Anomalous temperature-dependent band gaps in $CuInS_2$ studied by surface-barrier electroreflectance

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The lowest-energy gaps of $CuInS_2$ have been studied by low-field surface-barrier electroreflectance in the temperature range from 10 to 300 K. Anomalous temperature dependence of E_0 and $E_0+\Delta_0$ have been found. Below 120 K the temperature coefficient of the band gap is 4.3×10^{-5} eV/K for E_0 and 5.8×10^{-5} eV/K for $E_0+\Delta_0$. Above 120 K the coefficients become -8.7×10^{-5} eV/K and -4.4×10^{-5} eV/K for E_0 and $E_0+\Delta_0$. These temperature-dependent energy gaps are explained by the reduction of d levels in the upper valence band due to thermal expansion and the competition with the electron-phonon interaction. The temperature dependence of spin-orbit splitting in our experiment confirms this explanation.

INTRODUCTION

$CuInS_2$ is a ternary semiconductor $A^{I}B^{III}C_2^{VI}$, which crystallizes in the chalcopyrite structure.[1] The optical properties of $CuInS_2$ have been considered interesting due to the potential applications of this material to solar-energy photovolatic conversion devices.[2,3] The energy band transition of $CuInS_2$ near the fundamental energy gap has been studied by many authors.[4–12] The reported results indicate that the threefold degeneracy of the p-like valence band is not completely lifted under the influences of the crystal-field and spin-orbit interactions.[1] Instead, the valence- to conduction-band transition is a singlet and is independent of polarization at room temperature. Shay *et al.* had studied the optical transition of $CuInS_2$ at low temperatures.[13,14] These experiments showed that the singlet transition was removed by the spin-orbit interaction, which is quite similar to the behavior of binary II-VI semiconductors. From their experiments, a reduction in the energy band gap and in the spin-orbit splitting energy had also been found when compared to its binary analog. Shay and Kasper[5] had attributed these effects to the contribution of d levels in the upper valence band. The estimated value of the d contribution was roughly 45% in $CuInS_2$.[1,14] Recently, Jaffe and Zunger calculated the same d contributions; they obtained a lower d character of 22%.[15] The discrepancy between the two estimations needed to be studied further.

Besides the reduction of energy gap and spin-orbit splitting, the anomalous temperature dependence of the energy band gaps in some $A^{I}B^{III}C_2^{VI}$ compounds have also been related to the d levels in the upper valence band. Such temperature dependence of energy gaps has been observed by photoluminescence, reflectivity, absorption, and photocoductivity measurements in the semiconductors $AgGaS_2$,[16] $AgInSe_2$,[17] $AgGaTe_2$,[18] $CuGaS_2$,[19] $CuInSe_2$,[20,21] and $CuInS_2$.[8,22] In this paper we will study the energy transitions of $CuInS_2$ by the surface-barrier electroreflectance (SBER) in temperatures from 10 to 300 K.

Since the late 1960s and early 1970s electroreflectance spectroscopy has become a widely used technique for investigating the band structure of semiconductors and insulators.[23–27] Aspnes had demonstrated that the low-field electroreflectance revealed sharp and well-resolved features which were related to the third derivative of reflectance.[28–30] The purpose of this report is to use this third-derivative character to study the temperature dependence of the energy gaps in $CuInS_2$.

EXPERIMENT

The surface barrier electroreflectance was performed on single crystals of $CuInS_2$ grown by the traveling heater method.[11,31] These single crystals are of n type with the resistivities near 1 Ω cm, carrier concentrations $10^{16}-10^{17}$ cm^{-3}, and mobilities 40–300 $cm^2/V\,s$ at room temperature. The resistivities of the samples were measured by the Van der Pauw method, while the conductivity type, Hall mobilities, and carrier concentrations were obtained by Hall experiments. The front surface of the sample was evaporated on a layer of about 100-Å gold film to form a Schottky barrier. The back surface was in ohmic contact with a copper plate which was mounted on a sample holder in the closed-cycle cryogenic refrigerator system to ensure good thermal contact. Using this cryogenic system, the temperature was varied from 10 to 300 K. A thin mica plate was placed between the copper plate and sample holder for electrical insulation. The character of the Schottky barrier in our experiments was verified by I-V measurement.

The electroreflectance spectra of $CuInS_2$ were measured by standard optical and phase-sensitive detection techniques.[23] In our system, we used two lock-in amplifiers. One detected chopped signal proportional to the reflectance R. The other detected an ac signal of ΔR. The chopped signal was kept constant by a servosytem; this permits the ac signal to be proportional to $\Delta R/R$. The ac signal was obtained by applying an ac modulation voltage and dc bias across the sample cell. The modula-

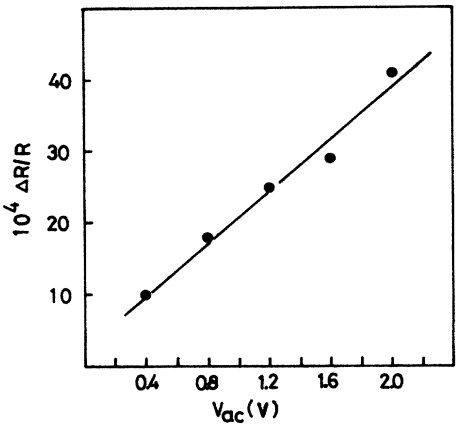

FIG. 1. The $\Delta R/R$ of SBER spectrum vs the modulation voltage V_{ac}.

tion field was a 23-Hz square wave with peak-to-peak voltage 0.4–2.0 V, and the dc bias was near 1 V. In order to make sure that our spectra were in the low-field region, the line shapes of $\Delta R/R$ were checked with the variation of modulation voltage according to the equation,[24]

$$\Delta R/R = -(2e/\epsilon_0)NV_{ac}L(\lambda) , \quad (1)$$

where ϵ_0 is the static dielectric constant, V_{ac} is the magnitude of the modulation voltage. N is the carrier concentration, and $L(\lambda)$ is a spectral-line-shape function which is related to the third derivative of the dielectric function. The magnitude of $\Delta R/R$ as a function of modulation voltage V_{ac} is shown in Fig. 1. The linear relationship and invariance of line shape indicate that the low-field region is in the range 0.4–2.0 V.

RESULTS AND DISCUSSIONS

The experimental SBER spectra of $CuInS_2$ at the temperature between 10 to 300 K is shown in Fig. 2. At low temperature, the line shape of the spectra exhibits two positive and one negative extrema at wavelengths near 7800, 8000, and 8200 Å. As the temperature is increased, only the extrema near 8000 and 8200 Å have been observed. The additional signal near 7800 Å is identified as the contribution from the spin-orbit interaction since the line shape of SBER is independent of the polarization of the incident light. Basically, these spectra agree with the experiments of Shay *et al.*[13,14] For the purpose of data analysis, we use the low-field approximation line shape given by Aspnes,[30]

$$\Delta R/R = \mathrm{Re}[Ce^{i\theta}(E-E_0+i\Gamma)^{-5/2}] , \quad (2)$$

where C and θ are amplitude and phase factor of line shape, E_0 is the energy gap, and Γ is the broadening parameter. At low temperature our spectrum is a combination of two transitions, E_0 and $E_0+\Delta_0$; we add two of the low-field line shapes in Eq. (2), and obtain[32]

$$\Delta R/R = C_1(\sin^{5/2}\phi_1/\Gamma_1^{5/2})\cos(5\phi_1/2-\theta_1) + C_2(\sin^{5/2}\phi_2/\Gamma_2^{5/2})\cos(5\phi_2/2-\theta_2) , \quad (3)$$

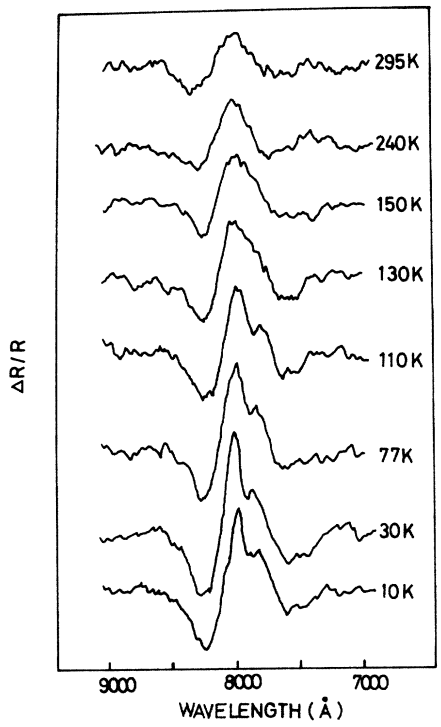

FIG. 2. The SBER spectra of $CuInS_2$ at temperatures between 10 to 300 K.

where 1,2 represent E_0 and $E_0+\Delta_0$ transitions,

$$\tan\phi_i = \Gamma_i/(E-E_i) , \quad (4)$$

$i=1,2$ and $E_1=E_0$, $E_2=E_0+\Delta_0$. A comparison between the experimental spectrum and the line-shape calculation is shown in Fig. 3. In this figure the dashed line represents the computer fitting of Eq. (3), and the arrows indicate the two transitions of E_0 and $E_0+\Delta_0$.

At higher temperature ($T>130$ K), the SBER spectrum shows only one transition feature. In general, this

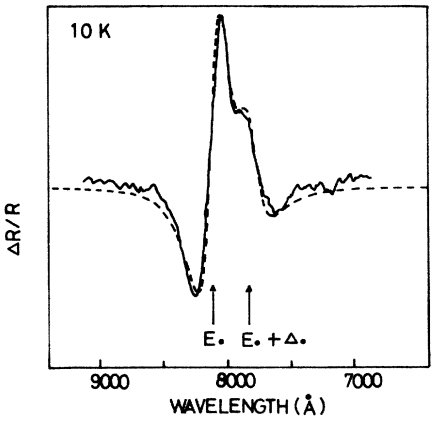

FIG. 3. A comparison between the experimental and calculated SBER line shape at 10 K. Solid line is the experimental data and dashed line is the calculated results.

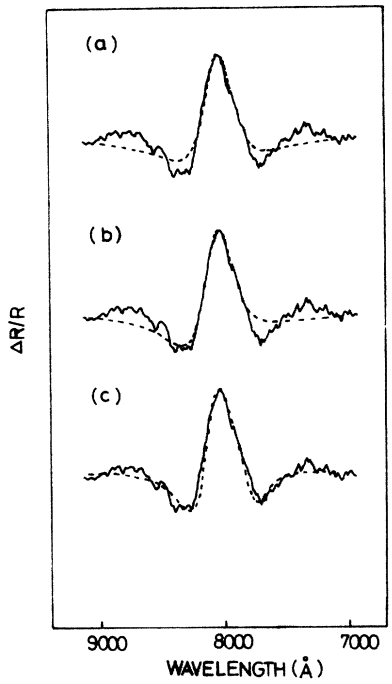

FIG. 4. A comparison between the experimental and calculated SBER line shape at 200 K. Solid line is the experimental data and dashed line is the calculated results. In (a) the one-transition line shape is used to fit the main peak and two lobes; (b) the one-transition line shape is used to fit the main peak and left-hand lobe; and (c) the two-transition line shape is used to fit the main peak and two lobes.

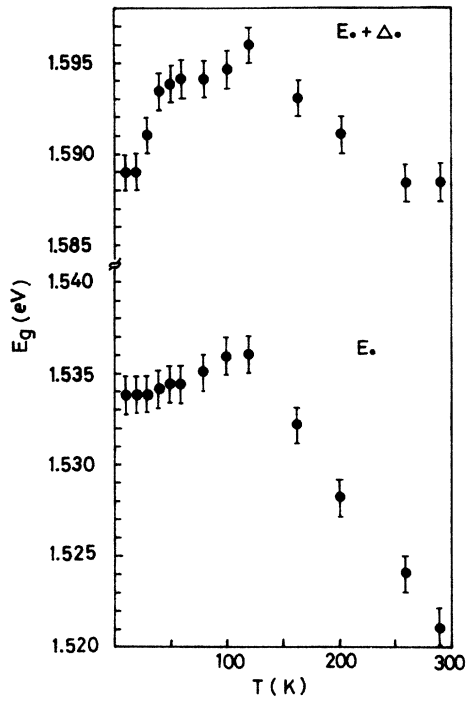

FIG. 5. The temperature-dependent band gaps of $CuInS_2$.

kind of spectrum can be calculated either by one-transition (E_0) or two-transition (E_0, $E_0+\Delta_0$) line shape. As shown in Figs. 4(a) and 4(b), the one-transition line shapes are unable to give satisfactory fits to the experiments. While the two-transition line shape, Fig. 4(c), fits to the experiment quite well. Therefore, we conclude that the two-transition line shape provides the best fit to the high-temperature data which is similar to the low-temperature analysis.

Listed in Table I are the energies and broadening parameters for E_0 and $E_0+\Delta_0$. The temperature dependence of the energy band gaps, as shown in Fig. 5, increases from 10 to 120 K, and starts to shrink as the temperature goes beyond 120 K. Such a temperature dependence of the energy gap is anomalous for semiconductors, and has been observed for several chalcopyrite semiconductors.[16–22] Our experiments show that the temperature coefficient of the band gap below 120 K is 4.3×10^{-5} eV/K for E_0 and 5.8×10^{-5} eV/K for $E_0+\Delta_0$. Above 120 K and up to room temperature, the temperature coefficient becomes -8.7×10^{-5} eV/K and -4.4×10^{-5} eV/K for E_0 and $E_0+\Delta_0$, respectively.

TABLE I. The experimental results of $CuInS_2$ for the average of four measurements. The error bars represent the standard deviation of the measurements.

T (K)	E_0 (eV) (±0.0010)	Γ_{E0} (meV) (±1.0)	$E_0+\Delta_0$ (eV) (±0.0010)	$\Gamma_{E0+\Delta_0}$ (meV) (±1.0)
10	1.5338	35.7	1.5890	36.9
20	1.5338	35.7	1.5890	36.9
30	1.5338	37.1	1.5910	38.1
40	1.5341	37.8	1.5935	39.3
50	1.5344	37.5	1.5938	38.8
60	1.5344	37.5	1.5941	38.8
80	1.5351	36.4	1.5941	37.9
100	1.5359	37.1	1.5946	39.1
120	1.5360	37.7	1.5960	39.7
163	1.5322	40.1	1.5931	41.1
202	1.5282	41.8	1.5911	42.8
260	1.5241	41.7	1.5885	42.7
291	1.5212	41.8	1.5885	42.8

The temperature dependence of the energy gaps has been considered as a consequence of thermal expansion of the lattice and the electron-phonon interactions.[33] The temperature coefficient due to the electron-phonon interaction has been expected to be negative,[33] whereas the positive contribution is probably due to the thermal expansion. As we have mentioned earlier, the d contributions in the upper valence band of $A^{I}B^{III}C_2^{VI}$ semiconductors will cause the downshift of energy gaps. Therefore, the increase of lattice constant due to thermal expansion will reduce the d levels in the valence band, and consequently increase the energy gaps. Using this argument, the observed anomalous positive and negative coefficients of energy gaps appear to be the results of competition between the thermal expansion and the electron-phonon interaction.

The spin-orbit splitting Δ_0 can also be used to verify the above explanations. According to Shay and Kasper,[5] the observed spin-orbit splitting is given as a weighted average of p-like binary analog Δ_p and d levels Δ_d,

$$\Delta_0=(1-x)\Delta_p+x\Delta_d \ , \tag{5}$$

where x is the fractional admixture of d levels in the valence bands, and $\Delta_p=0.07$ eV, $\Delta_d=-0.15$ eV for $CuInS_2$.[24] If the thermal expansions reduce the d level contributions, the observed spin-orbit splitting will be increased for p-like (positive), or decreased for d-like (negative), spin-orbit contributions. In Fig. 6 we show the temperature dependence of spin-orbit splitting Δ_0. We find that Δ_0 is 55 ± 2 meV at 10 K and increases slightly as the temperature goes up. This experiment indicates that Δ_0 is positive. From Eq. (5) the degree of d contributions can be calculated. They are 8% to 4% for 10 to 300 K. In general, the behavior of spin-orbit splitting in our experiment explains the effect of d contributions due to thermal expansion. Our estimated value for the d contributions (8%) is much smaller than the result of Shay and Kasper (45%).[5] However, our results agree with the prediction of Jaffe and Zunger that the d levels in the upper valence band of $CuInS_2$ are lower than the estimation of Shay and Kasper.[15]

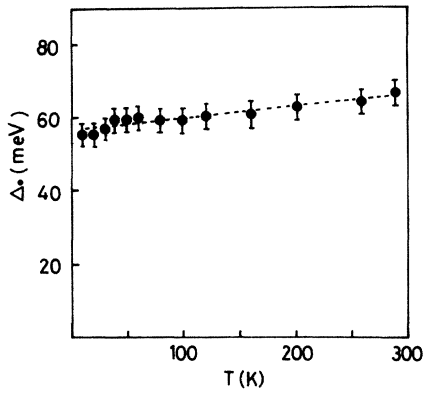

FIG. 6. The temperature-dependent spin-orbit splitting of $CuInS_2$. The dashed line indicates the increase of spin-orbit splitting as temperature goes up.

CONCLUSION

We have studied the energy-band-gap shifts of $CuInS_2$ single crystals as a function of temperature. The energy gaps and broadening parameters of E_0 and $E_0+\Delta_0$ were measured by the low-field surface-barrier electroreflectance. The anomalous temperature dependence of E_0 and $E_0+\Delta_0$ has been considered as the competition between the reduction of d levels by thermal expansion and the electron-phonon interactions. The temperature dependence of spin-orbit splitting confirms this explanation. The measurement of d-level contributions in our experiment is found to be much smaller than the estimation of Shay and Kasper. Our results agree with the prediction of Jaffe and Zunger that $CuInS_2$ has lower d contributions in the upper valence band.

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