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$CdIn_2S_2Se_2$: A New Semiconducting Compound

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The optical and electrical properties of $CdIn_2S_2Se_2$, a new layered semiconducting compound, were examined in the temperature range 10–300 K. The absorption edge at room temperature is observed at 1.95 eV, with a temperature shift of about 4.6×10^{-4} eV/K. Electrical transport is due to electrons, whose temperature independent density is about 3×10^{17} cm^{-3}. The room-temperature mobility is 130 cm^2/Vs, independent of the conduction direction. However, measurements parallel and perpendicular to c-axis show different linear decreases of the mobility with reciprocal temperature. Au/$CdIn_2S_2Se_2$/In Schottky diodes were produced.

I. Introduction

Considerable interest has recently been devoted to multinary compounds because of possible device applications. In particular, AB_2X_4 (A = II, B = III, X = VI) semiconductor crystals, show promising properties as photodetectors, switches, photovoltaic devices, light emitting diodes, nonlinear optical devices, and so on (*1, 2*).

The AB_2X_4 family includes ternary defective semiconductors of four different structures: cubic spinel, rhombohedral, pseudocubic, and tetragonal whose occurrence depends on the relative values of the cation and anion radii. Recently, a considerable effort has been devoted to the study of mixed crystals obtained by partial isoelectronic substitution for one of the three atomic species. Generally, the mixed compounds have the same structure as the pure ternary crystals: in this case their physical properties vary gradually from one end member to the other. Occasionally, different structures may be found of intermediate compositions (*3*). This is the case for $CdIn_2S_2Se_2$, where two anions with the same molar ratio are mixed in the corresponding sublattice. The end members $CdIn_2S_4$ and $CdIn_2Se_4$ have the spinel and pseudocubic structure, respectively. As reported by Haeuseler (*4*), the tetragonal pseudocubic form of $CdIn_2Se_4$ (space $P\bar{4}2m$) has a smaller homogeneity range than the spinel phase. Only up to 12% of $CdIn_2S_4$ is soluble in $CdIn_2Se_4$. Between 44 and 68 mole% $CdIn_2Se_4$ the mixed crystals crystallize in the rhombohedral $ZnIn_2S_4$-type structure (space group $R3m$). Thus, the $CdIn_2S_2Se_2$ compound has the same layered arrangement as $ZnIn_2S_4$ which generates thin single crystals, whose electrical and optical properties are easily examined. A compound, $CdInGaS_4$, of the same structure has been reported by Shand (*5*) for the system $CdS–In_2S_3–Ga_2S_3$.

Despite the many studies on ternary and pseudoternary layered compounds, as far as we know, the only published work on the $CdIn_2[S_xSe_{(1-x)}]_4$ system, deals with the X-

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ray investigation of polycrystals (*4*). No optical and electrical characteristics have been published to date. The aim of the present work is to report optical and electrical results, obtained from the first investigation on $CdIn_2S_2Se_2$ single crystals.

2. Experimental and Results

The crystals were obtained by chemical vapor deposition in LTVTP (linear time varying temperature profile) mode (*6*). They appear as dark red plates with reflecting surfaces. Powder X-ray diffraction analysis was performed; in agreement with Haeuseler's results (*4*), a complete correspondence with $ZnIn_2S_4$ X-ray spectrum is observed (*7*). The crystals may be represented in a hexagonal system, with the *c*-axis perpendicular to the cleavage plane. Monocrystalline samples approximately 1 cm long and 1 cm wide, whose thickness range from 10 to 500 μm, were obtained by cleaving the crystals and cutting the edges.

Optical transmission measurements were performed on the thinner samples in the temperature range 9–330 K. The average refraction index $\langle n \rangle$ was determined from the interference pattern in the region, of transparency, according to the relation

$$\langle n \rangle = \frac{1}{d\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right)} \qquad (1)$$

where d is the thickness, measured by a dial gauge; λ_1 and λ_2 are the wavelengths at which two adjacent maxima appear.

The absorption coefficient α is calculated from the multiple internal reflections according to the formula (*8*)

$$T = \frac{(1 - R)^2 \exp(-\alpha d)}{1 - R^2 \exp(-2\alpha d)} \qquad (2)$$

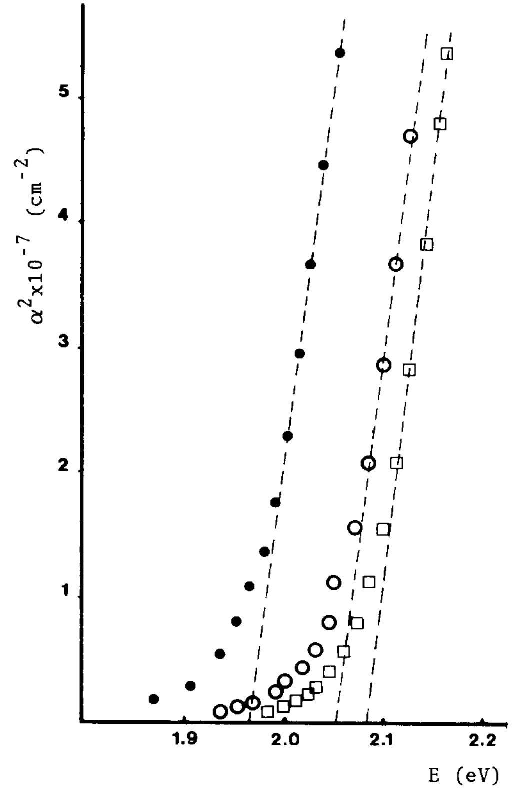

FIG. 1. Absorption edge at different temperatures: black dots, 290 K; white dots, 100 K; squares, 9 K.

where T is the optical transmission R is estimated by

$$R \simeq \frac{(n - 1)^2}{(n + 1)^2}. \qquad (3)$$

The power law $\alpha \sim (h\nu - E_g)^{1/2}$, has been used to fit the energy dependence of α. As shown in Fig. 1, straight lines with a nearly constant slope are obtained at different temperatures, indicating that allowed direct transitions are involved. Extrapolation of the α^2 vs $h\nu$ plot to zero yields the forbidden gap at different temperatures: E_g = 1.965, 2.052, and 2.085 eV at T = 290, 100, and 9 K respectively, with a thermal shift of about 4.6×10^{-4} eV/K.

Moreover, some structure was observed in the transmission spectra below the fundamental edge. Further studies are in progress to determine whether they are due to impurities.

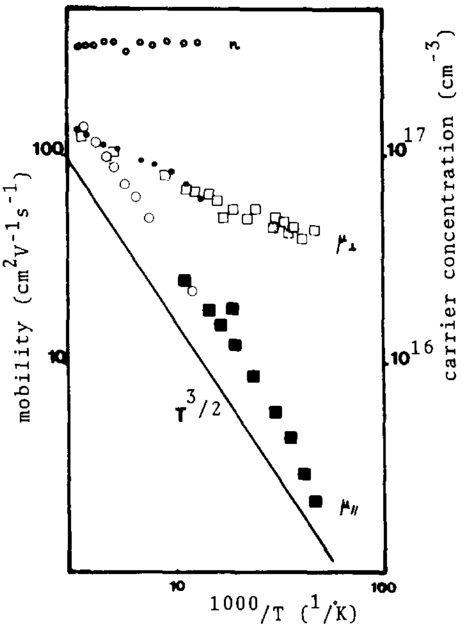

FIG. 2. Carrier concentration (n) and mobilities ($\mu_\perp$, $\mu_\parallel$) vs $1/T$. Dotted (white and black) values were obtained by the Van der Pauw technique. Measurements indicated by all other marks were carried out in the two-electrodes geometry: planar (white squares) and sandwich. Circle and black squares refer to different measurements performed with the sandwich configuration.

Thermoelectric measurements are consistent with n-type conduction. The room-temperature resistivity is ~0.1 ohm-cm.

Sandwich and planar contacts were used to investigate the electrical anisotropy. Indium ohmic electrodes were evaporated on one or both sides of freshly cleaved crystals. Electrical measurements were performed after checking the contacts for I-V linearity over the entire temperature range.

The Van der Pauw geometry (*9*) was used to evaluate the carrier concentration (n) and the mobility ($\mu_\perp$) in the direction perpendicular to the c-axis between 77 and 300 K. The results, shown in Fig. 2, indicate that n is constant and that $\mu_\perp$ changes according to a $T^{1/2}$ power law. To check the conduction anisotropy, the two-electrode geometry is used both in the planar and the sandwich configuration. These conductivity measurements were extended down to 20 K and mobilities obtained by supposing that the carrier concentration remains constant at temperatures lower than 80 K (Fig. 2). In this entire temperature range the mobility ($\mu_\parallel$) parallel to c-axis changes follows a $T^{3/2}$ dependence, while $\mu_\perp$ maintains the root square behavior observed at higher temperatures.

Schottky barrier diodes were prepared by evaporating gold on carefully cleaned surfaces. Notwithstanding the poor reproducibility, some remarkable results were obtained. Figure 3 shows a C^{-2} vs reverse bias plot gained at room temperature by capacitance measurements performed at 1 MHz. In the abrupt junction approximation, the net donor density is calculated from the slope of $1/C^2$ versus V curve by the relation (*10*)

$$N = \frac{-2}{q\varepsilon A^2}\frac{d}{dV}(1/C^2) \qquad (4)$$

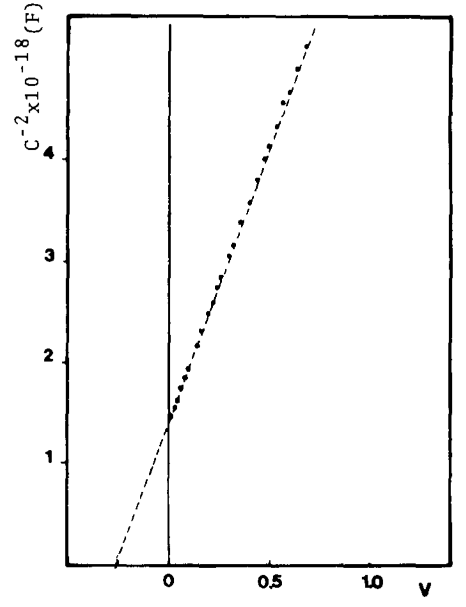

FIG. 3. Reciprocal square capacitance vs reverse bias at room temperature. Measurement frequency: 1 MHz. The intercept of $1/C^2$ with the x-axis yields V = 0.25 V.

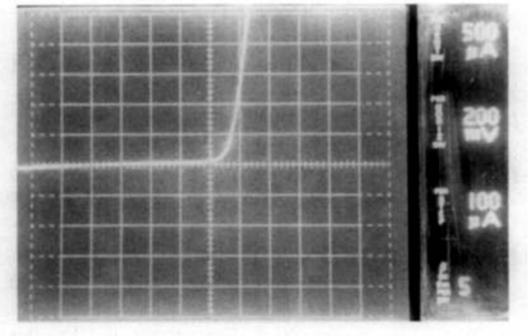

FIG. 4. I-V characteristic of $Au/CdIn_2S_2Se_2/In$ Schottky diode at room temperature: x sensitivity, 200 mV/div; y sensitivity, 500 μA/div.

where A and ε are, respectively, the junction area and the semiconductor static dielectric constant ($\varepsilon \sim n^2$). Thus, a donor concentration $N = 3 \times 10^{17}$ cm^{-3} is estimated, in good agreement with the previous calculation. The I-V characteristic of an $Au/CdIn_2S_2Se_2/In$ Schottky diode, exhibiting a pronounced rectifying effect, is illustrated in Fig. 4.

3. Discussion

An electrical conductivity anisotropy has earlier been reported in AB_2X_4 compounds (*11*). It is generally ascribed to a stacking disorder which limits the carrier transport perpendicular to the layers. A temperature dependent anisotropy, which is also a function of impurity density, has been proposed by Fivaz and Schmidth for III-VI layered compounds (*13*). In the present case, though direct experimental evidence of compositional faults is missing, the similarity of the morphology and of physical properties to previously investigated layered compounds (*3, 12*), suggests that the same explanation of electrical anisotropy applies here.

Moreover, the investigated samples are not intentionally doped and the room-temperature electrical anisotropy is low, but strongly temperature dependent. Conductivity measurements perpendicular to the layers show a $T^{3/2}$ mobility dependence, suggesting ionized impurity scattering. Along the layers the mobility varies as $T^{1/2}$, indicating a mixed lattice impurity scattering. A $1/T$ dependence of the anisotropy is thus obtained. This is not in disagreement with the Fivaz and Schimdth model; the high-impurity density, as determined from the previously calculated donor concentration, should reduce the anisotropy and decrease its temperature activation energy.

A high compensation effect is often proposed in AB_2X_4 to explain their high resistivity and their marked photosensitivity (*14–16*). On the contrary, $CdIn_2S_2Se_2$ is the first layered material showing low resistivity as grown; the reason for the weak compensation is still a matter of study.

4. Final Remarks

In conclusion, $CdIn_2S_2Se_2$ is a semiconducting compound whose optical and electrical characteristics are reported here for the first time. In particular: the fundamental optical edge, the electrical conductivity, the electron mobility, the electrical anisotropy, and their temperature dependence are studied.

A high density of intrinsic defects whose nature is still unknown, gives rise to almost degenerate semiconducting properties. Nevertheless, a remarkably high electron mobility is measured at room temperature. Further investigations are required for the identification of the defects. For instance, postgrowth annealing in controlled atmosphere could be performed to ascertain whether the chalcogen atom vacancy induces shallow donor levels as demonstrated in the case of $CdIn_2S_4$ and $CdIn_2Se_4$ ternary end members (*17, 18*).

Although an improved surface treatment has to be developed, the possibility for preparing a Schottky barrier device has been demonstrated.

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