CdIn_2S_4$ polycrystalls.

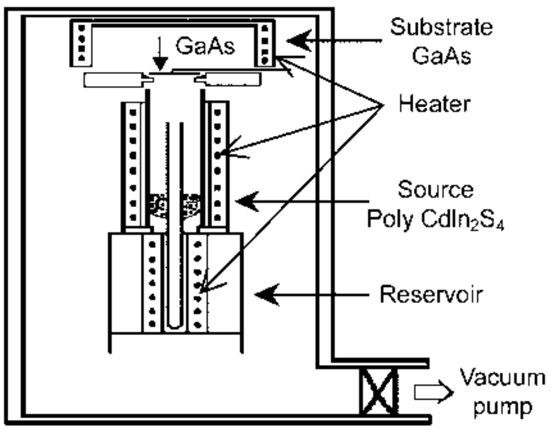

Fig. 2. Schematic diagram of a HWE apparatus.

was cleaned ultrasonically for 1 minute in successive baths of trichloroethylene, acetone, methanol and 2-propanol and etched for 1 minute in a solution of $H_2SO_4 : H_2O_2 :$ (5 : 1 : 1). The substrate was degreased in organic solvents, and rinsed with deionized water (18.2 MΩ). After the substrate was dried off, the substrate was immediately loaded onto the substrate holder in Fig. 2 and was annealed at 580 °C for 20 minute to remove the residual oxide on the surface of the substrate. To obtain the optimum growth conditions, the grown $CdIn_2S_4$/GaAs epilayers were analyzed by the PL and the DCXD measurements. The PL measurements of the samples were performed at 10 K in a low temperature cryostat (AP Inc. CSA 202B, DE 202S) with excitement by a He-Cd laser (Kimmon, 442 nm, 50 mW). The thickness of the $CdIn_2S_4$/GaAs was measured by an α-step profilometer (Tenco, α-step 200). Also, the electric properties were achieved from Hall effect measurements using the van der Pauw method at various temperatures. The optical absorption experiments to measure the energy band gap were performed with a UV-VIS-NIR spectrophotometer (Hitachi, U-3501) for a range from 400 nm to 800 nm with the temperature varied from 10 K to 293 K.

Result and Discussion

Optimum growth condition and structural properties

After heat treatment of the substrate surface, the $CdIn_2S_4$ epilayers were grown by changing the substrate temperature from 400 to 440 °C while the source temperature was fixed at 630 °C. To find the optimum growth conditions, PL measurements on the grown epilayers was performed at 10 K. Bound exciton, I_2, and self-activated (SA) emission were used as the crystal quality critera since the intensity of the I_2 peak tends to increase and the SA peak is inclined to decrease in the lower defect content at low temperature. As shown in Table 1, the highest I_2 peak and the very weak SA peak were observed from the epilayer which was grown while the substrate temperature was kept at 420 °C. Also, the $CdIn_2S_4$ epilayer only grown at the substrate temperature of 420 °C was measured by DCXD. Figure 3 shows the DCXD pattern of this $CdIn_2S_4$ epilayer. The full width at half maximum value of the $CdIn_2S_4$ epilayer was 127 arcsec. Therefore, to grow $CdIn_2S_4$/GaAs epilayers, the most suitable temperatures of the substrate and the source turned out to be 420 and 630 °C, respectively. Also, the thickness and the growth rate of the epilayer were 2.4 μm and 0.5 μm/h, respectively.

To confirm the orientation of the $CdIn_2S_4$ epilayer, X-ray diffraction (XRD) analysis was used. Figure 4 shows the XRD patterns of the $CdIn_2S_4$ epilayer grown on the GaAs substrate. These patterns correspond with diffraction peaks of the $CdIn_2S_4$ (110) and GaAs (400).

Table 1. Comparative PL intensity (in arbitrary units) as a function of substrate temperature when the source temperature was fixed at 630 °C (measured at 10 K)

Substrate temperature (°C)	I_2	SA
400	13.7	4.5
420	21.2	5.1
440	13.2	7.1

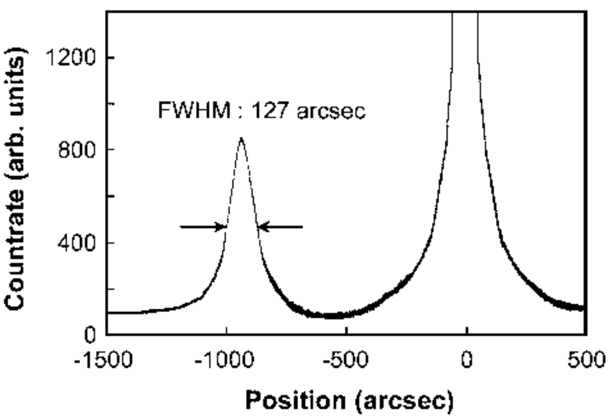

Fig. 3. The DCXD curves of a $CdIn_2S_4$ epilayer.

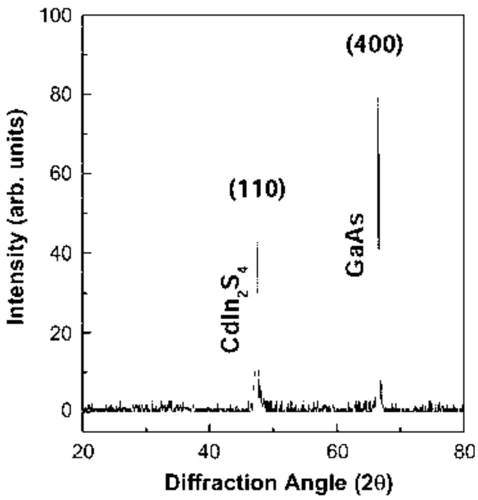

Fig. 4. XRD pattern of a $CdIn_2S_4$ epilayer grown on the GaAs substrate.

Thus, the observation of only the (110) peak indicates that the $CdIn_2S_4$ was grown epitaxially along the <110> direction onto the GaAs (100) substrate. Then, the orientation of the $CdIn_2S_4$ epilayer grown on the GaAs (100) substrate was converted to the (110) plane. This phenomenon has been observed in the CdTe epilayer grown on the GaAs (100) as well. Faurie *et al.* [17] 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) substrate was possible by controlling the different annealing temperatures and times.

Hall effect

Hall effect measurements on the $CdIn_2S_4$/GaAs epilayers were carried over a range of temperatures from 30 K to 293 K. The measured mobility and carrier density at 293 K were 219 $cm^2/V{\cdot}s$ and 9.01×10^{16} cm^{-3}, respectively. This mobility value is equal to the value obtained by Fiejeta and Okada [18]. Figure 5 shows the temperature dependence of the Hall mobility. As shown in Fig. 5, the mobility in the high temperature range tends to decrease as a function of $T^{-3/2}$ with increasing temperature and increase as a function of $T^{3/2}$ in the low temperature range. This indicates that the scattering at the high temperature range is mainly due to the acoustic mode of lattice vibrations and the scattering in low temperature range is most pronounced due to the impurity effect [2, 19]. The grown $CdIn_2S_4$/GaAs epilayer was confirmed to be n-type. The grown sample was always n-type presumably due to slight stoichiometric deviations originating from an excess of sulfur vacancies.

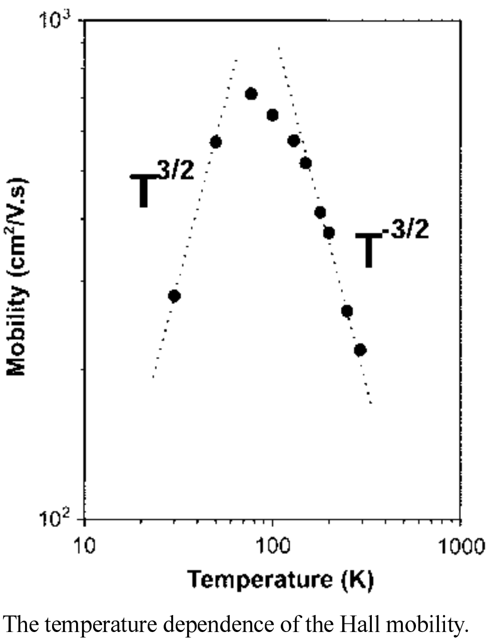

Fig. 5. The temperature dependence of the Hall mobility.

Optical absorption measurement

Figure 6 shows the optical absorption spectra obtained in the temperature range from 10 K to 293 K. In order to identify the energy band gap for $CdIn_2S_4$/GaAs, we carefully examined the relation between the optical absorption coefficient (α) and the incident photon energy (hν) from the optical absorption measurements in Fig. 6. The relation for a direct band gap between hν and α is given by :

$$(\alpha h\nu)^2 \sim (h\nu - E_g). \qquad (1)$$

Figure 7 displays the band gap energy variation of the $CdIn_2S_4$/GaAs epilayer using Eq. (1) as a function of temperature. This figure does not follow the convectional linear relationship. Generally, the energy gap varies proportionately to the square of the temperature when the measurement temperature is much lower than the Debye temperature, whereas the energy gap varies linearly with the temperature when the measurement temperature is much higher than the Debye temperature. Therefore, the temperature dependence of the optical energy band gap in our experiment is well described by

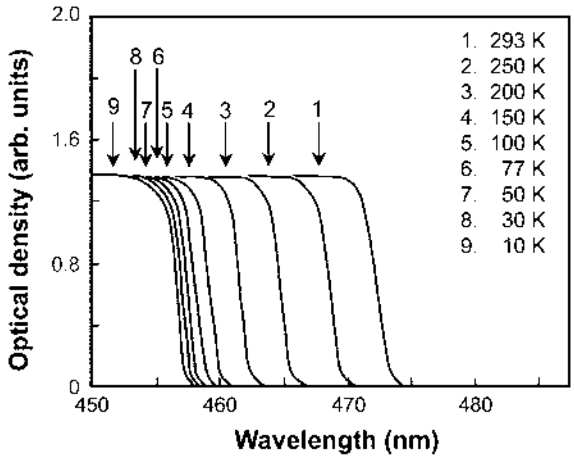

Fig. 6. Optical absorption spectra of $CdIn_2S_4$/GaAs epilayers measured at different temperatures.

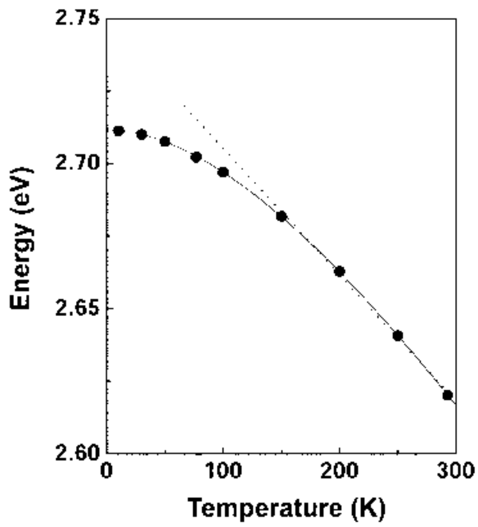

Fig. 7. Optical energy band gap of $CdIn_2S_4$/GaAs epilayers plotted as a function of temperature.

Varshni's equation [20] :

$$E_g(T) = E_g(0) - \alpha T^2/(T + \beta), \quad (2)$$

where α is a constant and β is approximately the Debye temperature. Also, $E_g(0)$ is the optical energy gap at absolute zero. From these experimental measurements, $E_g(0)$, α, and β are determined to be 2.7116 eV, 7.65 × 10^{-4} eV/K, and 425 K, respectively. Here, the Debye characteristic temperature [21] of $CdIn_2S_4$ was found to be 433 K at 160 K and this value reasonably agrees with our result. Therefore, the curve plotted from Eq. (2) follows well the experimental values at the higher and lower temperature of 160 K, as shown in Fig. 7. The energy band gap at 300 K fitted by Eq. (2) was 2.6166 eV, which is in good agreement with the value, 2.62 eV, measured at 300 K by Ref. [1]. Ordinarily, the band gap energy of $CdIn_2S_4$ at room temperature is known to be 2.2 to 2.7 eV [1, 2, 6].

Conclusions

The $CdIn_2S_4$ epilayers on the GaAs substrate have been first grown by using a HWE method. From the results of the PL and DCXD measurements, the grown $CdIn_2S_4$ epilayers were evaluated to be of high quality crystal. Simultaneously, the optimum growth temperatures of the substrate and the source turned out to be 420 and 630 °C, respectively. The $CdIn_2S_4$ was grown epitaxially along the <110> direction onto the GaAs (100) substrate. The Hall mobility and carrier density of the $CdIn_2S_4$ epilayer at 293 K were estimated to be 219 $cm^2/V{\cdot}s$ and 9.01 × 10^{16} cm^{-3}, respectively. From the temperature dependence of the Hall mobility, the scattering in the high temperature range was mainly due to the acoustic mode of lattice vibrations and the scattering in the low temperature range was more pronounced range due to the impurity effect. Also, the optical band gap obtained from the absorption measurement was well described by Varshni's relation, $Eg(T) = 2.7116\ eV\ (7.65 \times 10^{-4}\ eV/K)T^2/(425 + T)$. The energy band gap of the $CdIn_2S_4$ epilayers at 300 K was confirmed to 2.6166 eV.

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