Electrical properties of $\text{CdS}_x\text{Se}_{1-x}$ single crystals

D RAJA REDDY, B K REDDY and P J REDDY

Department of Physics, S V University College, Tirupati 517 502, India

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Abstract. Electrical conductivity and Hall effect were studied on vapour phase grown $\text{CdS}_x\text{Se}_{1-x}$ single crystals in the entire range of composition in the temperature range 90–300 K. The conductivities of the as-grown crystals varied significantly. High conducting samples were obtained by annealing either in vacuum or in cadmium vapour. Hall mobilities, carrier concentration and donor activation energies were calculated. No definite variation in mobility with composition was observed. Donor activation energy showed an increasing trend with increase of CdS content.

Keywords. Electrical properties; $\text{CdS}_x\text{Se}_{1-x}$ single crystals; Hall effect.

1. Introduction

Transport phenomena in II-VI compounds and their solid solutions are as important as their optical properties and provide valuable information regarding the nature of carriers, band structure and scattering mechanisms. The Hall mobilities of charge carriers in the binary compounds are known to be limited by piezoelectric/optical mode/impurity scatterings in different degrees at low temperatures (Devlin 1967). The activation energies of unidentified donors in CdS were reported by Piper and Halsted (1960) and Subhan *et al* (1972). Woodbury and Aven (1974) reported similar donor activation energies for CdSe. However, similar studies on $\text{CdS}_x\text{Se}_{1-x}$ single crystals are sporadic. Devlin and Shiozawa (1960) reported a mobility minimum at $x = 0.5$ in $\text{CdS}_x\text{Se}_{1-x}$ crystals. According to Weng (1971) the electrical properties of flash evaporated $\text{CdS}_x\text{Se}_{1-x}$ films are beyond control. Mochizuki and Igaki (1978) obtained an activation energy of 0.01 ± 0.02 eV for $\text{CdS}_{0.8}\text{Se}_{0.2}$ crystals. In the present work the Hall effect and conductivity on vapour phase grown $\text{CdS}_x\text{Se}_{1-x}$ single crystals were studied in the entire range of composition ($x = 1, 0.9, 0.7, 0.5, 0.3, 0.1$ and 0) in the temperature range 90–300 K. The Hall mobilities, carrier concentrations, and donor activation energies are calculated and their variation with composition is discussed.

2. Experimental

$\text{CdS}_x\text{Se}_{1-x}$ single crystal boules of 1 cm diameter and more than 2 cm in length were grown by a self-sealing vapour phase growth technique at about 1100°C in 100 torr argon pressure using 5 N pure CdS (M/s. Koch Light, England) and CdSe

(M/s Balzers, Switzerland). The charge for the growth was prepared by sintering appropriate quantities of CdS and CdSe at 1000°C in argon (100 torr) for about 24 hr. The final composition was checked by wet chemical methods to 1% accuracy and also from x-ray lattice parameter determination. The chemical composition and the lattice parameters are given in table 1 and figure 1 respectively. Typical samples of $5 \times 5 \times 0.5 \text{ mm}^3$ size were prepared by polishing the cut pieces from

Figure 1. Variation of lattice parameters a and c with composition for $\text{CdS}_x\text{Se}_{1-x}$ crystals.

Table 1. Results of chemical analysis of $\text{CdS}_x\text{Se}_{1-x}$ single crystals.

Target crystal	Estimated atomic percentage for 100 mol cadmium	
	Sulphur	Selenium
CdS	99.7	-
$\text{CdS}_{0.9}\text{Se}_{0.1}$	89.2	10.8
$\text{CdS}_{0.7}\text{Se}_{0.3}$	68.9	31.1
$\text{CdS}_{0.5}\text{Se}_{0.5}$	50.2	49.8
$\text{CdS}_{0.3}\text{Se}_{0.7}$	29.6	70.4
$\text{CdS}_{0.1}\text{Se}_{0.9}$	10.0	90.0
CdSe		99.8

the grown boules over chamois leather using chromium oxide powder. Four Indium ohmic contacts were applied and baked at 150°C for 2 hr in a vacuum of 10^{-4} torr. A magnetic field of 3 k gauss was applied for Hall measurements. A current of 5–10 mA was passed through the current leads and various voltages including the copper-constantan thermocouple emf were measured to $10\mu\text{V}$ accuracy using $4\frac{1}{2}$ digital multimeter. The measurements were made continuously from 90 K as the sample warmed up naturally in about 4 hr.

3. Results and discussion

The room temperature conductivities of as-grown crystals of different compositions varied significantly and conducting samples for some of the compositions could be obtained only after annealing at 700°C in vacuum or cadmium vapour for 24 hr (table 2). The high resistivity of $x = 0.7$ crystals did not show appreciable decrease and Hall mobilities could not be measured on these samples. Increase of conductivity by several orders of magnitude by just heat treatment is a peculiar phenomenon observed in $\text{CdS}_x\text{Se}_{1-x}$ crystals. The chemical analysis of conducting samples obtained after annealing in vacuum/Cd vapour by wet chemical methods did not show any appreciable deviation greater than the analysis accuracy of 1%. Hall mobilities of $\text{CdS}_x\text{Se}_{1-x}$ crystals at 300 K or 90 K (table 2) do not show any definite variation with composition. The mobility minimum at $x = 0.5$ reported by Devlin and Shiozawa (1960) is not clear in the present study and there is no other data to verify. The data on temporal variations of mobilities, not available in the report of Devlin and Shiozawa (1960), are presented in table 2. However, the mobilities, showed a definite increase with decreasing temperature in all the $\text{CdS}_x\text{Se}_{1-x}$ crystals.

Table 2. Electrical properties of $\text{CdS}_x\text{Se}_{1-x}$ single crystals.

Crystal	Conductivity of crystals ($\text{ohm. cm})^{-1}$			Hall mobility at ($\text{cm}^2/\text{v sec}$)	
	As grown	Annealed at 700°C in vacuum	Annealed at 700°C in Cd vapour	300 K	90 K
CdS	8.4	—	—	300	500
$\text{CdS}_{0.9}\text{Se}_{0.1}$	1×10^{-7}	1.4	—	130	380
$\text{CdS}_{0.7}\text{Se}_{0.3}$	1×10^{-10}	1×10^{-9}	1×10^{-7}	—	—
$\text{CdS}_{0.5}\text{Se}_{0.5}$	1×10^{-8}	1×10^{-8}	12.0	200	240
$\text{CdS}_{0.3}\text{Se}_{0.7}$	0.71	—	—	510	1650
$\text{CdS}_{0.1}\text{Se}_{0.9}$	1×10^{-6}	1.3	—	140	250
CdSe	0.16	—	—	480	4400

The temperature variations of Hall mobility (μ_H), carrier concentration (n) and conductivity (σ) for different compositions are shown in figures 2, 3 and 4 respectively. The mobility variation with temperature in the mixed crystals is similar to that in CdS and CdSe (Devlin 1967) for different degrees of compensation. As such the same scattering mechanisms namely piezoelectric/optical mode/impurity scatterings seem to be active in controlling the carrier mobilities. The donor activation energy (E_d) calculated from the slopes ($-E_d/k$, where k is the Boltzmann constant) of the straight line portions of the $\ln n$ vs $1/T$ plots for different compositions are shown in figure 5. It is clear that activation energy shows a decreasing trend from CdS to CdSe. Woodbury and Aven (1974) showed that the donors in II-VI compounds are more hydrogen like and the donor activation energy is given by $E_d = 13.6m^*/m_e \epsilon^2$ where m^*/m_e is the effective mass ratio and ϵ is the static dielectric constant. Moreover the activation energy of a particular donor is known to vary with the energy gap of the host crystal. The energy gap (eV), the effective mass

Figure 2. Temperature variation of Hall mobility in $\text{CdS}_x\text{Se}_{1-x}$ crystals.

Figure 3. Temperature variation of carrier concentration in $\text{CdS}_x\text{Se}_{1-x}$ crystals.

ratio (m^*/m_e) and static dielectric constant (ϵ) of CdS and CdSe are 2.37, 0.204, 9.3 and 1.7, 0.13, 9.63 respectively. Hence the observed decreasing trend in activation energy with increase in CdSe content is justified in all respects. As foreign impurities were not intentionally introduced these donors might be cadmium interstitials or sulphur vacancies. The carrier concentration in $x = 0.5$ did not change appreciably (figure 3) and this might be due to a heavy incorporation of cadmium atoms when these crystals were annealed in cadmium vapour.

No regular variation with composition was observed in the temperature variation of conductivity. For CdS the conductivity decreased as temperature was lowered whereas it increased for CdSe. This could be understood in terms of the rate of decrease of carrier concentration and the rate of increase of mobility as the temperature is lowered. If the former dominates a decrease in conductivity results

Figure 4. Temperature variation of electrical conductivity in $\text{CdS}_x\text{Se}_{1-x}$ crystals.

(CdS). If the latter dominates an increase in conductivity results (CdSe). The maxima observed for some of the compositions ($x = 0.1$ and 0.5) could be due to these two factors.

The type of conductivity observed from the sign of the Hall voltage and hot probe test is n -type for all the compositions. According to Mandel *et al* (1964) the lower limit of covalent radii ratio to have p -type conductivity of a semiconductor is 1.1. The covalent radii ratios of CdS and CdSe are 1.42 and 1.3 respectively. It was shown elsewhere (Reddy 1981) that CdS and CdSe are miscible in the entire range of composition and solid solution formation is of displacement type, and hence the covalent radii ratio of mixed crystals cannot become lower than 1.3 and hence the n -type conductivity observed is justified. Special conditions like quenching or chalcogen vapour annealing applied for some of the II-VI compounds (Sakalas 1975) were not used to achieve p -type conductivity.

Figure 5. Compositional variation of donor activation energy in $\text{CdS}_x\text{Se}_{1-x}$ crystals.

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