

PHOTOELECTRIC PROPERTIES OF $\text{CuGa}_{1-x}\text{In}_x\text{S}_2$

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ABSTRACT

Photovoltaic (PV) and photoconductivity (PC) excitation spectra are investigated at room temperature on $\text{CuGa}_{1-x}\text{In}_x\text{S}_2$ crystals by polarized light excitation. In PV mode, photocurrent spectra exhibit only intrinsic peaks corresponding to band to band transitions. In PC mode, structures due to a shallow and a deep donor states are observed in addition to the intrinsic ones found in PV mode.

Cancellation of spin-orbit splitting due to the p-d hybridization in this unique crystal system permits a direct observation of valence band crystal field splitting as a peak shift for polarized excitation. A copy of the splitting is also observed in the shallow extrinsic peak in PC mode.

INTRODUCTION

Progress toward device application of the I-III-VI₂ semiconductor is rather tardier than expected[1], except a limited compound such as CuInSe_2 [2]. A partial reason for this must exist in our abandonment of enduring investigation. Photoconductivity is such an ignored property for which, however, a series of examinations have been reported by Joshi et al.[3-7] very recently.

This report describes room temperature photovoltaic (PV) and photoconductivity (PC) properties of $\text{CuGa}_{1-x}\text{In}_x\text{S}_2$ crystals. Our emphasis is laid on their photocurrent response to polarized light excitation and phase-lag measurement of photocurrent. The results are compared with the earlier works on CuGaS_2 [8,9] and CuInS_2 [10], and some reasonable explanations are given on PV and PC characteristics of the crystal system.

EXPERIMENTAL

Vapour grown undoped $\text{CuGa}_{1-x}\text{In}_x\text{S}_2$ crystals were used for measurement without any annealing or etching treatment. Needle-like crystals having [111] growth direction with (112) mirror face were selected. Au-wire of 0.1mm in dia. was welded on both edges of the crystals by spark discharge method as electrical contacts[11]. All crystals used were highly compensated p-type ones with a resistivity typically of 10^6 ohm.cm. Because of imperfect ohmic character of the contacts, samples exhibited photocurrent both in PV mode (when light was irradiated onto either contact edge without bias voltage) and PC mode (when irradiated onto the middle part of the sample with bias voltage).

Polarized light excitation was made with either E parallel to [111] ($E//C$) and E normal to [111] ($E \perp C$) with a wave vector normal to (112) surface. The notation $E//Z$ is therefore only nominal in geometrical configuration, however, this gives rather perfect configuration for the $\text{CuGa}_{1-x}\text{In}_x\text{S}_2$ system where the spin-orbit splitting of the uppermost valence bands is almost cancelled due to the p-d hybridization[12].

Measurement of photocurrent was carried out by so-called intensity modulation method. Modulation frequency of the light chopper was typically 5Hz. By using an auto-phase lock-in amplifier, both the in-phase intensity

and the angle of phase-lag between the photocurrent and excitation light could be measured simultaneously as a function of wavelength. Since a photomemory effect was reported to be serious at low temperature[8,9], our measurement was carried out exclusively at room temperature.

RESULTS AND DISCUSSION

CuGaS₂

Figure 1 shows photocurrent excitation spectra in PV mode compared with those in PC mode with phase-lag characteristics at 5Hz. In PC mode, two sharp peaks of "I" (2.48eV for E//C and 2.57eV for E⊥C) and "S" (2.26eV for E//C and 2.35eV for E⊥C) are observed as well as a broad peak of "D₁" at 1.80eV. For reference, the location of exciton band gap and energies, A and B,C at room temperature[13] is marked by arrow on the abscissa.

The peak "I" is clearly attributed to the intrinsic transition from the uppermost valence band, A, to the conduction band. The energy shift (by about 90meV) due to the polarized excitation in this crystal corresponds to crystal field splitting between A and B,C valence bands because the oscillator strength of the transition from A valence band to the conduction band is negligibly small for E⊥C polarization. In other I-III-VI₂ compounds in which enough amount of spin-orbit splitting exists, however, the peak shift due to polarization excitation does not correspond to crystal field splitting[14]. Recent work on AgGaS₂[15] by polarized excitation may be such an example.

Since a minority carrier photocurrent dominates the PV mode[8]

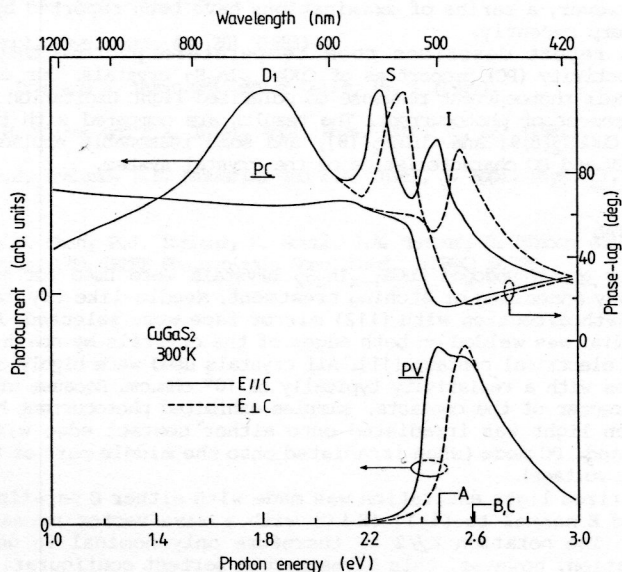


Fig. 1. Photocurrent excitation spectra of CuGaS₂ in PV and PC modes. Phase-lag spectra in PC mode is also shown.

(electron in this case), the photocurrent in PC mode was also mixed with electron current in addition to the majority carrier (hole) photocurrent (bimolecular photoconduction). Sublinear dependence of the photocurrent on excitation light intensity at this peak wavelength also supports this explanation.

The "S" peak, on the other hand, is observed only in PC mode. This indicates that the majority carrier (hole in this case) dominates the photocurrent (monomolecular photoconduction). Indeed at this peak wavelength, a linear dependence of photocurrent on excitation light intensity was observed. Also the polarization shift of this peak is just a copy of that of "I" peak. Therefore, the "S" peak is tempted to be attributed to the transition between the uppermost valence band, A, to a shallow donor state with an activation energy about 220meV. However, we can not find such a donor state for CuGaS₂ in the literature. Rather, an edge emission at 77K located at 2.41eV[16] may be related to this peak.

The phase-shift spectra is almost constant down to 600nm and decrease slightly at "S" peak followed by an abrupt decrease at "I" peak. In a compensated p-type semiconductor, response time of electron could be very smaller than that of hole. The abrupt decrease of phase-shift at "I" peak then indicates an onset of bimolecular photocurrent.

The broad "D₁" peak is speculatively attributed to the transition between the valence band to a deep donor state whose activation energy should be about 700meV. A broad red luminescence observed at the energy[16,17] may be related to this peak, however, the origin of the center is not known.

CuInS₂

Figure 2 shows photocurrent excitation spectra in PV and PC modes. The aspect of the structure is almost the same as for CuGaS₂, i.e., two sharp peaks of "I" (1.60eV) and "S" (1.55eV) are observed in PC mode whereas only

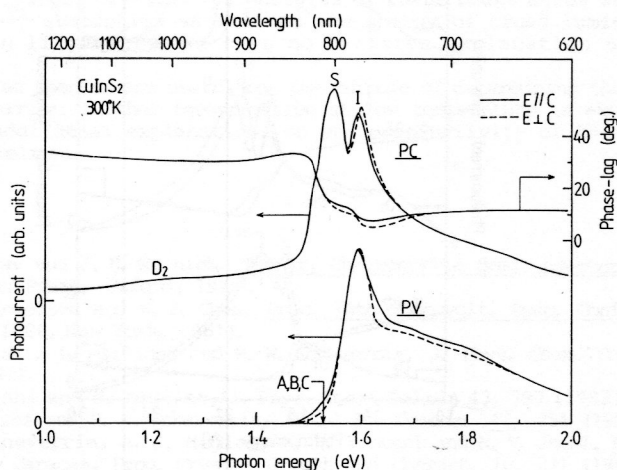


Fig. 2. Photocurrent excitation spectra of CuInS₂ in PV and PC modes. Phase-lag spectra in PC mode is also shown.

"I" peak in PV mode. Only the latter "S" peak has been reported in the previous work[10].

In CuInS_2 , however, peak shift due to the polarized excitation is not observed both for "I" and "S" peaks. This fact agrees with the feature of valence band degeneracy, i.e., in CuInS_2 , the p-like valence band (A,B and C) is triply degenerated due to the negligible spin-orbit splitting and crystal field splitting[1] within the limit of the experimental resolution. The transition from the valence band, respectively to the conduction band and to a shallow donor state, cause the "I" and "S" peaks. The sulfur vacancy state to be located at 35meV and/or 72meV[18] may be the origin. The extrinsic peak "D₂" is very weak and the location of it is near 1.2eV.

The phase-shift spectra in PC mode is almost constant down to 900nm and rather sharp decrease occurs at "S" peak followed by additional decrease at "I" peak.

$\text{CuGa}_{1-x}\text{In}_x\text{S}_2$ mixed crystals

Photocurrent excitation spectra and phase-shift spectra in PC mode are shown in fig. 3 on three mixed alloy crystals of compositions $x=0.3, 0.5$, and 0.7 . Only "I" peak was observed in PV mode also for these alloy crystals and the location of the peak energies are marked by arrow in the figure.

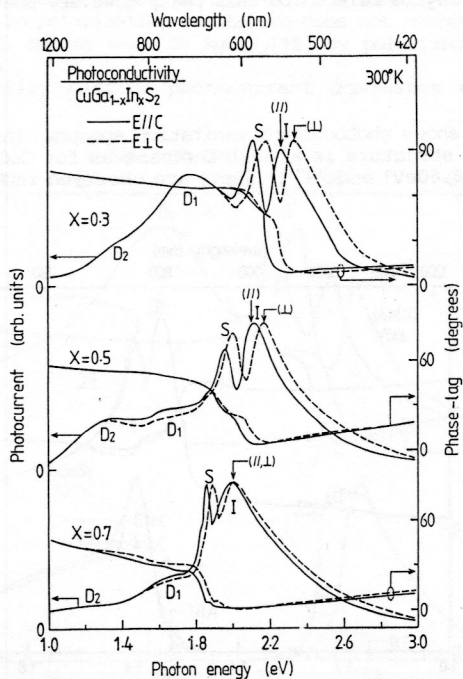


Fig. 3. Photocurrent excitation spectra and phase-lag spectra of mixed alloy crystals of $x=0.3, 0.5$ and 0.7 for either polarization. Location of peak energies in PV mode is marked by arrow.

Two remarkable features are clearly observed. First is that the energy shift due to the polarized excitation becomes smaller as the composition x increases. This agrees with the decrease in crystal field splitting from CuGaS_2 to CuInS_2 . Secondly, the decrease in phase-shift spectra at "S" peak becomes more abruptly as the composition x increases. The relation of photocurrent intensity against excitation light intensity varies linear (CuGaS_2) to sublinear (CuInS_2). These facts suggest that electron photocurrent can partly contribute to the photoconduction due to the thermal activation.

Throughout the crystal systems, the location of the broad peak "D₁" did not shift so much and the peak seems to hide out in CuInS_2 . The other broad peak "D₂" observed in CuInS_2 is seen as well in mixed alloy crystals. Hence it would be appropriate to consider that two different broad peaks "D₁" and "D₂" exist in all compositions of crystals. These energies agrees well those of Fe^{3+} absorption [19].

CONCLUSION

Polarized excitation spectra of photocurrent in PC and PV modes reveals that minority photocarrier conduction (by electron) dominates the "I" peak, which is due to the direct band to band transition. Photocurrent peak shift observed in CuGaS_2 by polarized excitation is due to the crystal field splitting rather than due to the oscillator strength difference of the single transition. Diminishing of the peak shift in CuInS_2 is a result of degeneracy of valence band.

The "S" peak which shows a copy of photocurrent peak shift by polarized excitation is attributed to the transition from the valence band to a shallow donor state. Majority photocarrier (by hole) conduction dominates in CuGaS_2 , however, onset of minority photocurrent conduction is also suggested in CuInS_2 . Sulfur vacancy state is the most appropriate candidate for the donor origin.

Two broad extrinsic peaks "D₁" and "D₂" are considered to exist in every $\text{CuGa}_{1-x}\text{In}_x\text{S}_2$ crystal. The energies of these peaks agree well with those of Fe^{3+} absorption as well as the energy of broad luminescence observed in literature. We have no decisive explanation on these transitions.

Phase-lag spectra are useful for the purpose of determining the type of main photocarrier. Further investigation at low temperature is expected to give some additional explanations on photoconductivity of the crystal system, we believe.

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