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Article *in* Solar Energy Materials and Solar Cells · March 2001

DOI: 10.1016/S0927-0248(00)00292-0

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ESR and PL characterization of point defects in $CuGaSe_2$ single crystals

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Abstract

Electron spin resonance (ESR) and photoluminescence (PL) spectra were employed to elucidate point defect features in $CuGaSe_2$ crystals grown by the traveling heater method. The isotropic paramagnetic center has been found in the crystals as-grown and annealed in various gas mediums. The PL bands have been observed in dependence on H_2-, O_2- and Se_2-annealings. The presence of donor singlet V_{Se}^{+} has been evidenced in the as-grown and H_2-annealed crystals. The ESR, PL data and appropriate models allow to add the point defect ensemble in $CuGaSe_2$ with other complex defects accordingly the treatments used in this work.

Keywords: $CuGaSe_2$ crystals; Photoluminescence (PL); Electron spin resonance (ESR); Selenium vacancy; Complex defects

1. Introduction

$CuGaSe_2$ is a promising absorber material for photovoltaic devices because of its appropriate band gap and high absorption coefficient in the solar spectrum. In spite of the considerable progress in research for its solar cell application, only a limited number of data are available about basic properties of this material. To improve the material quality, deeper knowledge of electronic structure are necessary via systematic study of point defects and impurities in the single crystals. There are only few studies for Cu-vacancies (V_{Cu}) and Fe- and Ni-related centers in $Cu(In,Ga)Se_2$ using the ESR

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0927-0248/01/$ - see front matter
PII: S0927-0248(00)00292-0

technique [1–3]. The sole available ESR data for polycrystalline $CuGaSe_2$ prepared by the melt growth method were reported by Birkholz et al. [2]. Recently, low-impurity-concentration single crystals were obtained by the traveling heater method (THM) [4]. However, unintentional donors and acceptors of a large concentration exist in $CuGaSe_2$ crystals and considerable efforts are being directed towards the defect control and characterization.

It was found earlier the post-growth annealing of Cu-containing ternary selenides in air or oxygen improves optical properties of eptaxial films [5] and increases the efficiency of polycrystalline solar cells [6,7]. The mechanism responsible for this oxygen annealing effect is not fully understood and explained till now.

The objective of this study is to provide with new information on point defects using ESR and PL spectra and to elucidate the annealing effect on $CuGaSe_2$ single crystals.

2. Experimental

The bulk $CuGaSe_2$ crystals were grown from the Ga solution using THM technique at the Mie University [4]. The samples for measurements were cut out of the bulk material and have typical sizes of $(4 \times 2 \times 2)$ mm^3. In order to manage the extrinsic/intrinsic defect concentration the samples were subjected to annealing in Se_2, O_2, and H_2 atmosphere. The Se_2-annealing was carried out in a closed processing tube and O_2- and H_2-treatments in an open processing tube. The tube was filled with the annealing gas of about 2 atm in pressure. The above annealings were carried out at 200°C for 1 h.

The JEOL JES-RE2X X-band spectrometer was employed in the ESR measurements at $T = 4.2$ K. The magnetic field up to 1.3 T and microwave power of 5 mW were used. PL measurements were performed using the Ar^+ laser (514.5 nm, 30 mW), JASCO CT-25C monochromator and North Coast EO-817L model Ge photodiode cooled with liquid nitrogen. The sample temperature of 20 K was maintained by the CryoMini type He-refrigerator cryostat.

3. Results and discussion

3.1. Electrical conductivity

The thermal probe method shows the p-type conductivity remains for all the samples under investigation. The estimation of a specific conductivity by the VA-ohm meter gives values $\sigma \leqslant 2 \times 10^{-7} \Omega^{-1} cm^{-1}$ for as-grown and H_2-annealed samples; $\sigma \leqslant 2 \times 10^{-5} \Omega^{-1} cm^{-1}$ for Se_2- and O_2-annealed samples at $T = 300$ K. The steady p-type and high resistivity indicate a high power of donor-acceptor (D–A) compensation in $CuGaSe_2$ crystals. The increase of σ value by > 2 orders as a result of Se_2- or O_2-annealing points out the change in free hole concentration and most likely by the donor V_{Se} point defect and oxygen-related defect complex. As known from previous investigations, e.g. [8–10], selenium and oxygen serve usually as an efficient chemical agent in Cu-III-Se_2 materials to suppress surplus donor-type point defects, like V_{Se}, therefore our treatments should result in a decrease of D–A compensation.

3.2. Annealing effect on ESR spectra

ESR spectra of samples as-grown and annealed in H_2, and O_2, Se_2 atmosphere are presented in Fig. 1. All the curves show the peak signal I_0 at the magnetic field $H = 320\,\text{mT}$. An additional ESR peak was detected in the low field region, noted as A. Details of the A-signal study will be published elsewhere. There are no other signals in the range $H = 0$–$1.3\,\text{T}$.

The g-factor was elucidated for I_0-signal as 2.006, close to $g = 2.003$ for free electrons. The narrow line ($\Delta H \cong 0.8$ mT) is characteristic of all ESR spectra excluding Se_2-treated crystal. This difference is associated with the concentration of selenium atoms or selenium vacancies in the crystals. Since the decrease of ESR I_0-signal is

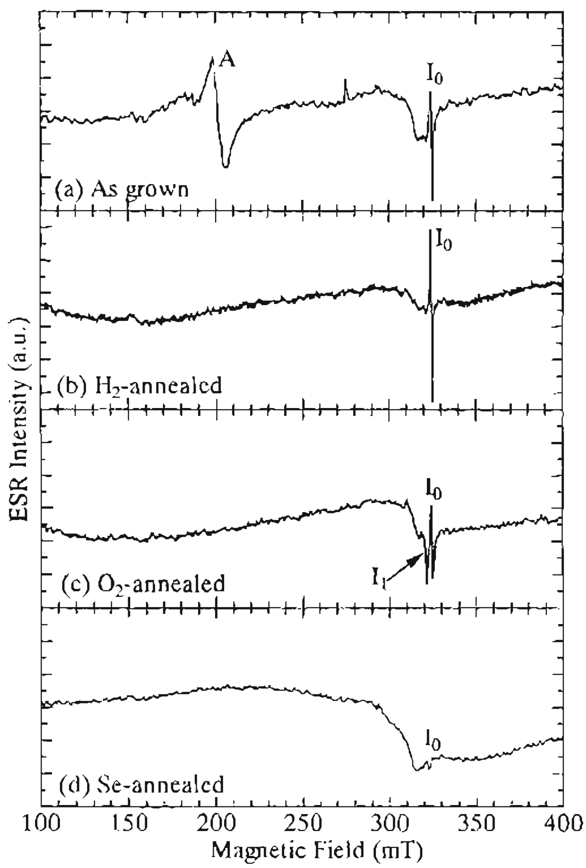

Fig. 1. ESR spectra of $CuGaSe_2$ single crystals at $T = 4.2\,\text{K}$. (a) as-grown, (b) H_2-, (c) O_2- and (d) Se_2-annealed samples.

observed only after annealing with VI group elements (oxygen, selenium) this effect may be ascribed to decreasing the V_{Se} concentration. Earlier the ESR signals were observed at around $g = 2.003$ in $Cu(In,Ga)Se_2$ and $CuIn_2Se_{3.5}$ compounds [2,3] and tentatively assigned to singly ionized donors as anticipated V_{Se}^{+} and Ga_{Cu}^{+}. For binary chalcogenides, the ESR signals at $g = 2.0027$ with the line-width of 0.58 mT in ZnSe epilayers, ZnS ($g = 2.0034$), CaSe (2.003) and SrSe (2.0032) were assigned also to the singly ionized vacancy V_{Se}^{+} [11,12].

As known from defect physics of the ternary compounds discussed in Refs. [13,14], the formation energy for various point defects in chalcopyrites differ strongly and for $CuGaSe_2$ by analogy with $CuInSe_2$, they may be ranged as

$$Ga_{Cu} < Cu_{Ga} < V_{Se} < V_{Cu} < V_{Ga} < Cu_i. \qquad (1)$$

Our crystals were grown by THM technique using Ga-solution then the presence of point defects as Cu_{Ga}, V_{Ga} and Cu_i is unlikely. On the other hand, the formation of some point defect complexes occurs to have the lower formation energy than that of single point defects [13]. Based on defect physics models, we suppose the main point defects in our $CuGaSe_2$ crystals are to be V_{Se}, $[2V_{Cu}^{-} + Ga_{Cu}^{2+}]$ defect pair, Ga_{Cu} and V_{Cu}. Obviously, the charge state may change with treatments. Because the neutral and doubly ionized centers are not paramagnetic, the ESR measurements show the presence of singly ionized defects like V_{Se}^{+} and $[V_{Cu}^{-} + Ga_{Cu}^{2+}]^{+}$ or V_{Cu}^{-}. It is mentioned that energetically the existence of the first two defects is preponderant in our crystals.

In case of Se_2-annealing the process of V_{Se} suppression flows more intensively, however in case of O_2-annealing, the additional formation of more complex defects like "oxide molecules" is possible. The similar production of "oxide molecules" in $CuInSe_2$ crystals was postulated for oxygen interaction with chalcopyrite lattice at the first stage of thermal oxidation and ion implantation [9,10].

As seen in Fig. 1(c), the I-peak signal occurs to be structured ($g_{av} = 2.04$, $\Delta H = 2$ mT). The arising additional I_1-peak may be responsible for Ga–O bonds electrically polarized. This fine structure appears due to changing the coordination of Ga atoms in chalcopyrite lattice because of reacting oxygen and formation of new molecular complexes Ga_2O_3, GaO^{+}, with V_{Cu}^{-}.

In contrast to above treatments, the H_2-annealing should result in opposite effect. The high concentration of acceptor-type defects V_{Cu} in the initial crystals should be suppressed partly by intensive H_2-annealing. It supposes the hydrogen in $CuGaSe_2$ passivates main defects responsible for p-type conductivity.

In other words, the H_2-annealing results in increasing concentration of singly charged point defect pairs $[V_{Cu}^{-} + Ga_{Cu}^{2+}]^{+}$ due to a passivation of copper vacancies. Indeed, the ESR I-signal in hydrogen treated crystals has the maximal amplitude, see Fig. 1(b). This indicates the elevated concentration of singlet paramagnetic centers after the H_2-annealing.

3.3. Photoluminescence

The PL spectra of all the samples under study are presented in Fig. 2. Two emission bands are observed at 1.57 and 1.616 eV. Similar PL emissions were reported earlier

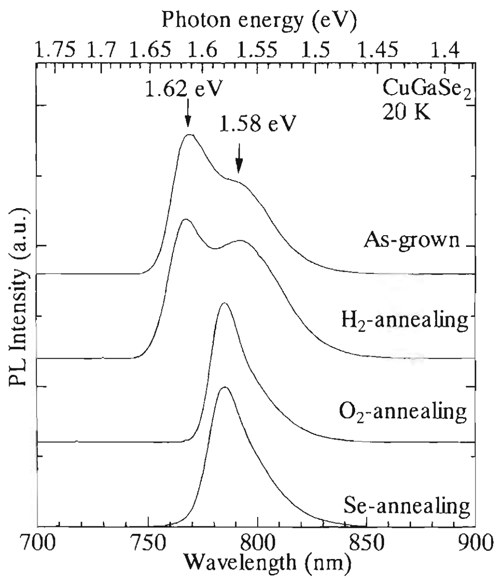

Fig. 2. Photoluminescence spectra at $T = 20\,K$ of $CuGaSe_2$ single crystals as-grown and annealed in various mediums.

for $CuGaSe_2$ epitaxial films grown by the MBE [15] and close to that for $CuGaSe_2$ single crystals grown by iodine vapor transport [16]. The main PL emission peaks at $h\nu = 1.616–1.618\,eV$ in as-grown and H_2-annealed samples. The annealing in different mediums (Se_2 and O_2) leads to disappearing this band and prevailing the 1.57–1.58 eV band over others. This long wave band may be associated with presence of Ga_{Cu} antisite defect. As follows from our ESR results and PL data of other authors [15,16] the short wavelength peak (1.62 eV) may be consistently ascribed to singly ionized V_{Se}^{+} point defect in the as-grown and H_2-annealed crystals. The existence of selenium vacancies in other charge states also is possible but their existence requires additional evidences. After Se_2- or O_2-treatments, the concentration of V_{Se} falls fast due to formation of neutral Se_{Se} or O_{Se} states, accordingly. The H_2-annealing in opposite effects a complex state, perhaps slightly activating the Ga_{Cu} point defect by charging the defect pair $[V_{Cu}^{-} + Ga_{Cu}^{2+}]^{+}$. When hydrogen effects the crystal, it is believed the change in V_{Se} concentration is minimal.

4. Conclusion

This paper describes new ESR and PL features of the point defect ensemble in $CuGaSe_2$ single crystals, grown by traveling heater method. ESR spectra showed variation in strength of isotropic *I*-signal for as-grown crystal and another ones subjected to annealing in H_2-, O_2- and Se_2-mediums. ESR spectra allowed to define paramagnetic properties and g-factor of point defect centers in $CuGaSe_2$ and to link them with the presence of singly ionized defects V_{Se}^{+} and defect pair $[V_{Cu}^{-} + Ga_{Cu}^{2+}]^{+}$. The formation the Ga-O bonds and oxygen related complexes, as a results of O_2-annealing was suggested by the additional ESR I_1-peak.

Photoluminescent properties of these $CuGaSe_2$ single crystals were examined and different emission bands have been found due to annealings. The 1.62 eV band was ascribed to optical transitions from V_{Se}^{+} donor level. The long wavelength emission has been found to do not effected by treatments and may be associated with some stable defect as Ga_{Cu} antisite.

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