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Photoluminescience properties for $CdIn_2Te_4$ single crystal grown by Bridgman method

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Abstract

Single crystal of p-$CdIn_2Te_4$ was grown in a three-stage vertical electric furnace by using Bridgman method. The quality of the grown crystal has been investigated by x-ray diffraction and photoluminescence measurements. From the photoluminescence spectra of the as-grown $CdIn_2Te_4$ crystal and the various heat-treated crystals, the (D^o, X) emission was found to be the dominant intensity in the photoluminescence spectrum of the $CdIn_2Te_4$:Cd, while the (A^o, X) emission completely disappeared in the $CdIn_2Te_4$:Cd. However, the (A^o, X) emission in the photoluminescence spectrum of the $CdIn_2Te_4$:Te was the dominant intensity like in the as-grown $CdIn_2Te_4$ crystal. These results indicated that the (D^o, X) is associated with V_{Te} which acted as donor and that the (A^o, X) emission is related to V_{Cd} which acted as acceptor, respectively. The p-$CdIn_2Te_4$ crystal was obviously found to be converted into n-type after annealing in Cd atmosphere. The origin of (D^o, A^o) emission and its to phonon replicas is related to the interaction between donors such as V_{Te} or Cd_{int}, and acceptors such as V_{Cd} or Te_{int}. Also, the In in the $CdIn_2Te_4$ was confirmed not to form the native defects because it existed in a stable bonding form.

Key Words : point defects, photoluminescence, annealing treatment, Bridgman technique, Cadmium indium telluride

1. Introduction

Cadmium indium telluride ($CdIn_2Te_4$), which has a defect chalcopyrite structure[1] with space group S^2_4-I4-, is one of the attractive materials because of its promised use in electro-optic devices[2-5]. Therefore, for device applications of $CdIn_2Te_4$, it is vital to know the electro-optical properties of this material. And, these properties are mainly determined by point defects associated with individual atoms forming the ternary compound. Especially, photoluminescence (PL) spectroscopy is a widely used method to analyze the defect structure of semiconductors. But, only several researchers have investigated the fundamental properties of $CdIn_2Te_4$ such as the crystallographic structure[6], the phase diagram[7], and the electrical and optical properties[3-7]. However, the point defect analyses of the $CdIn_2Te_4$ crystal by using PL experiments have not yet been well understood.

In the $CdIn_2Te_4$ growth, cadmium and tellurium have higher vapor pressure compared to that of indium. This indicates that the native defects in the $CdIn_2Te_4$ were generated by non-stoichiometric composition during high temperature growth. It has been known that these native defects, such as cadmium vacancy (V_{Cd}), tellurium vacancy (V_{Te}), cadmium interstitial (Cd_{int}), tellurium interstitial (Te_{int}), and complex of these point defects were formed while the crystal cooled down after crystal growth. Among the defects, V_{Te} and Cd_{int} are plausible defects because they act as donors. Other defects such as V_{Cd} and Te_{int} may form deep levels and/or acceptors.

In this paper, a three-stage vertical electric furnace was used to grow single crystal of $CdIn_2Te_4$ by using the Bridgman method. The predominant point defects in the as-grown $CdIn_2Te_4$ crystal and the various heat-treated crystals were investigated by PL measurement. Based on these results, we will discuss the origin of native defects in $CdIn_2Te_4$.

2. Experimental Procedures

Prior to crystal growth, polycrystalline $CdIn_2Te_4$ was formed as follows. The starting materials were shot type Cd, In, and Te with 6 N purity. After these materials were weighed in stoichiometric proportions, they were sealed in a quartz tube. After the sealed ampoule was placed in the synthesis furnace, this ampoule was con-

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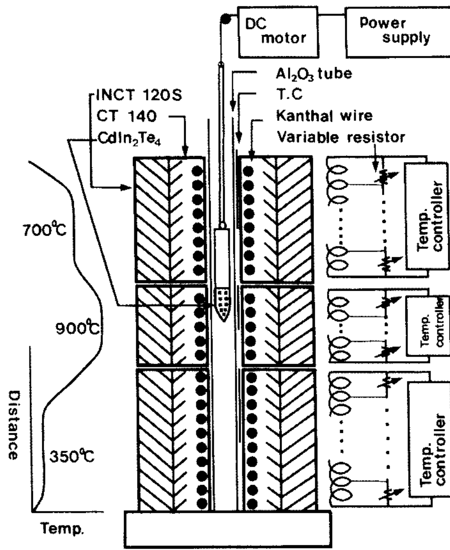

Fig. 1. Block diagram of the three-stage vertical electric furnace.

tinually oscillated to the right and left at the rate of 1 period per minute. In order to avoid the explosion of the ampoule due to the vapor pressure of cadmium or tellurium, the temperature of the ampoule was increased gradually to 1050 °C and then was maintained for 24 h. After the growth of the polycrystalline $CdIn_2Te_4$ ingot, the $CdIn_2Te_4$ ingot was sealed in the ampoule whose tip was processed sharply. A spiral type ampoule was placed in the three-stage vertical electric Bridgman furnace, as shown in Fig. 1.

The top, middle, and bottom temperatures of the furnace were gradually increased to 700, 900, and 350 °C, respectively, and then, these temperatures were maintained for 48 h to keep the uniform molten $CdIn_2Te_4$. To grow the undoped $CdIn_2Te_4$, the pull-down speed of the ampoule was 0.75 mm/h. The temperature was kept within ± 1 °C during growth. We pulled down the ampoule further and lowered the temperature of the ampoule at the rate of 20 °C/h for 10 h in order to avoid the crack of the crystal. The ampoule was then removed from the electric furnace. Fig. 2 shows the grown cone-shaped $CdIn_2Te_4$ crystal.

The structural properties of the grown $CdIn_2Te_4$ crystal were analyzed using the x-ray powder method and the back-reflection Laue method. Also, in the measurement of the PL, the exciton emitted from the band edge has been reported to be strongly dependent on the sur-

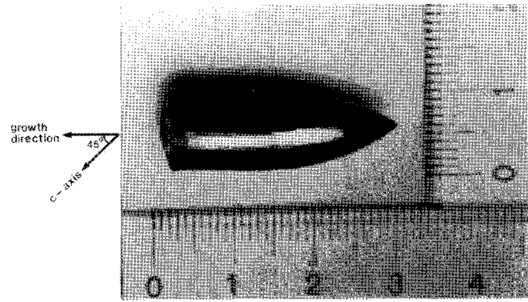

Fig. 2. Photograph of the grown $CdIn_2Te_4$ crystal. The c-axis of crystal tilted an angle of 45 degrees on the growth direction.

face condition of the crystal. Thus, only those samples cleaved off the bulk $CdIn_2Te_4$ along (110) plane were used in this experiment, since the crystal surface ground and polished has a possibility of affecting the PL spectra[8]. To prepare the PL samples of $CdIn_2Te_4$:Cd (annealed in the Cd vapor atmosphere), $CdIn_2Te_4$:Te (annealed in the Te vapor atmosphere), and $CdIn_2Te_4$:In (annealed in the In vapor atmosphere), the as-grown $CdIn_2Te_4$ crystal with adding each of Cd, Te, and In shots was sealed in a quartz ampoule at $\sim 10^{-6}$ torr. The samples of $CdIn_2Te_4$:Cd, $CdIn_2Te_4$:Te, and $CdIn_2Te_4$:In were annealed for 30 min at 400 °C, for 1 h at 650 °C, and 30 min at 850 °C, respectively. The PL measurement of the samples was performed at 10 K in the low temperature cryostat equipment (AP Inc. CSA 202B, DE 202S). The surface of the $CdIn_2Te_4$ sample was illuminated by 514.5 nm emitted from a Ar+ laser (USA, Coherent, INNOVA 300, 8.8 W) in which the light was polarized parallel to the c-axis of the (110) plane, and the light coming from the sample was dispersed with a monochromator. The dispersed light was detected with a photomultiplier tube (RCA, C3-1034) and then converted into a current. This current was recorded on an x-y recorder with amplification by a lock-in amplifier (EG&G 5210). Also, the Hall effect of the as-grown sample with the (110) plane was measured by the van der Pauw method. The sample temperature was varied from 10 K to 300 K during the measurement.

3. Results and Discussion

3.1. Structural and electrical properties

The crystal structure of $CdIn_2Te_4$ chalcopyrite as seen

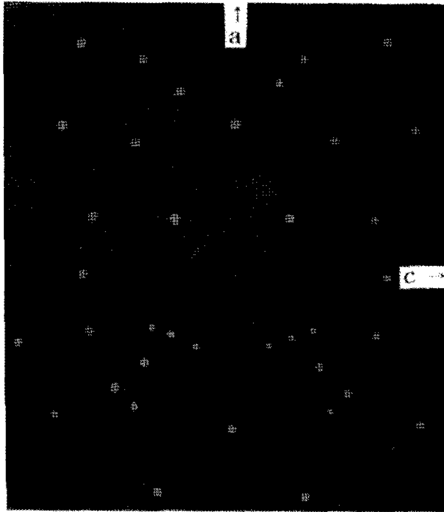

Fig. 3. Photograph of back-reflection Laue pattern of the {110} plane cut perpendicular to the c-axis of crystal.

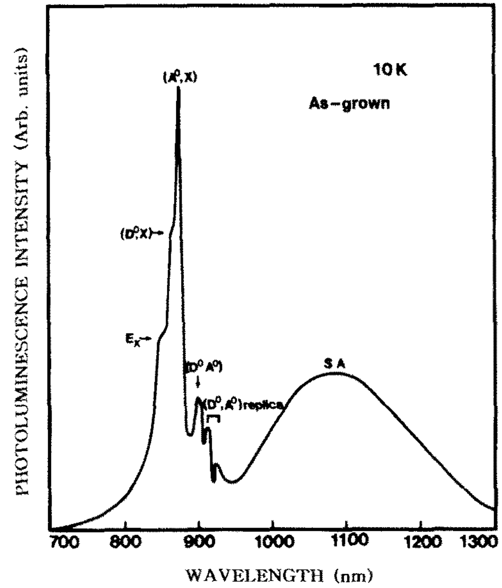

Fig. 4. A typical PL spectrum of the as-grown $CdIn_2Te_4$ crystal measured at 10 K.

from the typical diffraction peaks from planes such as (112), (103), (202), and (211) using the x-ray powder method. From these patterns, the lattice constant a_o and c_o were obtained by the extrapolation method and found to be 6.219 and 12.396 Å, respectively. This value agrees well with the values obtained by Nikolic *et al.*[9]. The plane perpendicular to the c-axis of the crystal was the {110} plane, which was determined by the back-reflection Laue method of Fig. 3.

The measured Laue patterns showed that the c-axis of the grown crystal is tilted with an angle of 45 degree to the growth direction, as shown in Fig. 2.

The measurement of the Hall effect was carried out at the temperature range from 10 to 300 K. Here, the carrier density, Hall mobility, and conductivity of the crystal at 300 K were determined to be 8.61×10^{17} cm^{-3}, 2.42×10^2 $cm^2/V \cdot sec$, and 33.38 $\Omega^{-1}cm^{-1}$, respectively, and confirmed to be p-type. These values measured at 10 K were 1.01×10^{15} cm^{-3}, 2.64×10^2 $cm^2/V \cdot sec$, and 4.27×10^{-2} $\Omega^{-1}cm^{-1}$, respectively.

3.2. Photoluminescence spectroscopy

3.2.1. As-grown $CdIn_2Te_4$ crystal

Fig. 4 shows a typical PL spectrum of the as-grown $CdIn_2Te_4$ crystal measured at 10 K. The two peaks on the shoulder appear at 846.5 nm (1.4647 eV) and 864.2 nm (1.4347 eV) toward the shorter-wavelength region. These peaks are associated with the free exciton (E_x) and with the neutral donor bound exciton (D^o, X) due to the recombination from bound exciton to neutral donor. The binding energy of E_x^b, can be obtained from the following Eq. (1):

$$E_x^b = E(10) - E_x, \quad (1)$$

where E(10), which has the value of 1.4746 eV[10], is the energy band gap at 10 K. Therefore, the E_x^b was calculated to be 9.9 meV (=1.4746−1.4647). The strong peak of the exciton (A^o, X) corresponding to the neutral acceptor appears at 871.5 nm (1.4226 eV). This belongs to the typical p-type configuration of the PL spectrum observed in the as-grown $CdIn_2Te_4$ crystal. Also, the full width at half maximum (FWHM) is taken to be 15 meV. It has been known that this exciton is related to the recombination from bound exciton to neutral acceptor. Like the above-mentioned, the V_{Cd} and V_{Te} are probably present in the $CdIn_2Te_4$ since the Cd and Te have higher vapor pressure then that of In. But, the Cd atoms have lower vapor pressure than the Te atoms. Therefore, the concentration of the V_{Cd} may be lower then that of the V_{Te}. Thus, this indicates that the native defects of the $CdIn_2Te_4$ crystal were generated due to the non-stoichiometric composition during high temperature growth. The binding energy, E_{bx}^b, for the (A^o, X)

emission is

$$E_{bx}^{b} = E(E_x) - E(A^o, X) \text{ or } E(D^o, X). \quad (2)$$

Here, E_{bx}^{b} was calculated to be 42.1 meV (=1.4647−1.4226). Also, the ionization energy[11] of the neutral acceptor level, E_A, is 421 meV, which is denoted to E_{bx}^{b}/E_A 0.1. This responds to the acceptor states of the V_{Cd} or Te_{int}, which are located at 421 meV upper the edge of the valence band. At the same time, this value is nearly equal to the activation energy, 0.431 eV, of the p-type sample obtained by the Hall effect measurement. In the PL measurement, the observance of the E_x and the bound excitons suggests that the crystal grown in this laboratory has a very high optical quality, because the emission peak of the exciton can be observed only due to the interaction of the long-range Coulomb coupling between the electron and the hole. And the neutral donor-acceptor pair, (D^o, A^o), emission at 897.0 nm (1.3822 eV) and its TO phonon replicas were observed. The (D^o, A^o) emission occurred due to the interaction between the neutral donor and the neutral acceptor states in the energy band gap. Also, the energy difference between the (D^o, A^o) emission and its replicas is 17.1 meV, which corresponds to the to phonon[9]. The relatively strong and broad peak at 1070.1 nm (1.1586 eV) in the longer-wavelength region can be attributed to a self-activated (SA) emission.

3.2.2. Annealing effect of the $CdIn_2Te_4$ crystal

In order to understand the origins of the several peaks of the as-grown $CdIn_2Te_4$ crystal, we measured the PL spectra for the samples after annealing in a In-, Te-, and Cd-atmosphere, respectively. First, in order to find a role of In, we prepared the $CdIn_2Te_4$:In sample annealed in a In atmosphere for 30 min at 850 °C. Fig. 5 shows the PL spectrum of $CdIn_2Te_4$:In measured at 10 K.

This spectrum is close to that as shown in Fig. 4. This means that In is not related to the formation of native defects because In forms more covalent bonds than Cd and Te in the $CdIn_2Te_4$, i.e., In participates in the formation of pre-covalent and less-ionic chalcopyrite compounds than Cd and Te. Therefore, this indicates that In is the stable element in $CdIn_2Te_4$.

Second, Fig. 6 displays the PL spectrum of the $CdIn_2Te_4$:Te annealed in the Te-atmosphere for 1 h at 650 °C. This shows that the dominant (A^o, X) peak is still observed as shown in the PL configuration of the as-grown $CdIn_2Te_4$, while the peaks of the E_x and (D^o, X) completely disappeared. Therefore, the (A^o, X) peak is not related to Te because the V_{Te} sites should be substituted with saturated Te. It has been known that small stoichiometric deviations in the crystal can be adjusted by compensating for the concentration of vacancies in the appropriate sublattice. Probably the V_{Cd} and V_{In} are

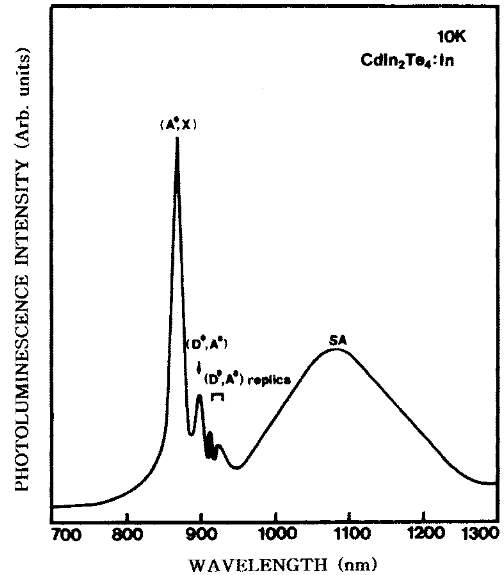

Fig. 5. The PL spectrum of $CdIn_2Te_4$:In measured at 10 K.

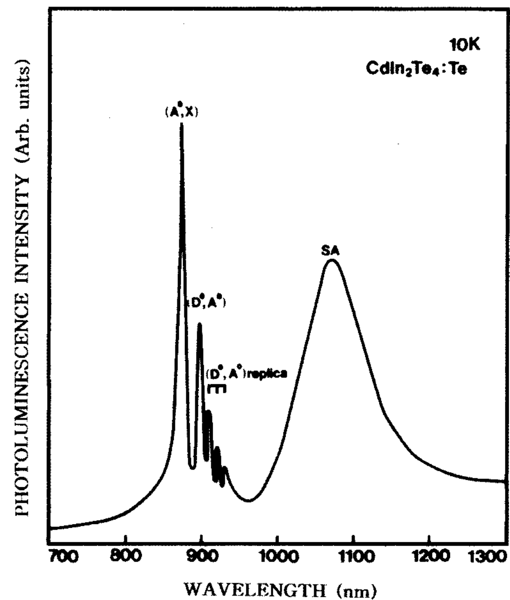

Fig. 6. The PL spectrum of $CdIn_2Te_4$:Te measured at 10 K.

present and also excess Te atoms in $CdIn_2Te_4$. But, in the starting material in order to form $CdIn_2Te_4$, the concentration of the In atoms must be equal to that of Cd atoms.

However, the concentration of V_{In} will be lower then that of V_{Cd}. Because the Cd atoms participate only weakly in the covalent bonding, most of the covalent bonding occurs between In and Te. Consequently, the V_{Cd} is likely to be the more dominant vacancy candidates rather than that of V_{In}. Therefore, the (A^o, X) origin can be ascribed to the acceptor level, which originated from V_{Cd} or Te_{int} due to stoichiometric deviation. And the (D^o, A^o) emission and its to phonon replicas in the $CdIn_2Te_4$:Te were dominantly observed to the intensities more than that in as-grown $CdIn_2Te_4$. Therefore, those peaks are related to the V_{Cd}, Te_{int}, or their complexes, which acted as acceptors. Also, the intensity of the SA emission increased after the Te-atmosphere treatment. This means that the origin of the SA emission is related to the V_{Cd} or Te_{int}.

Lastly, we prepared the $CdIn_2Te_4$:Cd sample annealed in Cd-atmosphere for 30 min at 400 °C. This annealing would saturate the $CdIn_2Te_4$ with Cd. Fig. 7 shows the PL spectrum of the $CdIn_2Te_4$:Cd measured at 10 K. By comparing the PL spectrum of the as-grown $CdIn_2Te_4$

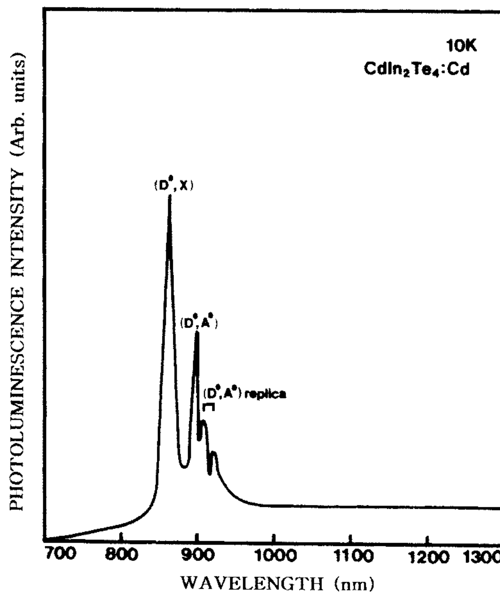

Fig. 7. The PL spectrum of $CdIn_2Te_4$:Cd measured at 10 K.

as shown in Fig. 4, the peaks corresponding to the E_x and the (A^o, X) completely disappeared in the $CdIn_2Te_4$:Cd.

This disappearance indicates that the (A^o, X) is certainly associated with an acceptor level of the V_{Cd} or levels of antisite native defects such as In_{Cd} and Cd_{In}. On the other hand, the (D^o, X) emission became the most dominant intensity in the PL spectrum of the $CdIn_2Te_4$:Cd and the FWHM was 13 meV. It has been known that this peak was observed in a typical n-type $CdIn_2Te_4$. Therefore, the (D^o, X) peak is not related to Cd because the V_{Cd} sites should be substituted with the saturated Cd. However, (D^o, X) may be related to the V_{Te}. The (D^o, X) origin can be ascribed to the donor level which originated from the V_{Te} or Cd_{int} due to stoichiometric deviation. And this suggests that only Cd-atmosphere annealing at 400 °C could convert the as-grown $CdIn_2Te_4$ crystal into n-type. The binding energy, E_{bx}^b, for the (D^o, X) emission can be calculated by using Eq. (2). Therefore, the E_{bx}^b turned out to be 30.1 meV. Also, the ionization energy[11] of the neutral donor level, E_D, is denoted to E_{bx}^b/E_D 0.15 and the E_D is determined to be 201 meV. A similar donor level located at 0.2 eV below the conduction band in CdTe has been reported in the literature and is associated with a Cd_{int}[12-14]. Ou *et al.*[3] reported that the level at 0.21 eV observed in the n-type $CdIn_2Te_4$ might be associated with a similar native defect or these complexes. The (D^o, A^o) emission and its to phonon replicas were dominantly observed in the sample which had been annealed in the Cd-atmosphere. The origin of these (D^o, A^o) emissions may be associated with the point defects of the V_{Te}, Cd_{int}, or their complexes, which acted as donors. On the other hand, the SA peak completely disappeared in $CdIn_2Te_4$:Cd. This may mean that the $CdIn_2Te_4$:Cd crystal is purified by annealing in the Cd-atmosphere. Also, the disappearance of the SA emission indicates that this peak is certainly associated with the V_{Cd}.

4. Conclusions

We grew high quality $CdIn_2Te_4$ crystal in a three-stage vertical electric furnace by using the Bridgman method. From the Hall effect measurement, the carrier density, and Hall mobility of the crystal at 300 K were determined to be 8.61×10^{17} cm^{-3} and 2.42×10^2 cm^2/V·sec, respectively, and it was confirmed to be a p-

type.

The PL spectra of the as-grown $CdIn_2Te_4$ crystal and the various heat-treated crystals showed that the (D^o, X) emission became the most dominant intensity in the PL spectrum of the $CdIn_2Te_4$:Cd, while the (A^o, X) emission completely disappeared in the $CdIn_2Te_4$:Cd. However, the (A^o, X) emission maintained the dominant intensity in the $CdIn_2Te_4$:Te. Based on these results, the (D^o, X) and the (A^o, X) emissions were found to originate from the V_{Te} acting as a donor and the V_{Cd} acted as an acceptor, respectively. Also, the binding energies of these emissions turned out to be 30.1 meV and 42.1 meV, respectively. Thus, we confirmed that the $CdIn_2Te_4$ crystal obviously converted into n-type after the Cd atmosphere treatment. The origin of emissions related to (D^o, A^o) is caused by the interaction between donors such as V_{Te} or Cd_{int}, and acceptors such as V_{Cd} or Te_{int}.

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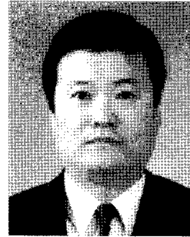

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