

Characterization of I–III–VI₂ bulk crystals grown by chemical vapor deposition: application of phase-shift-difference spectroscopy

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Chalcopyrite type crystals, CuAlS₂ and CuGaS₂, were prepared by the iodine transport technique, for which the energy gaps were determined at temperatures between 20 and 300 K by phase-shift-difference spectroscopy for oblique incidence reflection using a piezobirefringent modulator. The temperature coefficient of the energy gap and the temperature dependence of crystal-field splitting are discussed in terms of the energy band structure.

1. Introduction

Recently chalcopyrite type semiconductors such as AgGaS₂, CuAlS₂, CuGaS₂ and their alloys have been drawing considerable attention due to their potentiality as materials for blue-light emitting devices and nonlinear optical elements [1]. Accordingly, the temperature dependence of the energy gap (E_g) in these semiconductors also gains interest because of the temperature shift giving the possibility of tuning the energy gaps to the photon energies of interest.

Studies on temperature-dependence as well as on pressure-dependence of E_g in the chalcopyrite crystals also offer information on the electronic band structure. The temperature coefficients of the energy gap in the chalcopyrites have been known to be much reduced from those in their binary analogues [2]. Although the band structure calculations by Jaffe and Zunger [3] elucidated that the band gap narrowing seen in chalcopyrites can be explained by the hybridization of the Cu 3d electrons into the valence band as well as by the structural peculiarity due to the

anion displacement, the anomalous temperature variation of E_g has not yet been explained in terms of these factors. Therefore, detailed temperature variation studies on I–III–VI₂ compounds are of significance since they offer an interesting challenge to physicists.

A number of techniques have been employed to determine E_g in these materials. Yamamoto and his colleagues [4,5] have developed the phase-shift-difference (PSD) spectroscopy technique and applied it to various solid solution systems, such as CuAl_{1-x}Ga_xS₂ [6] and CuGaS_{2-x}Se_x [7], from which they evaluated the composition-dependence and the temperature-dependence of E_g , as well as the crystal-field splitting Δ_{crys} . However, no detailed data are available on the temperature variations of E_g in CuAlS₂. This is partly due to the difficulty in obtaining single crystals of CuAlS₂ with a good quality.

Therefore, we have grown single crystals of CuAlS₂ and CuGaS₂ using the chemical vapor deposition technique and measured the PSD spectra at various temperatures between 20 K and room temperature, utilizing a retardation

modulation technique with a piezobirefringent modulator. The temperature coefficients of E_g and Δ_{cryst} in these crystals were determined.

2. Experimental procedure

2.1. Crystal growth

Single crystals of the CuGaS₂ and CuAlS₂ were prepared by the iodine vapor transport method. The starting materials were polycrystalline powders of the respective compounds synthesized from the constituent elements of 6N purity.

These materials were sealed into evacuated (about 10^{-6} Torr) quartz ampoules (13 or 18 mm in diameter, 200 mm in length) with an appropriate amount of iodine (15–18 mg/cm³). The ampoule was heated in a two-temperature-zone furnace. For the first two days of the growth experiments, the temperature of the growth zone was raised higher than that of the source zone to reduce the number of nuclei, which was followed by the normal transport conditions with 900 °C for the source zone and with 750 °C for the growth zone for 3–5 days.

Single crystals with a specular surface were obtained. The typical size of the crystals obtained was $5 \times 2 \times 0.5$ mm³. X-ray analysis showed that these crystals had the chalcopyrite structure, and the growth surface can be indexed as {112} plane.

2.2. Phase-shift-difference (PSD) spectroscopy

A schematic experimental layout illustrating the modulated PSD spectroscopy is shown in fig. 1. The light from a 150 W Xe lamp was dispersed by a JASCO type CT25C monochromator with a grating of 1200 grooves/mm blazed at 300 nm, and was polarized by a polarizer of which the direction of transmission axis was set at 45° from the plane of incidence. The polarized light passed through a piezobirefringent modulator (Hinds International, PEM-CF3) by which the retardation δ was modulated with an amplitude δ_0 and angular frequency ω . The modulated light was reflected by the sample with an incidence angle of

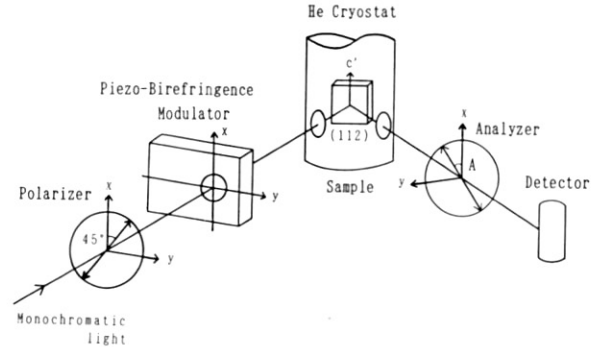


Fig. 1. Schematic illustration of the system for modulated phase-shift-difference spectroscopy for oblique incidence.

45°. The reflected beam was analyzed by an analyzer of which the transmission axis made an angle A with the vertical axis. The analyzed light was detected by a photomultiplier (Hamamatsu R928A).

We assume that the Jones 2×2 matrix for the Fresnel reflection coefficient of the sample is expressed by

$$\hat{r} = \begin{pmatrix} r_{ss} & r_{sp} \\ r_{ps} & r_{pp} \end{pmatrix}.$$

Assuming the retardation caused by the modulator to be δ , we get for the output signal:

$$\begin{aligned} I = \frac{1}{2} E_i^2 \{ & [|r_{ss}|^2 + |r_{sp}|^2 \\ & - 2 |r_{ss}||r_{sp}| \cos(\theta_{ss} - \theta_{sp} + \delta)] \cos^2 A \\ & + [|r_{ps}|^2 + |r_{pp}|^2 \\ & - 2 |r_{ps}||r_{pp}| \cos(\theta_{ps} - \theta_{pp} + \delta)] \sin^2 A \\ & + [|r_{ss}||r_{ps}| \cos(\theta_{ss} - \theta_{ps}) \\ & + |r_{sp}||r_{pp}| \cos(\theta_{sp} - \theta_{pp}) \\ & - |r_{ss}||r_{pp}| \cos(\theta_{ss} - \theta_{pp} + \delta) \\ & - |r_{sp}||r_{ps}| \cos(\theta_{ps} - \theta_{sp} + \delta)] \sin 2A \}, \end{aligned}$$

where $|r_{ij}|$ and θ_{ij} express the absolute value and the phase shift of the Fresnel coefficient r_{ij} , respectively, and E_i denotes the amplitude of the incident light.

Provided that A is zero, the above equation becomes quite simple as follows:

$$I = \frac{1}{2} E_i^2 \left[|r_{ss}|^2 + |r_{sp}|^2 - 2 |r_{ss}||r_{sp}| \cos(\theta_{ss} - \theta_{sp} + \delta) \right].$$

Applying the retardation δ , expressed as

$$\delta = \delta_0 \sin \omega t,$$

to the above equation, we get as ω component of the signal:

$$I(\omega) = E_i^2 |r_{ss}||r_{sp}| J(\delta_0) \sin(\theta_{ss} - \theta_{sp}).$$

The ω component has a finite value when the off-diagonal component of the Fresnel coefficient has non-zero value. This is the case in our experimental condition in which the c -axis of the tetragonal lattice makes a finite angle (54.19° for CuAlS₂ and 54.16° for CuGaS₂) with the normal of the sample surface.

It should be noted that for the normal incidence layout, the analyzer angle A should be taken as 45° in order to get a non-zero ω component of the output.

The phase-shift-difference $\theta_{ss} - \theta_{sp}$ can be connected with the difference in absorption coefficient for the two polarizations ($E \parallel c$ and $E \perp c$), according to the electromagnetic theories. Details will be published elsewhere. In chalcopyrite crystals, the top of the valence band is subject to the crystal-field splitting, which causes the difference in the polarization dependence of the absorption by band-edge excitons, as shown in the inset of fig. 2 thus giving rise to structures associated with the E_g in the PSD spectrum.

In fig. 2, the PSD spectra of CuGaS₂ measured at room temperature are illustrated. Curves (a) and (b) represent those for normal incidence conditions with $A = 45^\circ$ and for 45° incidence with $A = 0^\circ$, respectively. The similarity of those two curves allows us to conclude that they provide the same information on the energy positions of the exciton transitions associated with E_g . The 45° incidence layout provides versatile experimental conditions, especially for low tem-

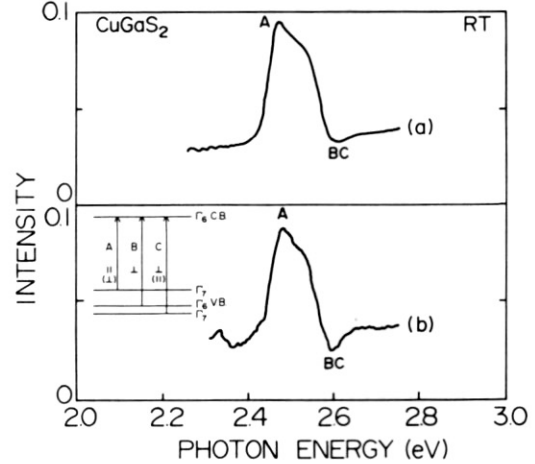


Fig. 2. Comparison of PSD spectra in CuGaS₂ for (a) normal incidence layout with $A = 45^\circ$ and (b) 45° incidence layout with $A = 0^\circ$. Inset: energy diagram for the band edge exciton transitions.

perature measurements where limitations in the window arrangement usually exist.

3. Results and discussion

We illustrate in fig. 3 the PSD spectra for an undoped CuAlS₂ single crystal measured be-

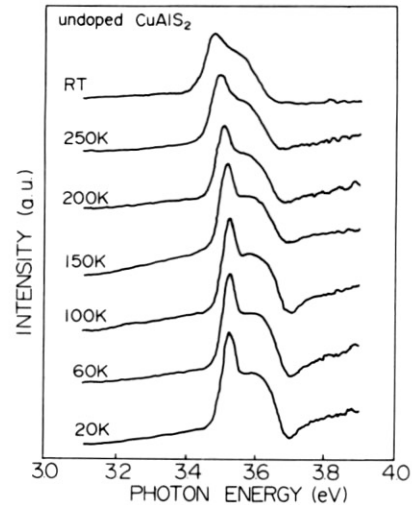


Fig. 3. Phase-shift-difference spectra in an undoped single crystal of CuAlS₂ for temperatures between 20 K and room temperature.

tween 20 K and room temperature. The line shape at 20 K is quite identical to that reported by Bettini [8], which was measured with the normal incidence arrangement, although a slight discrepancy is observed in the baseline. The positive peak A and the negative peak BC are observed over the whole temperature range of measurement. These are considered to be related to free exciton peaks associated with the crystal-field-split valence bands. The fact that the free exciton peak remains even at room temperature is related to the large binding energy (30 meV) of excitons in this material.

From the PSD spectra we deduced the temperature coefficient dE_g/dT in both crystals for A- and BC-exciton transitions. They were approximately constant below 100 K. The average values of dE_g/dT of A- and BC-excitons in CuGaS₂ for temperatures between 100 and 295 K were deduced as -2.0×10^{-4} eV/K and -2.3×10^{-4} eV/K, respectively. These values are quite reasonable compared with published values [5]. In CuAlS₂, the values of dE_g/dT we determined were -2.3×10^{-4} eV/K and -1.5×10^{-4} eV/K for A- and BC-peaks, respectively, which were quite similar to those of CuGaS₂.

The crystal-field splittings Δ_{crys} are shown as functions of the temperature in fig. 4. Δ_{crys} in CuGaS₂ at 20 K was about 120 meV showing only a slight temperature dependence ($d\Delta_{\text{crys}}/dT = -3 \times 10^{-5}$), consistent with the published data [9], whereas in CuAlS₂ it was about 180 meV, showing a positive temperature coefficient of approximately $+8 \times 10^{-5}$ eV/K.

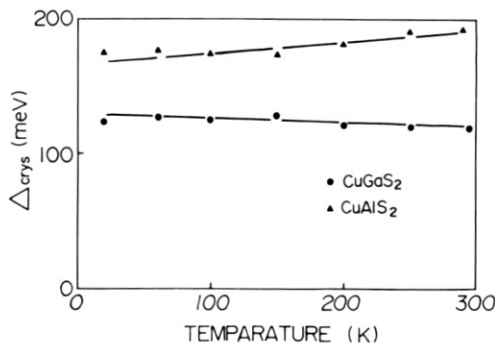


Fig. 4. Temperature dependence of the crystal-field splitting Δ_{crys} in CuAlS₂ and CuGaS₂.

It is generally accepted that the wavefunction in the top of the valence band is composed mostly of 3p orbitals from S atoms and 3d orbitals from Cu atoms, while the contributions from Ga and Al atoms are small. In addition, the degree of tetragonal distortion estimated from $1 - c/2a$ has the same value ($= 0.02$) in both crystals. Therefore, it is natural to consider that Δ_{crys} should show an identical behavior in both CuGaS₂ and CuAlS₂. The clear difference observed in the temperature dependences of the crystal-field parameter between the two crystals should be attributed to a difference in lattice properties of these crystals. For further discussions, detailed measurements on the temperature variation of the lattice constants are strongly required.

We also carried out PSD measurements for the solid solution between the two crystals. The PSD spectral shape becomes broader and less structured than it is in the case of the two constituent crystals, although in some of the cases it consists of a number of structures which cannot be identified. This indicates that the crystallinity in these alloys is very poor compared to the constituent crystals.

In addition to these materials, we also examined single crystals of Mn-doped CuAlS₂. We observed a distinct peak at the A-exciton edge, of which the temperature dependence was found slightly reduced compared to that of undoped crystals. However, PSD structures associated with the BC-exciton were smeared out. Since the splitting between A and BC peaks has been associated with the tetragonal crystal field, this result suggests that the incorporation of Mn atoms leads to the disorder in the atomic arrangements in the vicinity of Mn atoms breaking the tetragonal symmetry, although it is not clearly observed in the conventional X-ray diffraction analysis.

4. Conclusion

A modulated phase-shift-difference spectroscopy system for oblique incidence reflection was constructed. Using this apparatus, the temperature dependence of the energy gaps was observed in CuAlS₂ and CuGaS₂. The temperature

coefficient of the crystal-field splitting energy in CuAlS₂ was determined for the first time as being equal to 8×10^{-5} eV/K.

The technique also proved to be a convenient and sensitive tool for evaluation of the crystallinity and the local atomic disorder in chalcopyrite crystals.

Acknowledgments

The authors express their sincere gratitude to Professor N. Yamamoto and Dr. H. Horinaka for kind discussion on PSD spectra. This work has been supported in part by a Grant-in-Aid for Priority Areas from the Ministry of Education, Science and Culture.

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