Properties for the $CdIn_2Te_4$ Single Crystal

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Abstract.

The p-$CdIn_2Te_4$ single crystal was grown in the three-stage vertical electric furnace by using Bridgman method. The quality of the grown crystal has been investigated by the x-ray diffraction and the 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 an as-grown $CdIn_2Te_4$ crystal. These results indicated that the (D^o, X) is associated with V_{Te} acted as donor and that the (A^o, X) emission is related to V_{Cd} acted as acceptor, respectively. The p-$CdIn_2Te_4$ crystal was found to be obviously converted into the n-type after annealing in the 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 the stable form of bonds.

Keywords: p-$CdIn_2Te_4$ single crystal, photoluminescence, photocurrent, crystal field splitting, spin orbit splitting, band gap energy.

1. Introduction

Cadmium indium telluride ($CdIn_2Te_4$), which is the defect chalcopyrite structure [1] with space group S^2_4I4-, is one of the attractive materials because it shows promise for practical use in electro-optic devices [2-5]. Therefore, for device applications of the $CdIn_2Te_4$, 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], the electrical and optical properties [3-7]. However, the point defect analyses of the $CdIn_2Te_4$ crystal by using PL experiments have not been well understood yet. 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 the 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, the three-stage vertical electric furnace was used to grow the single crystal of $CdIn_2Te_4$ by using Bridgman method. The predominant point defects in the as-grown

$CdIn_2Te_4$ crystal and the various heat-treated crystals were investigated by the PL measurement. Based on these results, we will discuss the origin of native defects in the $CdIn_2Te_4$.

2. Experimental Procedure

Prior to the crystal growth, polycrystalline $CdIn_2Te_4$ was formed as follows. The starting materials such as Cd, In, and Te were the shot type of 6N purity. After these materials were weighed in stoichiometric proportions, they were sealed in a quartz tube. After the sealed ampoule was putted in the synthesis furnace, this ampoule was continually 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. And, the ampoule which the spire tip was existed to the below of it was placed in the three-stage vertical electric furnace of Bridgman method. The three-stage vertical electric furnace is shown in Fig. 1. The top, middle, and bottom temperatures of the three-stage vertical electric furnace to grow the undoped $CdIn_2Te_4$ 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 with the spire tip posited in the middle temperature region was controlled to be 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.

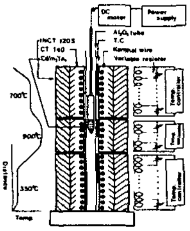

Fig. 1. Block diagram of the three-stage vertical electric furnace.

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 surface 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 ~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, 8.8W) 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 as-grown sample with the (110) plane was measured the Hall effect 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 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 obtained from the extrapolation method is 6.219 and 12.396 , 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 angle of 45 degree on the growth direction, as shown in Fig. 2.

The electrical properties of the as-grown $CdIn_2Te_4$ crystal were obtained from the Hall effect measurement using the van der Pauw technique. The measurement of 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}/Vsec, and 33.38 ^{1}cm ^{1}, respectively, and confirmed to be a p-type. These values measured at 10 K were 1.01 10^{15} cm ^{3}, 2.64 10^{2} cm^{2}/Vsec, and 4.27 10 ^{2} ^{1}cm ^{1}, respectively.

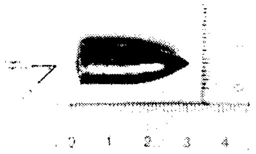

Fig. 2. Photograph of the grown $CdIn_2Te_4$ crystal. The c-axis of crystal tilted an angle of 45 degrees on the growth direction

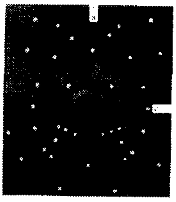

Fig. 3. Photograph of back-reflection Laue pattern of the {110} plane cut perpendicular to the c-axis of crystal.

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):

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

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

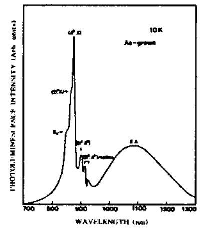

Fig. 4. A typical PL spectrum of the as-grown $CdIn_2Te_4$ crystal measured at 10 K.

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

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

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 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 is 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 is 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.

Conclusions

We grew the $CdIn_2Te_4$ crystal in the three-stage vertical electric furnace by using Bridgman method. From the x-ray diffraction experiments, the $CdIn_2Te_4$ crystal was confirmed to be the single crystal and the chalcopyrite structure. 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 $2.42\ \ 10^{2}$ $cm^{2}/Vsec$, respectively, and it was confirmed to be a p-type.

From the PL measurement, the observance of the E_x and bound excitons in the as-grown $CdIn_2Te_4$ crystal indicates that the grown crystal is a very high optical quality.

References

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