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Deep Level Photoluminescence in $CuIn_{1-x}Ga_xSe_2$

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Deep level photoluminescence (PL) bands are studied in $CuIn_{1-x}Ga_xSe_2$ solid solutions at T=8K. These PL bands had peak positions at 0.4-0.5 eV below the bandgap energy E_g. In $CuInSe_2$ these bands have a peak position at $h\nu \approx 0.58$ eV and in $CuGaSe_2$ they can be found at $h\nu \approx 1.1$ eV. The energy of these deep PL bands shifts with the In/Ga ratio in the same way as E_g. It is shown that these bands arise from recombination within deep donor-deep acceptor pairs, where the donor defect is probably an interstitial copper and the acceptor defect is V_{In} or V_{Ga}.

KEYWORDS: $CuInGaSe_2$, deep levels, photoluminescence, donor-acceptor pairs

1. Introduction

Due to the very short optical absorption length, the $CuIn_{1-x}Ga_xSe_2$ (CIGS) system is probably one of the most promising materials for low-cost thin film solar cells. At the same time, there still remain many unsolved problems related to the defect structure of these multinary compounds. Among other things, it is necessary to study more carefully the deep defect levels. Photoluminescence (PL) is certainly one of the most powerful methods in defect studies. Recently we discovered the new D1 and D2 deep PL bands in $CuInS_2$ and $CuGaSe_2$.[1-2)] These PL bands had peak positions at 0.4-0.5 eV below the bandgap energy E_g. The experimental results for the D1 and D2 PL emissions could be consistently explained by a model of donor-acceptor pair luminescence where both donor and acceptor levels are relatively deep, and where the D1 and D2 bands are due to recombination within pairs of the closest neighbors (D1), and between pairs of the next-closest neighbors (D2), respectively.

In the present work we studied PL properties of these deep bands in $CuInSe_2$ and $CuGaSe_2$ solid solutions.

2. Experimental

Different samples (single crystals, polycrystalline samples, thin films) were studied. It was found that the PL intensity of these bands was higher in polycrystalline samples. It is known that the polycrystalline material contains more intrinsic and structural defects than single crystals. Therefore we believe that these defects play a major role in our deep PL bands. The compositional analysis of the samples was carried out by the energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) measurements. For the PL measurements reported here, a He-Cd laser with a wavelength of λ=441 nm was used for excitation. The samples were mounted inside a closed cycle He cryostat (T= 8-300K). The PL spectra were recorded with a computer controlled SPM-2 grating monochromator (f = 0.4m). The chopped signal was detected with an InGaAs, PbS detectors, or with a photomultiplier tube with S1-characteristics for the edge emission region, using a conventional lock-in technique. The emission spectra were corrected for grating efficiency variations and for the spectral response of the detectors.

3. Results and discussion

Fig. 1. shows some of the PL results of the $CuIn_{1-x}Ga_xSe_2$ samples from the "deep" spectral region. The structured deep band shifts with Ga content x toward high energy and the band shape changes. This is a proof, albeit indirect, that we indeed have two PL bands (D1 and D2), the same way as was found for $CuGaSe_2$ in Ref. 1. However, the D1 and D2 PL bands were not resolved in samples where x<1. We were able to find deep PL bands for the whole range of the solid solution and the relative intensity of these bands increases with Ga content. In $CuInSe_2$ these bands have a peak position at $h\nu \approx 0.58$ eV and in $CuGaSe_2$ they can be found at $h\nu \approx 1.1$ eV. The energy of these deep PL bands shifts with the In/Ga ratio in the same way as the edge emission band and as the band gap energy E_g, see Fig. 2. Previous results have shown [1,2)] that conduction or valence band states are not involved in the recombination process. This fact indicates that the deep PL emission must be connected with defect levels, the depth of which does not depend on the In/Ga ratio. According to the deep donor- deep acceptor pair model [1)] the peak position of the deep PL band depends mainly on the depth of these defect levels and only a slight influence of lattice parameters and of the dielectric constant change with x can be observed.

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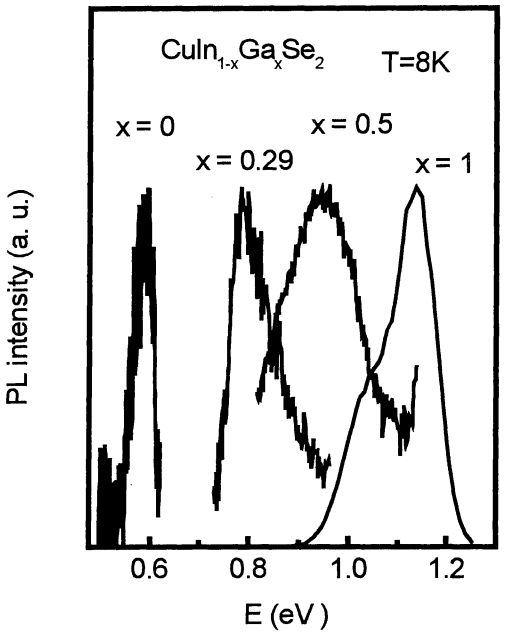

Fig. 1. Normalized PL spectra from the deep region of our $CuIn_{1-x}Ga_xSe_2$ samples as a function of the Ga content x.

Moreover, in several materials we observed even deeper PL bands which correspond to next distances between donor and acceptor defects [2]. These results have shown that we are dealing with DA pairs where the donor defect occupies an intrstitial position.

Latest theoretical calculations [3] show that the depth of at least one donor defect does not change with the In/Ga ratio and this is an interstitial copper ion. The behavior of the second possible interstitial defect In_i (or Ga_i) is not known. According to our previous results [1,2] both interstitial donor defects could be involved in these deep DA pairs, but the most probable is an interstitial copper. It is known [2] that the intensity of these deep PL bands increases after thermal treatment with the presence of Cu. It is interesting that in $AgInS_2$ we observed very similar deep PL bands where the donor defect was Ag_i [5].

The most probable acceptor defect in this DA pair is V_{In} or V_{Ga} . According to the latest calculations of defect structure in the CIS related ternary compounds these vacancies are responsible for the A3 level with $E_{A3} \approx 150$ meV [6].

Deep PL bands in chalcopyrite ternaries are not so often measured and at this moment very little is known about the defects causing them. Deep DA pairs like (Cu_i-$V_{Ga/In}$) are believed to form more easily than the individual defects Cu_i or $V_{Ga/In}$, because the formation energy of a defect pair is remarkably lower than the sum of the energy of two individual defects [6] and therefore the relative role of complexes can be far more relevant than it has been assumed before.

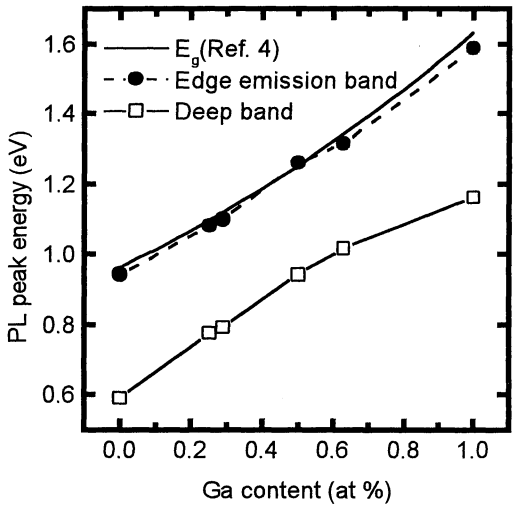

Fig. 2. Relationship between PL peak positions and Ga content in $CuIn_{1-x}Ga_xSe_2$ at T=8K. The room temperature bandgap energy, as given in Ref. 4, is drawn as a continous line, and appears to closely follow the edge emission band energy measured at T=8K in the present work.

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