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MATERIALS SCIENCE IN SEMICONDUCTOR PROCESSING

EPR studies of point defects in Cu-III–VI_2 chalcopyrite semiconductors

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Abstract

EPR and PL spectra were measured to investigate point defects in I–III–VI_2 type chalcopyrite semiconductors where the group I element is Cu. Taking into account various optical spectra, the EPR signals observed were assigned to defect centers involving residual Fe impurities and Cu-vacancies. Some of the point defects were found to form defect-complexes.

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Keywords: Chalcopyrite semiconductors; Electron paramagnetic resonance; Photoluminescence

1. Introduction

Chalcopyrite semiconductors of both I–III–VI_2 and II–IV–V_2 types have been attracting attention as potential materials for next-generation electro-optical and spin-electronics devices [1,2]. Among these chalcopyrite crystals most intensive studies have been performed in the series of compounds belonging to the I–III–VI_2 family, where Cu is involved as a group I element. In particular, $CuInSe_2$ has been proved to be one of the best materials for thin film solar cells, where the control of conductivity type and carrier density has been achieved by the non-stoichiometry introduced intentionally, although few knowledge has been accumulated on the physical properties of intrinsic defects in chalcopyrites.

We have been working with electron paramagnetic resonance (EPR) and optical studies of intrinsic point defects in single crystals of $CuAlS_2$ [3], $CuAlSe_2$ [4], $CuInSe_2$ [5] and $CuGaSe_2$ [6,7], as well as many transition-metal impurities in these crystals [8]. Sources of these transition-metal impurities are either those introduced intentionally during growth or those found as residual impurities, the content of the latter being as large as 20–50 ppm in iodine-transport samples [9]. Thermal treatments in different environments often lead to the coloration of these crystals. The coloration is closely related with the change in the valency of transition elements due to thermal treatments. A defect whose energy level is located close to the center of the band gap will gain or lose electrons as the Fermi level passes through the demarcation (or recharging) level associated with this defect.

The position of the Fermi level in the band gap can be influenced by thermal treatments of the crystal. If the charged states of defects are paramagnetic (with unpaired spins), then the electron paramagnetic resonance technique can be applied to monitor the motion of the Fermi level near the demarcation level of the defects. Even in the case where no unpaired spins exist, optical excitation can make them paramagnetic.

2. Experiments

Single crystals of $CuAlS_2$, $CuAlSe_2$ and $CuGaSe_2$ were grown in our laboratory by chemical transport reaction using iodine as a transporting agent, while single crystals of $CuInSe_2$ were grown at Science University of Tokyo by normal freezing technique from the melt [10]. Single crystal of $CuGaSe_2$ was prepared at

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Mie University by traveling heater method (THM) from the solution [11].

EPR spectra were measured using a JEOL JES-RE2X X-band spectrometer at temperatures between 4.2 K and room temperature. Photoluminescence (PL) spectra were measured using 514-nm line of an Ar-ion laser or 530-nm line of LD-pumped YAG SHG laser as light sources, a JASCO CT-25C monochromator or a JASCO CT-50C monochromator and a Hamamatsu R928 photomultiplier or a Northcoast EO-817L liquid nitrogen-cooled Ge diode as a photo-detector. Temperature was maintained at 20 K using a He-refrigerator cryostat.

3. Results and discussion

Fig. 1(a) shows EPR spectra of $CuAlS_2$ single crystals before and after white light illumination. The signals marked with black dots have been assigned to isolated Fe^{3+} centers [12]. In addition to these Fe-related EPR signals, a light-induced EPR signal was observed at $g = 2.019$ and was ascribed to a hole that is bound to a copper vacancy V_{Cu} [3]. From the temperature dependence measurement of the EPR intensity shown in Fig. 1(b), the activation energy of the center was determined to be 190 ± 10 meV. This value is quite close to the value of 180 ± 10 meV determined as the binding energy of a V_{Cu}-acceptor by photoluminescence measurements [13]. A peak of the EPR excitation spectrum for the V_{Cu} signal was observed at 365 nm (3.40 eV), which was associated with the photoionization energy of the center as shown in Fig. 1(c). The sum of the photoionization energy 3.40 eV and the V_{Cu} accepter binding energy 0.19 eV amounts to 3.59 eV, which is quite close to the energy gap of $CuAlS_2$($E_g = 3.55$ eV). After the light is switched on, the intensity of the V_{Cu} signal gradually increases while that of Fe^{3+} signal decreases. Switching-off of the light results in an opposite behavior. Electrons, optically excited from the V_{Cu} into the conduction band, are found to be trapped mainly by Fe-related deep levels, making the intensity of Fe^{3+} signal decrease.

In $CuAlSe_2$ the similar light-induced EPR signal was observed at $g = 2.032$, the activation energy being 40 meV close to the value 52 meV determined by PL measurements [4]. A peak of the EPR excitation spectrum was observed at 2.64 eV. The sum of 2.64 and 0.04 eV is quite consistent with the energy gap value (2.70 eV) of $CuAlSe_2$.

In $CuInSe_2$, a broad isotropic signal at $g = 2.12$ with $\Delta H_{pp} = 10$ mT was observed when the crystal was annealed in vacuum or in Se-atmosphere and was completely quenched by annealing in Cu-atmosphere, the annealing temperature and time being 650°C and 50 h, respectively [5]. The Cu/In ratio of vacuum-annealed, Se-annealed and Cu-annealed sample was determined by EDX as 0.89, 0.92 (In-rich) and 1.115 (Cu-rich), respectively. Therefore, we tentatively assigned that the EPR signal is due to a single Cu-vacancy (V_{Cu}). A similar EPR signal was already assigned to a hole trapped at a single V_{Cu}-defect and broadening of the signal was interpreted in terms of the hyperfine interaction with In nuclei (nuclear spin $I = 9/2$) in the second shell surrounding the V_{Cu}-defect by Tchapkui-Niat et al. [14]. However, their assignment seems contradictory to the positron-annihilation results in MBE-grown $CuInSe_2$ thin films, which showed that V_{Cu}–V_{Se} complex-defects prevail in the In-rich samples, while V_{Cu} single-vacancies predominate in Cu-rich samples [15]. Concerning Fe-related signals, broad EPR signals with fine structures have been related to Fe^{3+}-X complex defects. On the other hand, a highly anisotropic EPR signal observed in a vacuum-annealed $CuInSe_2$ has been assigned to Fe^{2+}. Infrared absorption showed a broad band ranging between 2000 and 4500 cm^{-1}, which was assigned to ^5E–$^5T_2$

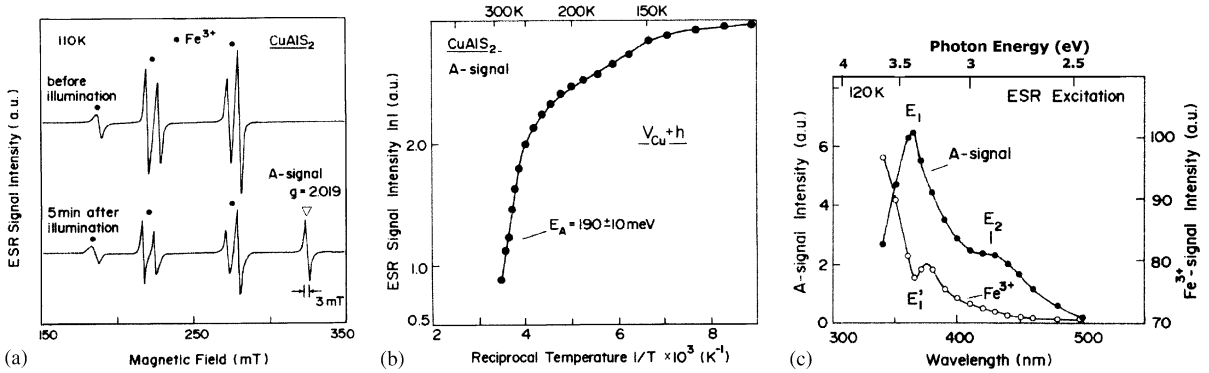

Fig. 1. (a) EPR spectrum of $CuAlS_2$ single crystals before and after light illumination. (b) Temperature dependence of the intensity of A signal. (c) Excitation spectrum of A signal.

crystal field transition in $3d^6$ manifold of Fe^{2+} in Td symmetry [16].

EPR spectra of $CuGaSe_2$ single crystals as-grown and annealed in H_2, and O_2, Se_2 atmosphere are presented in Fig. 2. Both isotropic and anisotropic paramagnetic centers were found in as-grown and annealed samples. All the curves show a peak I_0 at the magnetic field $H = 320\,\text{mT}$. An additional EPR peak was detected in the low field region, noted as A. There are no another signals in the range $H = 0-1.3\,\text{T}$. The A signal is considerably anisotropic and was assigned to Fe^{3+}-related center. A signal was completely quenched by H_2- and O_2-annealing. The H_2-annealing produces V_{Se}, which pushes up the Fermi level above the Fe^{2+}/Fe^{3+} demarcation level changing the Fe valence from Fe^{3+} to Fe^{2+}, which can explain the disappearance of the Fe^{3+}-related signal. The reduction of the signal A by O_2-annealing may be explained if the signal is related to Fe^{3+}–V_{Se} complexes, since O_2-annealing is known to reduce the concentration of V_{Se} [17].

The g-factor of the I_0-signal was found to be 2.006, close to $g = 2.003$ for free electrons. The narrow line width ($\Delta H \cong 0.8\,\text{mT}$) is characteristic of all EPR spectra except for Se_2-treated crystals. The disappearance of the I_0-signal in the latter shows that the signal may be associated with the non-stoichiometry in the crystals. Similar EPR signals were observed around $g = 2.003$ in a Cu(In,Ga)Se_2 compound and tentatively assigned to singly ionized donors V_{Se}^{+} and Ga_{Cu}^{+} [18]. Since our THM-crystals were grown under a strongly Ga-rich condition, the presence of point defects as Cu_{Ga}, V_{Ga} and Cu_i may be ruled out. In $CuInSe_2$, it has been revealed through a theoretical research by Zhang et al. that defect-complexes such as $(2V_{Cu}^{-} + In_{Cu}^{2+})$ and $(Cu_{In}^{2-} + In_{Cu}^{2+})$ can more easily be created than single point defects [19]. Based on defect physics models, we suppose the main point defects in our $CuGaSe_2$ crystals are isolated vacancies V_{Se} (either V_{Se}^{0}, V_{Se}^{+} or V_{Se}^{2+}) and V_{Cu}^{-}, and defect pairs $(2V_{Cu}^{-} + Ga_{Cu}^{2+})$. Since the neutral and doubly ionized centers are not paramagnetic, EPR measurements detect the singly ionized defects like V_{Se}^{+} and $(V_{Cu}^{-} + Ga_{Cu}^{2+})^{+}$ or V_{Cu}^{-}, the first two defects being more probable in our crystals from formation-energy considerations.

The PL spectra of all the $CuGaSe_2$ samples under study are presented in Fig. 3. Two emission bands are observed at 1.58 and 1.62 eV in both as-grown and H_2-annealed crystals. Similar PL emissions were reported in $CuGaSe_2$ epitaxial films grown by MBE [20]. The spectral shape can be decomposed into three uniformly broadened single Gaussian lines at 1.614–1.618 eV (main peak), 1.570–1.580 eV (shoulder) and 1.545–1.548 eV (foot). Annealing in Se_2 and O_2 atmosphere leads to

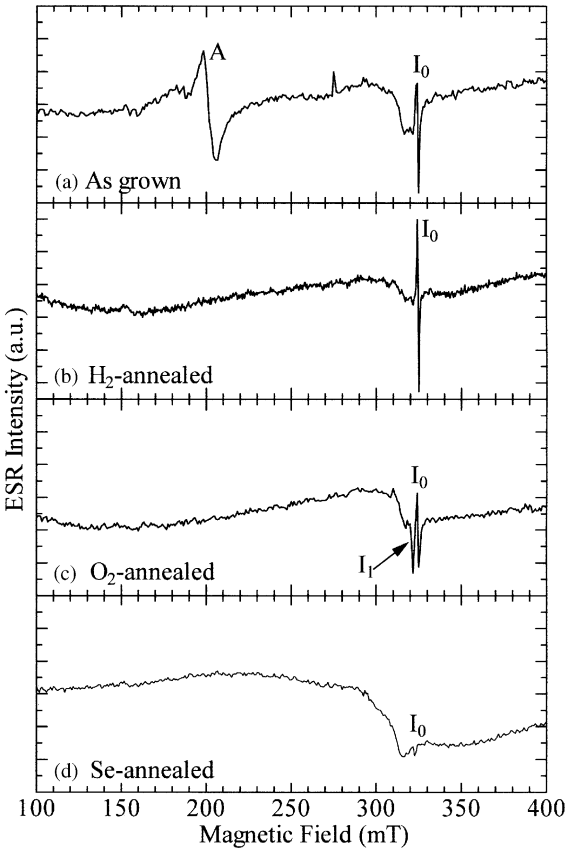

Fig. 2. EPR spectra of $CuGaSe_2$ single crystals.

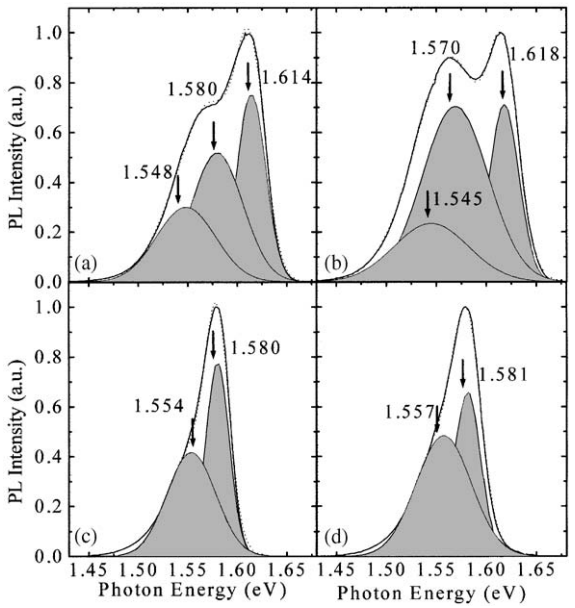

Fig. 3. Multi-peak Gaussian fit to photoluminescence spectra of $CuGaSe_2$ single crystals as-grown (a) and annealed in vacuum (b)–(d). The common fitting curve well traces the experimental points. Shadowed contours: uniformly broadened lines.

disappearance of the 1.62-eV peak showing that a band is composed of two uniformly broadened single Gaussian lines at 1.580–1.581 and 1.554–1.557 eV. These two low-energy emissions may be ascribed to the optical transitions related to some point defect states that are not affected by any treatments used in this work. They are possibly stable-defect complexes in $CuGaSe_2$ with a very low formation energy, for example $(Cu_{Ga}^{2-} + Ga_{Cu}^{2+})$, as predicted theoretically for $CuInSe_2$ [19].

In view of our EPR results and PL data of other authors the high-energy peak (1.62 eV) may be consistently ascribed to V_{Se}^{+} point defect in as-grown and H_2-annealed crystals. After Se_2- or O_2-treatments, the concentration of V_{Se} rapidly decreases with the formation of neutral Se_{Se} or $(V_{Se}^{2+} + O^{2-})$ states, accordingly. The H_2-annealing results in the $(2V_{Cu}^{-} + Ga_{Cu}^{2+})$ state, slightly activating the Ga_{Cu} point defect by the charged defect pair $(V_{Cu}^{-} + Ga_{Cu}^{2+})^{+}$. The change in the concentration of V_{Se} seems not very large in the H_2-annealing.

4. Conclusion

Characterization of point defect by means of EPR and PL was carried out in series of Cu-III–VI_2 chalcopyrite type compounds. Isolated copper vacancies were clearly observed by photo-EPR in $CuAlS_2$ and $CuAlSe_2$ prepared by iodine transport. EPR signals related to copper vacancies have been observed in a vacuum-annealed $CuInSe_2$. Defect-complexes involving copper vacancy have been found from EPR and PL studies in an as-grown and H_2-annealed $CuGaSe_2$.

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