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ANALYSIS OF PHOTOLUMINESCENCE SPECTRA ON $CuInS_2$ CRYSTALS

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The bound exciton and defect-related donor-acceptor pair emissions in photoluminescence (PL) spectra of $CuInS_2$ crystals grown by traveling heater method were investigated to characterize defects in these crystals. After the $CuInS_2$ crystals had been annealed in vacuum at 400 °C, the bound exciton emission at 1.525 eV (E_{x2}) was found to be completely quenched and a new bound exciton peak (E_{x3}) appeared at 1.520 eV. At the same time, annealing in contact with In_2S_3 powder did not lead to any significant changes of PL spectra in exciton emission region. By the analyses of donor-acceptor pair emissions the energy levels of donors were deduced to be 36 and 63 ~ 69 meV. Acceptors were found to lie much deeper with energy levels at 113, 150, 180 and 220 meV. The origin of the defects associated with bound excitons, donors and acceptors in $CuInS_2$ is discussed.

1. INTRODUCTION

Ternary semiconductor $CuInS_2$ has attracted much attention as a promising photovoltaic material for application in thin-film solar cells because of its optimal band gap of 1.5 eV. However, the conversion efficiency of the $CuInS_2$-based solar cells is still at the level of 12.5% [1], or by 6.3% smaller than efficiency (18.8%) of $Cu(InGa)Se_2$ solar cells [2]. One of the obstacles to achieving further efficiency increase is insufficient understanding of the defect-related properties of this material. For example, a unified view on the nature of bound excitons and donor-acceptor pair emissions in photoluminescence (PL) spectra is not developed as yet, because of the variety of the obtained results, and the differences in both the crystallinity of the studied samples and the employed experimental techniques [3-6].

Recently, we have grown high quality bulk single crystals of $CuInS_2$ and have examined their excitonic properties [7-11]. In addition, sharp and pronounceable donor-acceptor pair emissions have been observed on these crystals. In this work the annealing effects on bound exciton emissions in PL spectra of the above crystals have been investigated. Further to the data obtained previously [7-11], we report the obtained donor and acceptor level energies and subsequent analyses of the excitation intensity dependence of the donor-acceptor pair emissions. We also discuss the nature of the defects associated with the observed defect levels.

2. EXPERIMENTAL DETAILS

The samples for PL measurements were prepared from bulk single crystals of $CuInS_2$ grown by the traveling heater method (THM) [7]. For annealing, crystals were sealed into an evacuated quartz ampoule. Annealing was performed in vacuum or in contact with In_2S_3 powder at 400 °C for 15 min. The surfaces of the investigated samples were mechanically polished using alumina powder (particle size of 0.1 μm). The samples were then secured in a closed-cycle helium cryostat (JANIS CCS-100) and kept at a temperature of 10 K. Photoluminescence excited by a Ti: sapphire laser (Spectra Physics 3950/3960) with a wavelength of 760 nm was detected by a cooled photomultiplier.

3. RESULTS AND DISCUSSION

3.1 Bound exciton emission

A photoluminescence spectrum of as-grown crystals at 10 K in the band-edge region is shown in Fig. 1. The spectrum exhibits three sharp peaks (the A free exciton, E_A at 1.535 eV, and two bound excitons, E_{x1} at 1.531 eV and E_{x2} at 1.525 eV) with a weak shoulder (a donor-to-valence band transition, DV at 1.520 eV) [4]. After $CuInS_2$ crystals had been annealed in vacuum (V-annealing), the total exciton intensities were reduced down to one-twelfth the original values; the E_{x2}-emission peak was completely quenched and intensities of E_A and E_{x1} emissions were also largely decreased. At the same time, a new high intensity bound exciton (E_{x3}) peak appeared at 1.520 eV (as shown in Fig. 1).

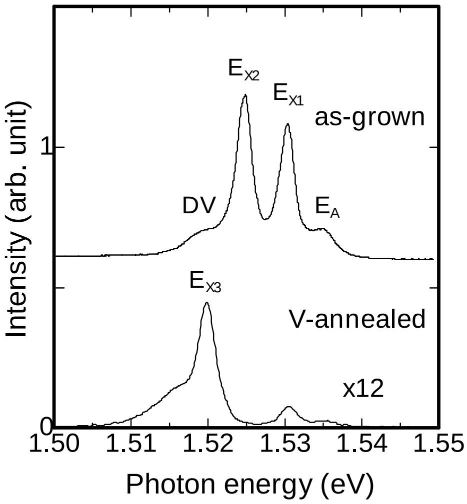

Fig. 1. PL spectra of as-grown and V-annealed crystals at 10 K in the band-edge region.

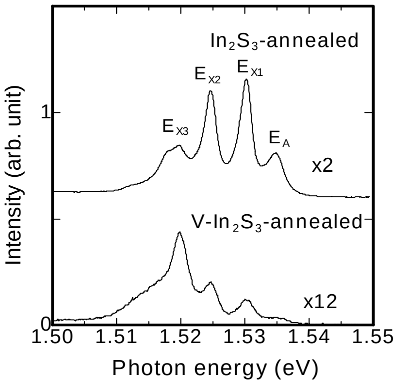

Fig. 2. PL spectra of In_2S_3-annealed and V-In_2S_3-annealed crystals at 10 K in the band-edge region.

$CuInS_2$ crystals were also annealed in contact with In_2S_3 powder (In_2S_3-annealing). After the In_2S_3-annealing, the total exciton intensities decreased only to a half the original values and the PL spectrum of excitons (Fig.2) did not undergo a significant change in comparison with that of as-grown crystals, although a small E_{x3} peak appeared. From the obtained results, we can consider the V-annealing treatment extracts S and/or In atoms from the crystals while the In_2S_3-annealing treatment preserves the crystals from the release of S and/or In atoms. In order to confirm the effect of the In_2S_3-annealing, crystals were annealed in contact with In_2S_3 powder further to the V-annealing (V-In_2S_3-annealing). After the V-In_2S_3-annealing, the quenched E_{x2} peak reappeared with a smaller intensity, whereas the E_{x3} peak did not undergo any change as shown in Fig. 2. These results indicate that the In_2S_3-annealing produces a strong effect on the E_{x2} emission and creates a defect state associated with the E_{x2} bound exciton.

Since the E_{x2}-emission peak is eliminated by the V-annealing, which is supposed to draw out S and/or In atoms, we propose that for the E_{x2} bound exciton, a defect binding this exciton is an interstitial S-atoms (S_i). Lewerenz and Dietz reported that the acceptor level of S_i is located at 170 to 180 meV [12]. This energy level is close to the one with energy of 192 meV [13] for the neutral acceptor that is assumed to be a binding center for the E_{x2} bound exciton.

On the other hand, we can speculate that for the E_{x3} bound exciton the defects binding an exciton are In-vacancies (V_{In}) or substitutional Cu-atoms at In-site (Cu_{In}). The reason for this is that the E_{x3} emission appears only after V-annealing that extracts S and/or In atoms, and is not observed in the as-grown crystals which are In-rich due to the growth method using an In solvent. Assuming that the E_{x3} emission is also caused by an exciton bound to neutral acceptors, the neutral acceptor level is estimated to be at 303 meV [13]. Kneisel *et al.* did really find the trap level at 0.3 eV in p-type $CuInS_2$ [14]. Furthermore, it is reported from the results of the first principle calculations on $CuInSe_2$ that In-vacancies have an acceptor level at 0.17 eV above the valence band and substitutional Cu-atoms at In-site have an acceptor level at 0.29 eV [15]. Above energies of the acceptor levels also support our speculation.

3.2 Donor-acceptor pair emission

Figure 3 shows the excitation intensity dependence of the normalized PL spectra for the low-energy region in which a manifestation of the defect-related properties is most likely. The spectrum with a normalization constant of 1 mainly consists of three peaks at 1.44 eV (I), 1.40 eV (II) and 1.36 eV (III), which all shift towards lower energies with decreasing excitation intensity (Fig. 3). This red-shift is indicative of the donor-acceptor nature of the observed emission. Since energy differences between both peaks I and II, and peaks II and III are about 40 meV, peaks II and III might be assigned to a phonon replica of peak I. However, these peaks were also observed on crystals grown by the iodine vapor transport method and the intensity of peak II was larger than that of the other peaks [7,8]. Therefore, peaks I, II and III have to be considered independent.

The spectra of donor-acceptor emission were resolved into Gaussians. Two Gaussians (I and II) having the highest intensity were used to evaluate the parameters of the donor and acceptor levels associated with the observed emissions.

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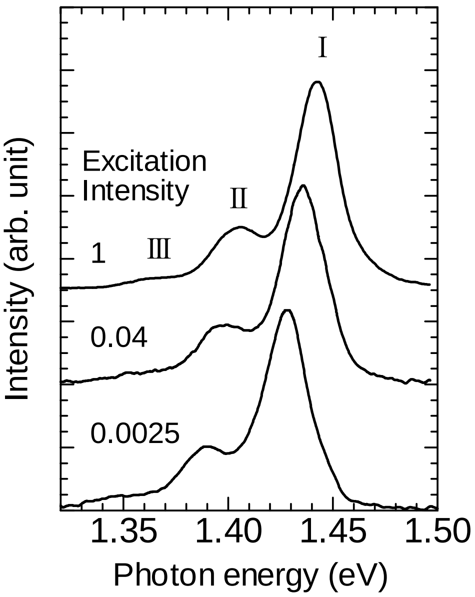

Fig. 3. Excitation intensity dependence of normalized PL spectra for as-grown crystals in the low-energy region.

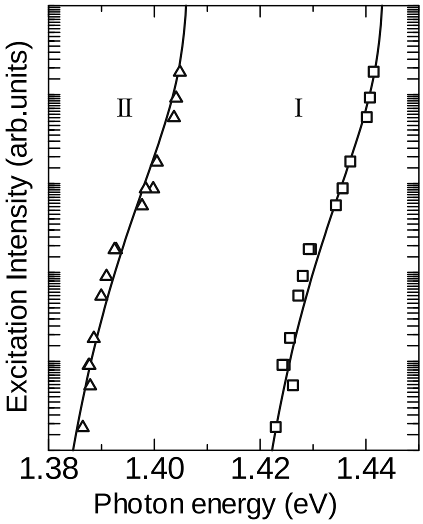

Fig. 4. Experimental points for energies of peaks I and II (as shown in Fig. 3 plotted as function of excitation intensity. Solid curves were obtained by fitting to the equation of donor-acceptor recombination.

Figure 4 displays experimental data on peak energy as a function of excitation intensity of the emissions I and II. The solid curves obtained by fitting to the equation of donor-acceptor recombination [16] allow us to estimate the energies of the donors and acceptors associated with peak I at 36 and 113 meV, and those associated with peak II at 36 and 150 meV, respectively. The donor level of 35 meV has already been reported [3,6] to be in perfect match with the above estimates (36 meV). Therefore we believe that the energies of 113 and 150 meV indeed correspond to the energies of acceptor levels.

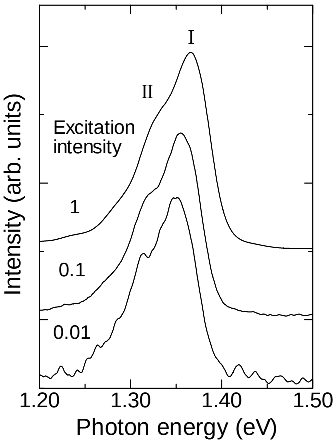

Fig. 5. Excitation intensity dependence of normalized PL spectra of annealed crystals in the low-energy region.

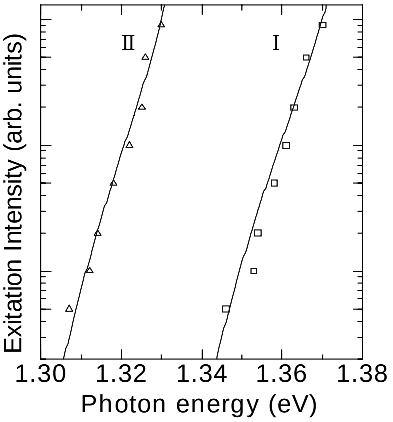

Fig. 6. Experimental points for energies of peaks I and II (as shown in Fig. 5) plotted as function of excitation intensity. Solid curves were obtained by fitting to the equation of donor-acceptor recombination.

The above procedure of the evaluation of the energy position of the donor and acceptor levels from PL has also been applied to annealed crystals. In the low-energy region of the spectrum shown in Fig. 5, we can observe two main peaks at 1.33 and 1.37 eV, which shift towards lower energies with decreasing excitation intensity and are also caused by donor-acceptor pair transitions. The relationship between the peak energies of emissions I and II and the excitation intensity is shown in Fig. 6. By a similar fitting as above, the energies of the donors and acceptors associated with peak I have been estimated to be 63 and 180 meV, and those with peak II to be 69 and 220 meV. Within the accuracy of the performed Gaussian decomposition, the obtained values of 63 and 69 meV can be viewed as the same donor level energy, which is in excellent agreement with the reported energy, 60 ~ 70 meV [3,6,17], of the donors in $CuInS_2$. Consequently, the acceptor levels related to peaks I and II have energies of 180 and 220 meV, respectively.

All above results are summarized in an energy level diagram in Fig. 7.

Since the compositional changes of the annealed samples could not be displayed by electron probe X-ray microanalysis (EPMA), we are in the following opinion concerning these changes. First, it is reasonable to expect that the annealed crystals would be S poor rather than S rich (at least) by comparison with as-grown samples since the annealed composition should be S-depleted because of the release of some fraction of S into vacuum during annealing.

Second, our results display that as-grown crystals with the ascertained In-poor composition, and the annealed samples have the same PL spectra in the region of both exciton and donor-acceptor pair emissions [17]. Such tendency in the emission of $CuInS_2$ has previosly been reported by Binsma *et al*. [3], and we can expect that the annealed crystals are In poor in comparison with the as-grown crystals with stoichiometric composition.

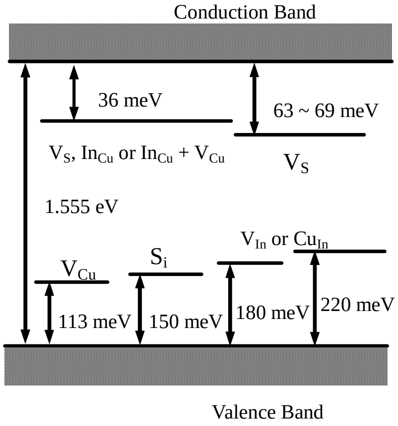

Fig. 7 Energy level diagram of $CuInS_2$ crystals.

The donor level of 63 ~ 69 meV in the annealed samples can be an S vacancy (V_S) or a defect related to V_S, since the annealed crystals are S and In depleted. A candidate for the donor level of 35 meV is also V_S or a defect related to V_S or the substitutional In atom at the Cu site (In_{Cu}) or a complex of In_{Cu} and a Cu vacancy (V_{Cu}), as they all are expected to form donor levels [15].

On the basis of the available data for as-grown crystals, including S- and In-rich compositions, the acceptor level of 113 meV might be ascribed to the Cu vacancy (V_{Cu}) with the reported energy of 100 meV [3]. A candidate for the acceptor level of 150 meV is an interstitial S atom (S_i), whose energy is estimated to be 170 ~ 180 meV [12] and which are expected to be pronounceable only in S-rich compositions. On the other hand, first-principles calculations for $CuInSe_2$ have revealed that In vacancies (V_{In}) and substitutional Cu atoms at In sites (Cu_{In}) should be acceptors with energies of 0.17 and 0.29 eV, respectively [15]. As the probability of defect creation is higher in the annealed samples, which are In poor, the acceptor levels of 180 and 220 meV are likely to be attributed to V_{In} or Cu_{In}.

5. CONCLUSIONS

The effects of annealing on the emissions of the bound excitons in $CuInS_2$ crystals grown by THM have been examined. The V-annealing is found to completely eliminate the emission of the E_{x2} bound exciton and to lead to the appearance of the E_{x3} bound exciton emission. On the other hand, the In_2S_3-annealing does not affect appreciably the bound exciton emissions observed in as-grown crystals. From the obtained results, we propose that the defects associated with E_{x2} and E_{x3} bound excitons are interstitial S-atoms and In-vacancies or substitutional Cu-atoms at In-site, respectively.

We have also examined the excitation intensity dependence of the donor-acceptor pair emissions in as-grown and annealed $CuInS_2$ crystals to characterize and determine the energy of the defects. For as-grown crystals, a donor level of 36 meV and the acceptor levels of 113 and 150 meV have been identified, while for annealed crystals, a donor level of 63 ~ 69 meV and the acceptor levels of 180 and 220 meV have been found. The nature of the energy levels found in this study has been discussed under an assumption that annealed samples are S and In poor in comparison with as-grown crystals.

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