ESR and Optical Studies of CuInS$_2$ Single Crystals

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Infrared (IR) absorption and ESR spectra of iron and chromium impurities were studied in CuInS$_2$ crystals. Both iron in its divalent and trivalent valence states and chromium in its divalent state were observed. The charged states of these ions showed a drastic change in accordance with the Fermi level movement in the band gap introduced by vacuum- and sulfur vapor-annealing. The g-values of these divalent ions determined from ESR ($g_{\parallel}=2.20$ in Fe^{2+} and $\langle g \rangle=1.935$ in Cr^{2+}) were in good agreement with those estimated theoretically using approximate values of crystal-field parameters ($Dq \sim 350$ cm^{-1} in Fe^{2+} and $Dq \sim 570$ cm^{-1} in Cr^{2+}) deduced from optical absorption spectra.

1. Introduction

Ternary chalcopyrite semiconductor CuInS$_2$ is one of the most promising materials for solar cells application due to its large absorption coefficient, its direct energy band gap value ($E_g=1.55$ eV)[1] suitable for achieving high photovoltaic energy conversion efficiency, as well as a small lattice mismatch of this compound with another prospective photovoltaic material having narrower band gap-CuInSe$_2$.[2]

For device application of CuInS$_2$ it is vital to know the electro-optical properties of this material, which are dominated by structure, stoichiometry, as well as intrinsic and extrinsic defects, including those formed by transition atom ions, which are known to be present in the ternary compounds and introduce deep levels in the band gaps of these materials.[3]

In this study we present the results of the ESR and optical absorption investigations of the CuInS$_2$ single crystals grown by the chemical vapor transport technique.

2. Experimental

Single crystals of CuInS$_2$ were grown by the chemical vapor transport (CVT) in a closed system using iodine as a transporting agent (the source and growth zone temperatures were 820°C and 700°C, respectively, and the duration of CVT was 6 days). The source material for CVT was a powder of CuInS$_2$ obtained by the direct melting of constituent elements (Cu, In, S-99.9999%) in a BN crucible held in a sealed quartz ampoule. The resulting crystals exhibited p-type conductivity with the resistivity values $\rho \geq 10^3 \Omega \cdot$cm. The electron probe microanalysis (EPMA) showed that the concentration of the dominant TA impurities (Fe and Cr) in the obtained crystals was less tha 0.01 at% (the sensitivity limit of our EPMA system).

Thermal annealings of the samples in vacuum and S-vapor were carried out for 50 h at 650°C and 700°C, with the pressure of sulfur being about 3 atm. Optical absorption measurements were carried out at room temperature (RT) by using a HITACHI U-3410 spectrometer and a BOMEM Type MB 100 Fourier Trasform IR spectrometer, the optical beam diameter being about 2 mm. ESR spectra were taken at 4.2 K with a JEOL JES-RE2X X-band spectrometer with the microwave power of 5 mW.

3. Results and Discussion

The typical IR absorption spectra are shown in Fig. 1 for the as-grown, as well as vacuum-annealed and sulfur vapor-annealed CuInS$_2$ crystals, whereas the ESR spectra for the same crystals are shown in Fig. 2. The absorption spectrum of the as-grown crystals exhibits a broad absorption band "A" peaked at 5700 cm^{-1}
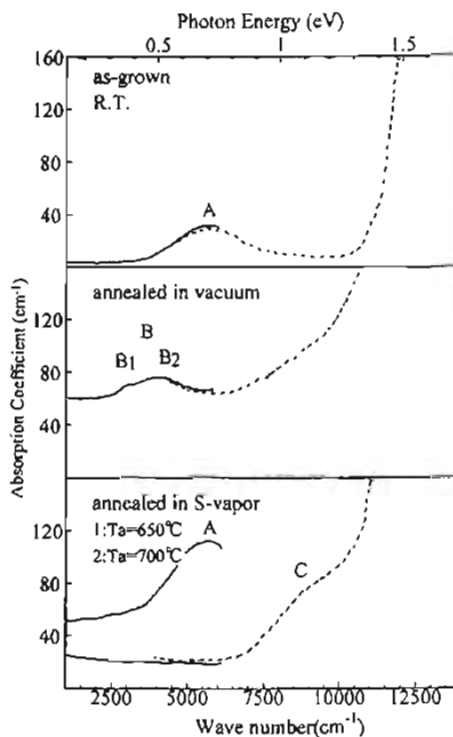

Fig. 1. The IR absorption spectra of the as-grown, as well as vacuum and S-vapor annealed CuInS$_2$ crystals. The solid lines show the results obtained by using the Fourier Transform IR spectrometer, whereas the broken lines show that obtained using a HITACHI spectrometer

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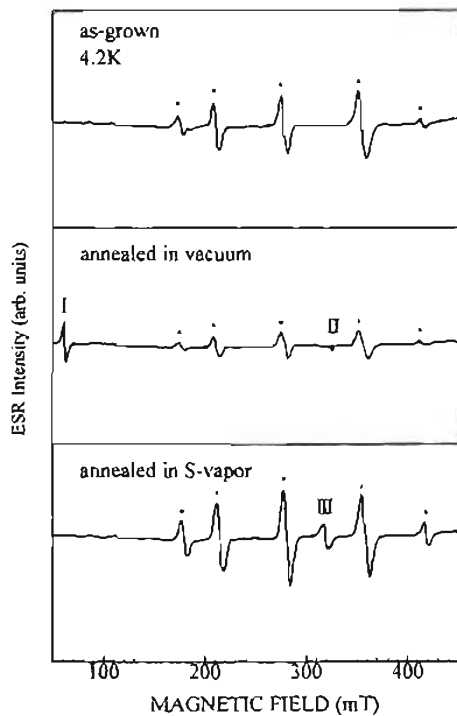
Fig. 2. The ESR spectra of the as-grown, as well as vacuum and S-vapor annealed CuInS$_2$ crystals.
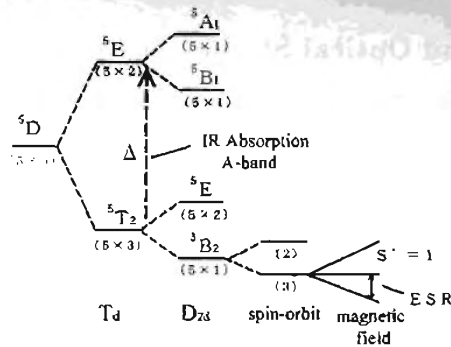

Fig. 3. The splitting of the ground ^5D term of the Cr^{2+} ion in a tetragonal crystal field. The numbers below the energy levels show the spin degeneracy x orbital degeneracy of the levels.

(0.707 eV) which can be assigned, on the basis of the previous studies,[4] to the $^5T_2 \Rightarrow {}^5E$ electronic transitions between 3d-shell originated orbitals of Cr^{2+} ion. By the effect of the tetragonal (D$_{2d}$) crystal field the ground state ($^5T_2$) of the Cr^{2+} ion is split into the orbital singlet $^5B_1$ and doublet ^5E. the singlet being the lowest, while the excited state (^5E) is split into orbital singlets $^5A_1$ and $^5B_1$ (see Fig. 3). The optically induced zero-phonon and phonon-assisted transitions from the $^5T_2$-originated ground state to the ^5E-originated excited state results, at RT, in a broad absorption band denoted as A. The energy position of the barricenter of the A-band provides an approximate value of the cubic crystal-field parameter $Dq \sim 570$ cm^{-1}.

The ESR spectrum exhibits a well-known signal of the subtitutional Fe^{3+} ion with 3d^5 electronic configuration,[3,5] consisting of five fine-structure lines broadened due to the effects of random crystalline fields and unresolved hyperfine interaction with nuclear moments of ^{63}Cu and ^{113}In, ^{115}In nuclei.

Annealing of the crystals in vacuum results in a quenching of the Cr^{2+}-related absorption band A and a simultaneous appearance of another broad band B centered around 3500 cm^{-1} and exhibiting two subbands peaked at 3200 cm^{-1} (B$_1$) and 3900 cm^{-1} (B$_2$). The B-band can be assigned to the $^5E \Rightarrow {}^5T_2$ transitions in the 3d^6 manifold of Fe^{2+} ion, the assignment being in accordance with the results of the previous studies in the CuInSe$_2$ and CuGaS$_2$[4] compounds. The energy level splitting for the Fe^{2+} (3d^6) ion is opposite to that for the Cr^{2+} (3d^4) ion shown in Fig. 3, with the transitions occuring beween the lowest $^5B_1$-state split from the ground orbital doublet state (^5E), and the states with the ^5E- and $^5B_2$-representations split from the first excited triplet level of the $^5T_2$-symmetry, these transitions

corresponding to absorption bands B$_2$ and B$_1$, respectively. Similarly to the above discussed case of Cr^{2+} ion, absorption lines due to these crystal-field transitions are broadened due to phonons at RT, which explains the broad absorption spectra observed experimentally.

It should be noted that, since both transition metal ions under consideration, i.e., Cr^{2+} and Fe^{2+}, are situated in the crystal field of the tetragonal (D$_{2d}$) symmetry, which results in the orbital singlet ground states in both systems, we can neglect the Jahn-Teller effect in the ESR spectra. The Jahn-Teller effect, however, can cause an additional splitting of the orbital doublet ^5E and, therefore, can affect the absorption spectra. In our absorption spectra, taken at RT, the effect, however, is indiscernable.

The ESR spectrum in the vacuum-annealed sample (Fig. 2) exhibits three signals, i.e. (1) the signal from Fe^{3+}, the intensity of which decreases compared with that in the as-grown samples, (2) a highly anisotropic signal l, the g-factor of which takes its maximum value of $g_{eff} \sim 14.5$ when the tetragonal c-axis of the crystal is parallel to the external magnetic field direction, as well as (3) a narrow nearly isotropic signal with $g = 2.0012 \pm 0.0015$, marked as signal II.

Taking into account the results of our studies in CuInSe$_2$ compound,[6] the I-signal has been attributed to the microwave transitions within the lowest $M_s = \pm 2$ non-Kramers doublet of the Fe^{2+}. Since the noncubic crystal-field splitting working on the ground state ^5E of the Fe^{2+} ion in CuInS$_2$ is expected to be small due to a small tetragonal distortion in this compound ($c/a = 2.0158$),[2] we can estimate the g-factor for Fe^{2+} on the basis of the crystal-field theory for the predominant cubic crystal field as[7]

$$g_{//} = g_e - \frac{8k\lambda_0}{\Delta_1} \qquad (1)$$

where λ_0 is the spin-orbit coupling constant for the free Fe^{2+} ion and $k(<1)$ the reduction factor due to the effect of covalency, $g_e = 2.0023$ is the free electron g-factor and Δ_1 is the energy position of the IR absorption B$_1$-band due to Fe^{2+}. Assuming $k = 0.8$[8] and taking $\lambda_0 = -100$ cm^{-1} and $\Delta_1 = 3200$ cm^{-1} we then obtain $g = 2.26$, which is close to the value of $g_{//}$ for the Fe^{2+} ion in CuInSe$_2$ ($g_{//} = 2.19$)[7] and CuAlS$_2$ ($g_{//} = 2.19$).[8]

Next, since under $H//c$ the resonance condition for the transition within the $M_s = +1/2$ doublet is $(h\nu)^2 = (4g_{//}\beta H)^2 + \alpha^2$ (where α is the cubic field splitting parameter and $h\nu$ is the microwave energy),[8] we calculated the value of α from the known values of $g_{eff_{//}}$ and $g_{//}$ using the expression

$$g_{eff_{//}} = 4g_{//}[1-(\alpha/h\nu)^2]^{-1/2} \qquad (2)$$

the resulting value of α being $|\alpha| = 0.24$ cm^{-1}, which is comparable with that for CuInSe$_2$ ($|\alpha| = 0.28$ cm^{-1})[6] and CuAlS$_2$ ($|\alpha| = 0.45$ cm^{-1}).[8]

The signal II in the ESR spectrum may safely be attributed to that from an electron bound to a donor since the averaged g-value of this signal is smaller than g_e. The most probable donor states, which bind electrons giving rise to the signal II, are thought to be the ones formed by V_s (sulfur vacancy) since the large concentration of V_s is expected to be formed due to vacuum annealing. The high concentration of donors is also evidenced by the narrowness of the signal II ($\Delta H_{pp} \sim 0.6$ mT) which requires an exchange interaction between closely situated donor states.

Annealing in vacuum, therefore, results in the upward motion of the Fermi level in the band gap of CuInS$_2$. The observed vacuum annealing-induced effects of the quenching of the Cr^{2+} absorption and the appearance of the Fe^{2+} absorption in the IR spectra, as well as a decrease in intensity of the Fe^{3+}-related signal and, again, the appearance of the Fe^{2+}-originated signal in the ESR spectra, are then a result of a change in the Fermi level energy position from that in the as-grown samples. We believe that in the vacuum-annealed crystals the Fermi level is shifted upwards from its original position and is situated above the Cr$^{+/2+}$ and near Fe$^{2+/3+}$ demarcation levels.

Annealing of the crystals in the sulfur vapor at $T_a = 650°C$ results in the strengthening of the Cr^{2+}-originated A-absorption, whereas the thermal treatment at $T_a = 700°C$ leads to a quenching of the Cr^{2+}-originated A-absorption and an appearance of the Fe$^{3+} \Rightarrow$ Fe^{2+} charge-transfer band C peaked at 9000 cm^{-1} (Fig. 1). The intensity of the Fe^{3+}-originated signal in the ESR spectra increases after the S-annealing (Fig. 2). In addition, the ESR spectrum exhibits an anisotropic signal III with the g-factor being in the range $g = 1.925–1.960$.

The anisotropic signal III may be assigned to the microwave transitions within the lowest spin triplet state of the Cr^{2+} ion in a tetragonal crystal field. This assignment is made on the basis of the g-value described below and the expected anisotropy without knowing the exact orientation of the sample. Since the resulting ground state is three-fold spin degenerate, the Cr^{2+} ion is described by the effective spin $S' = 1$ with the g-factor given by eq. (1), in which $g_{//}$ should be changed to an averaged g-value $\langle g \rangle$ and Δ_1 should be replaced by the approximate value of the cubic field splitting $(10Dq)$ estimated from the baricenter of the absorption band A due to Cr^{2+}. Then, taking again $k = 0.8$, as well as the values $\lambda_0 = 57$ cm^{-1} and $10Dq \sim 570$ cm^{-1} we obtain the averaged g-factor as

$\langle g \rangle = 1.935$, which is in the range of the experimentally observed g-factors for the III-signal. It should be noted that in some of the investigated CuInS$_2$ samples the ESR signal due to Cr^{2+} is so strong that it dominantes the spectra at low (4.2 K) temperature.

Annealing in the vapor of S at 650°C, therefore, causes the downward shift of the Fermi level below the Cr$^{+/2+}$ and Fe$^{2+/3+}$ demarcation levels, which results in the observed strengthening of the Cr^{2+}-related absorption and the Fe^{3+}-originated ESR signal, as well as in the appearance of the Fe$^{3+} \Rightarrow$ Fe^{2+} charge-transfer band. Since the Cr^{2+}-originated A-absorption is quenched in the sample annealed in S-vapor at 700°C, we believe that the Fermi level in that sample is situated not only below the Cr$^{+/2+}$ demarcation level (the Fermi level position in the as-grown crystals), but also below the Cr$^{2+/3+}$ demarcation level. The last assumption is supported by the fact that Cr is known to exist in several charged states even in semiconductors having not very large band gap energy. For example, in GaAs, having the band gap energy very close to that of CuInS$_2$, the Cr ion has been found to exist in three charged states: Cr^{2+}, Cr^{3+} and Cr^{4+}.[10]

4. Conclusions

In conclusion, we have detected Fe and Cr transition atom impurities of less than 0.01 mol% in the CuInS$_2$ single crystals grown by the CVT method. Both the divalent and trivalent valence states of Fe and the divalent state of Cr were identified by the IR absorption and ESR methods, the charged states of these ions being determined by the position of the Fermi level in the band gap of CuInS$_2$. The g-values of these impurity ions determined from ESR ($g_{//} = 2.20$ in Fe^{2+} and $\langle g \rangle = 1.935$ in Cr^{2+}) were in good agreement with those estimated theoretically using approximate values of crystal-field parameters ($Dq \sim 350$ cm^{-1} in Fe^{2+} and $Dq \sim 570$ cm^{-1} in Cr^{2+}) deduced from optical absorption spectra. More precise determination of crystal-field parameters requires low temperature absorption measurements, which is scheduled to be carried out in the near future.

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