ESR Characterization of CuAlSe₂ Single Crystals

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High-quality single crystals of CuAlSe₂ were grown by the chemical vapor transport technique starting from a polycrystalline CuAlSe₂ powder prepared by heating constituent elements above their melting points. The defect states of the crystals were characterized using photoinduced ESR technique at 120 K. An isotropic ESR signal "A" due to a hole trapped by an acceptor was found at the g value of 2 032. The activation energy obtained from the temperature-quenching curve of the A-signal was 40 meV ± 10 meV. This value was consistent with the level position determined from the difference between the band gap and the peak position of the excitation spectrum of the A-signal. The signal was tentatively assigned to a hole trapped by the Cu vacancy.

KEYWORDS: CuAlSe₂, chemical transport technique, photo-induced ESR, excitation spectrum, copper vacancy

1. Introduction

Chalcopyrite type compounds, such as CuAlS₂, CuAlSe₂, CuGaS₂, CuGaSe₂ and CuInSe₂, have been attracting interest as possible candidates for new optoelectronic devices.[1] Recent progress in metal organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) techniques has enabled growth of high-quality epitaxial films of these materials, which gives promising insight into device applications.[2] However, only a few studies have been carried out on the fundamental properties of these materials, especially on the electric structures of defects and impurities which are of critical importance in the realization of devices.

For this purpose, characterization by PL and ESR using well-defined single crystals is required. In previous studies we obtained high-quality single crystals of CuAlS₂, which showed free exciton luminescence[3] and were used for photo-ESR experiments. An ESR signal due to Cu vacancy was found, and the location of the energy level of this defect in the gap was determined.[4]

Only a few ESR studies have been performed in selenides among the chalcopyrite series. This is presumably due to lack of high-quality single-crystal samples suitable for ESR characterization. However, ESR data in well-defined single crystals of selenides are strongly required, since most recent applied research in the chalcopyrite materials is carried out on selenides, of which both p-type and n-type are easily prepared. We therefore began studies on selenides in the chalcopyrite series. We initially selected CuAlSe₂ because of the ease of comparison with the results of previous studies on CuAlS₂.

In the present paper we report on the preparation of high-quality single crystals of CuAlSe₂ and the observation of the photo-induced ESR signal from a hole trapped at a defect, which is assumed to be a vacancy of copper, in CuAlSe₂ crystals grown by the chemical vapor transport technique.

2. Experimental

Single crystals were grown by the chemical vapor transport method with iodine as a transporting agent. Usually, iodine-transported crystals of CuAlSe₂ show poor crystallinity, with twins and precipitations, when Cu, Al and Se are used as starting materials. In order to obtain crystals of better quality, we followed the procedure described in our previous paper for the growth of CuAlS₂.[5] The starting material for the transport was a powder ground from a polycrystalline ingot of CuAlSe₂ synthesized by means of direct melting of constituent elements of 99.9999% purity at 900°C in a pyrolytic BN crucible sealed in a fused silica ampoule. Iodine of 10 mg per cm³ of the inner volume of the ampoule was added to the starting material. Single crystals obtained showed well-developed facets of {112} crystal plane and were transparent with slightly yellowish color. Typical size of the single crystals was 5 mm × 2 mm × 1 mm. X-ray studies using a four-crystal diffractometer (Philips MRD High-Resolution X-ray Diffraction) revealed that the full width at half maximum (FWHM) of the 112 diffraction rocking curve was 72 s, which is smaller than the FWHM (usually on the order of 1 degree) in crystals obtained by the conventional iodine transport technique.

The difference in crystal quality between the two cases (one prepared starting from elements and the other from the ternary compound) may be attributed to the different modes of transport; iodides may be the dominant gas species when preparation started from the elements, while selenides may play the main role in the transport process when preparation started from the ternary compound. Iodine may only act to decompose the compound into two binary compounds in the latter process.

All as-grown crystals have been found to exhibit p-type conductivity with resistivity values as high as 10⁵–10⁶ Ω·cm due to the very pronounced effects of charge compensation, which usually takes place in wide-band-gap ternary chalcopyrites and results in the Fermi level position being close to the middle of the band gap.[6]

ESR spectra were obtained using a JEOL JES-RE2X X-band spectrometer between 120 and 300 K with microwave power of 5 mW. The magnetic field was modulated at 100 kHz with the modulation width (0.79 mT) kept below the width of ESR signals to avoid any distortion of line shapes. As a standard of the g value, a

$Mn^{3+}:MgO_2$ standard sample was used. Optical excitation spectrum of ESR has been measured by using white light of a 150 W Xe lamp, monochromated by a Ritsu MC-10 grating monochromator (focal length = 10 cm), the spectral resolution being about 1 nm. The photo-ESR excitation spectra were taken at 120 K after 5 min of optical excitation. The time interval of 5 min was chosen simply to save the experimental time, since temporal dependences of the ESR signal have been found to be the same for excitation at various energies used in our study, the ESR signal being saturated after about 1 h of continuous optical illumination, which is similar to the previously studied case of $CuAlS_2$.[4] The measurement was carried out point by point at each particular wavelength of optical excitation. In order to avoid the effects of trapping by the previous optical excitation, the sample temperature was increased to 300 K before each change of wavelength, to completely quench the photo-induced signal.

Photoluminescence (PL) spectra were measured using a 325-nm line of a Kimmon Electric CD3101R-1M HeCd laser (10 mW) as a light source, a JASCO CT-25C grating monochromator and a Hamamatsu R928 photomultiplier. Temperature was controlled between 70 and 300 K using an Oxford CF1104 continuous-flow cryostat.

All spectra were corrected for the spectral response of the optical system.

3.   Results and Discussion

No ESR signal was observed in as-grown $CuAlSe_2$ crystals at 300 K and 120 K. Only after irradiation at low temperature did an isotropic signal appear as shown in Fig. 1. Microwave power saturation of the signal could not be reached up to 50 mW at 120 K. We did not use higher magnitudes of the microwave power. We named this signal "A". The g value and the peak-to-peak field width ΔH_{pp} of A-signal were 2.032 and ~3.5 mT, respectively. Although we did not know exactly the orientation of the tetragonal c-axis of our samples in relation to the external magnetic field, the said isotropy of the A-signal has been verified by the ab-

sence of any change in the position of the A-signal at various orientations of the samples. As was discussed in §2, the intensity of the A-signal under constant optical excitation progressively saturates and reaches its final level after about one hour at 120 K. The signal could be quenched by heating the sample up to room temperature.

The A-signal can be definitely attributed to a hole trapped on some highly symmetric center since the observed g value of the A-signal is isotropic and larger than that of a free electron ($g_e = 2.0023$). It seems surprising to observe an isotropic signal in the tetragonal crystal lattice of a chalcopyrite compound. However, as reported for $CuAlS_2$ in our previous paper,[4] the isotropic behavior of the A-signal is understandable if we consider the possibility of a defect being located at the center of the less tetragonally distorted selenium tetrahedron, and that the remaining small anisotropy of the signal may be reduced by thermally stimulated hopping of a hole between four selenium ions, resulting in an averaged isotropic spectrum.

Since the linewidth of the A-signal is quite small, we can exclude the possibility of this signal arising from holes trapped on Cu or Al ions, since the nuclear moment of Cu leads to a linewidth of about 10 mT in ZnS,[7] and the nuclear moment of Al is even larger than that of Cu.

According to the above considerations, we propose an intrinsic defect center which originates from a hole trapped by a copper vacancy V_{Cu}, whose existence may reasonably be assumed from the observed p-type conductivity of $CuAlSe_2$. It consists of a p-hole centered on the V_{Cu} and equally shared by the nearest Se ions of the anion sublattice.

To be precise, the A-signal should be slightly anisotropic, with the anisotropy being caused by the distortion of the chalcopyrite crystal lattice from a perfect superstructure of the cubic ZnS lattice.[4] The expected anisotropy of the g value for $CuAlSe_2$, however, is as small as 0.0015, which is less than the error of our ESR experiment.

The observed broadening of the A-signal up to about 3.5 mT (which is similar in value to that of a hole trapped in V_{Cu} in $CuAlS_2$[4] and $CuGaS_2$[5] compounds) has been attributed to unresolved hyperfine interaction with Cu and Al ions in the second shell surrounding the copper vacancy.

Figure 2 shows an Arrhenius plot of the temperature dependence of the A-signal for the temperature range between 120 and 300 K. In the Hartree-Fock approximation, the energy level of an acceptor state is assumed to remain at the same position before and after an ionized acceptor traps a hole to become a neutral center. Therefore, the activation energy E_A can be estimated from the thermal quenching curve of the A-signal, which reflects the process of thermal release of captured holes into the valence band. Taking into account the above considerations, we determined the value of the activation energy E_A from the slope of the Arrhenius plot of the A-signal as $E_A = 40 \pm 10$ meV. This result is consistent with the reported value 62 meV obtained
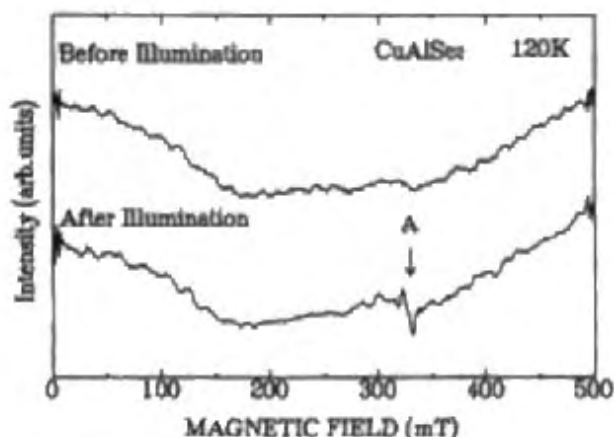

Fig. 1.   ESR spectra of a $CuAlSe_2$ single crystal before and after illumination with white light at 120 K.
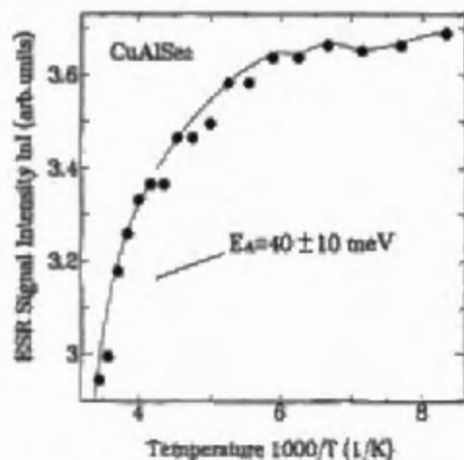
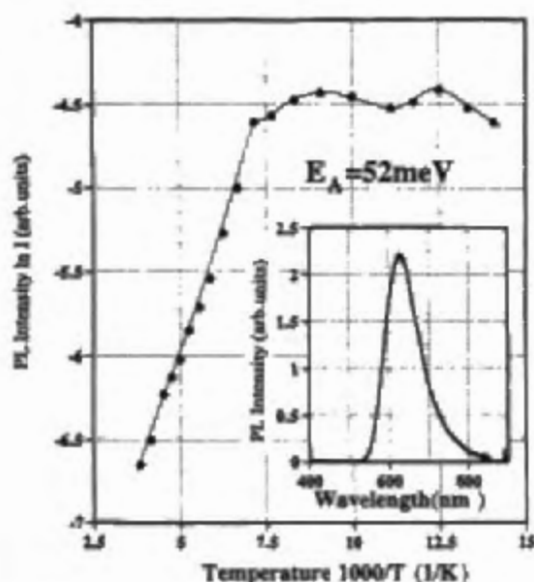Fig. 2.   Thermal quenching curve of the A-signal.

Fig. 3.   An Arrhenius plot of the temperature dependence of the PL peak intensity. The PL spectrum at 70 K is plotted in the inset.

Fig. 4.   ESR excitation spectrum of the A-signal, each point being measured after 5 min of irradiation with monochromatic light.

by Hall measurements.[9]

Figure 3 shows an Arrhenius plot of the temperature dependence of PL peak intensity in the single crystal, the PL band at 70 K, which is similar to that reported by Chichibu,[9] being shown in the inset. The activation energy of 52 meV was determined from the slope of the Arrhenius plot. This value is believed to represent the activation energy of the shallower level (V_{Cu}-acceptor), which takes part in the formation of a broad PL band peaking at 620 nm together with a deeper donor level of unknown nature. The value of the activation energy is also consistent with the value of E_A (40 meV) determined by ESR measurement.

Figure 4 illustrates the ESR excitation spectrum of the A-signal measured at 120 K. The spectrum exhibits a broad peak E at about 470 nm (~ 2.64 eV) with a tail towards longer wavelength region. The band-gap energy E_g (2.70 eV) of the CuAlSe$_2$ is 60 meV higher than the peak E (2.64 eV), which is consistent with the activation energy obtained from the thermal quenching
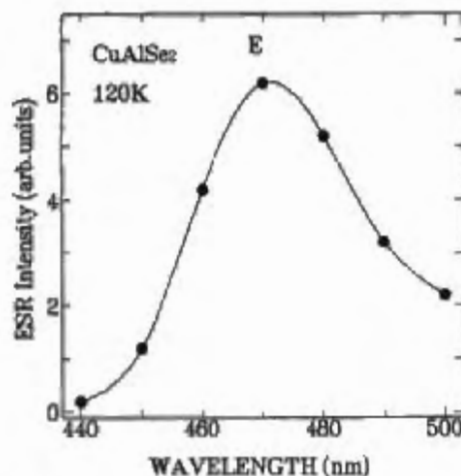
curve for the A-signal.

The photoexcitation process may be understood as follows. Upon excitation with 470 nm light, an electron is emitted from V_{Cu} into the conduction band, or, in other words, V_{Cu} traps a hole from the valence band, producing an unpaired hole resulting in the observed spin resonance signal.

It is quite surprising that the binding energy of the copper vacancy in CuAlSe$_2$ is much less than the value of 180 meV in CuAlS$_2$. This may be understood if one takes into account the higher covalency of selenides compared with that of sulfides, which makes the effective-mass approximation valid in this material.

4.   Conclusions

We have observed for the first time in CuAlSe$_2$ crystal an isotropic photosensitive ESR signal at $g = 2.032$, which has been assigned to a hole trapped in a copper vacancy, the hole being equally shared by four surrounding selenium ions. The activation energy of the V_{Cu} defect $E_A = 40$ meV, estimated from the thermal quenching of the hole-originated ESR signal, showed good agreement with the value of the activation energy deduced from the excitation spectrum and that obtained from the thermal quenching curve of photoluminescence, as well as with the value obtained from the Hall effect. The smallness of the binding energy of V_{Cu} compared with the corresponding value of 180 meV in CuAlS$_2$ may be attributed to higher covalency of selenides than of sulfides.

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