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Short communication

Optical and electrical studies of vapour phase grown $Cd_{1-x}Co_xTe$ crystals

Y. Dwarakanadha Reddy*, B.K. Reddy, D. Sreekantha Reddy, D.R. Reddy

Department of Physics, Sri Venkateswara University, Tirupati, Andhra Pradesh 517502, India Received 24 June 2007; accepted 26 November 2007

Abstract

The optical properties of vapour phase grown crystals of diluted magnetic semiconductor (DMS) $Cd_{1-x}Co_xTe$ were investigated for x = 0.001, 0.003, 0.005, 0.007 and 0.009. The reflectivity spectra exhibited a regular shift in the fundamental absorption edge (E_0) with composition x. The reflectivity spectra for the present samples of $Cd_{1-x}Co_xTe$ of all compositions exhibit broad bands at 5300 and 11,100 cm⁻¹ due to the transitions of ${}^{4}A_{2} \rightarrow {}^{4}T_{1}$ (F) and ${}^{4}A_{2} \rightarrow {}^{4}T_{1}$ (P), respectively. Temperature dependence of resistivity revealed semiconducting behaviour of the samples. Hot probe test revealed that all the samples exhibited p-type conductivity. © 2008 Published by Elsevier B.V.

Keywords: Vapour phase growth technique; DMS; $Cd_{1-x}Co_xTe$ crystals; Reflectivity studies; Band gap; Electrical properties

1. Introduction

Diluted magnetic semiconductors (DMS) are a class of semiconducting materials formed by randomly replacing some fraction of the cation in compound semiconductors with a magnetic ion like Mn²⁺, Fe²⁺or Co²⁺. The presence of the magnetic ion leads to a number of unusual electronic and magnetic properties, including a magnetically tunable band gap, resulting from the large sp-d exchange interaction between the magnetic ions and the band electrons. These interactions are strongly influenced by the ground state of the particular substitutional magnetic ion used [1,2]. DMS are expected to play an important role in interdisciplinary materials science and future electronics because charge and spin degrees of freedom accommodated into a single material exhibit interesting magnetic, magnetooptical and magneto-electronic and other properties [3]. It has been attempted to make use of not only the charge but also the spin degree of freedom in modern semiconductor electronics for information processing. This new developing field is called spintronics [4]. The possibility of using electron spins in electronic devices known as spintronic devices has attracted a growing interest in DMS. In these devices both charge and spin of the electrons are utilized as carriers of information. The interest greatly increased after the discovery of ferromagnetic DMS as they can be used in spintronic devices as an effective source of

* Corresponding author. Tel.: +91 9885532989.

E-mail address: ydreddy64@yahoomail.com (Y.D. Reddy).

spin-polarized electrons. Though II–VI DMS have been studied extensively, the experimental data published on $Cd_{1-x}Co_xTe$ to date are very limited and sporadic. This could perhaps be due to the difficulties in preparing homogeneous crystals with sufficient amounts of substitutionally incorporated Co due to its very low solubility. Also it is obvious from literature that no single paper reports a systematic study on preparation and complete characterization of this system. The dispersed results reported in literature and the interesting properties exhibited by $Cd_{1-x}Co_xTe$ system motivated the present authors to take up the present study. This paper reports the results of the investigations on diffuse reflectance spectra and electrical conductivity.

2. Experimental

Cd_{1-x}Co_xTe crystals with x=0, 0.001, 0.003, 0.005, 0.00 7and 0.009 were grown from CdTe and CoTe (99.99%, M/s Sigma–Aldrich) by the modified vapour phase growth technique [5]. The required cubic phase of CoTe was prepared afresh and was used immediately as cubic CoTe is not stable. Pure Co and Te (99.99%, M/S Sigma–Aldrich) were used to prepare CoTe. Appropriate quantities of Co and Te were weighed, mixed and ground thoroughly and heated in vacuum (~10⁻⁶ Torr) sealed graphitized quartz tube at 1000 °C for about 5 min. It was then quickly withdrawn to yield the desired poly crystalline CoTe. Appropriate quantities of freshly prepared CoTe and CdTe (99.99%, M/S Sigma–Aldrich) were mixed and ground thoroughly to ensure homogeneity. The powder was packed tightly

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Fig. 1. $Cd_{1-x}Co_x$ Te crystals with x = 0.001, 0.003, 0.005, 0.007 and 0.009 prepared using vapour phase growth technique.

in the quartz growth tube and was used for crystal growth in a vapour phase growth setup described else where [5]. Good quality crystals of $Cd_{1-x}Co_x$ Te were obtained after trial and error method. A growth temperature of 1100 °C, a temperature gradient of 30–40 °C/cm and pulling rates of 0.4–0.6 mm/h were used. Each growth run lasted for about 5–7 days. Good quality crystals of 1-2 cm long were grown in the present study and the photographs of the as-grown boules are shown in Fig. 1. Samples of appropriate dimensions cut from the as-grown boules were used for chemical analysis and structural studies using EDAX (Model JSM-840A), and XRD (Seifert 3003 TT) techniques The room temperature diffuse reflectance spectra of the powdered samples of all compositions were recorded using optical Carey-5E Spectrophotometer in the wavelength range 200-2000 nm. Electrical conductivity measurements were made by the two-probe technique.

3. Results and discussion

3.1. Chemical analysis

The typical EDAX spectrum for Cd_{0.997}Co_{0.003}Te crystal is shown in Fig. 2. The average compositions obtained from EDAX were within ± 0.03 at.% of the target compositions for all the samples. Incongruent melting and the differences in the vapourization of various chemical species present in the samples might have resulted in the observed microscopic deviations in compositions. This could also be due to the differences in the saturated vapour pressures of transition metal dopants and those of the II-VI compounds. Thus slight inhomogeneities and stoichiometric deviations are common in II-VI based DMS. Such minor deviations in chemical compositions have been reported by earlier workers also [6–9] in Bridgman grown $Cd_{1-x}Co_xTe$ crystals. There are no reports on the vapour phase growth of $Cd_{1-x}Co_xTe$ crystals for comparison. In view of the minor differences between the nominal and the estimated compositions, in all the future discussions only the nominal compositions are used.



Fig. 2. EDAX spectrum of Cd_{0.997}Co_{0.003}Te crystal.

3.2. Structural analysis

X-ray diffractograms of $Cd_{1-x}Co_xTe$ powdered samples of all compositions obtained using "Seifert Rayflex" and "Powder" X-ray powder pattern indexing softwares. A typical XRD spectrum for Cd_{0.995}Co_{0.005}Te crystal is shown in Fig. 3. The diffraction spectra of $Cd_{1-x}Co_xTe$ samples exhibit sharp peaks at 23.45°, 39.18°, 46.25°, 56.49°, 62.20° and 71.21°, which correspond to diffraction from (100), (220), (311), (400), (331) and (422) cubic planes, respectively. The diffracting planes were indexed using JCPDS data of pure CdTe and CoTe. It was found that crystals of all compositions exhibited zinc blende structure. That there is no appearance of new X-ray diffraction peaks indicates that Co is substituted in CdTe. A gradual shift in the angular positions of the XRD peaks corresponding to the host CdTe lattice is observed, which indicates changes in the lattice parameters of the host because of the incorporation of the dopant ions into the basic unit cell.



Fig. 3. XRD spectrum of Cd_{0.995}Co_{0.005}Te crystal.



Fig. 4. Reflectivity spectrum of pure CdTe at room temperature.

3.3. Reflectivity studies

The diffuse Reflectance spectrum of undoped CdTe is as shown in Fig. 4. The observed transitions are labeled as $\Gamma_{15} \rightarrow \Gamma_1$ (*E*₀), $\Lambda_3 \rightarrow \Lambda_1$ (*E*₁) and $X_5 \rightarrow X_1$ (*E*₂). These are due to the transitions from the highest valence band (Γ_{15}) to the lowest and second lowest conduction bands (Γ_1), respectively. Transitions at the fundamental absorption edge (E_0) mark the beginning of this structure. The pronounced structures found in the energy region 1.4–6 eV are due to E_0 , $E_0 + \Delta_0$, E_1 , $E_1 + \Delta_1$ and E_2 transitions. The present experimental values of $E_0, E_0 + \Delta_0, E_1, E_1 + \Delta_1$ and E_2 are in good agreement with the values reported by Greenway [10] in CdTe. Fig. 5 shows the reflectance spectra of $Cd_{1-x}Co_xTe$ samples of all compositions in the wavelength range 300–1300 nm. It is obvious from Fig. 5 that there is a regular shifting of the fundamental absorption edge (E_0) to lower energies (higher wavelengths) with increasing Co concentration. The band gap energy decreases linearly



Fig. 5. Shift in the position of absorption edge (E_0) with composition (x).



Fig. 6. Variation of band gap energy with composition of $Cd_{1-x}Co_xTe$ crystals.

with x in the present samples and is shown in Fig. 6. Similar linear dependence of band gap on x was reported by Kim et al. [11,12] in $Cd_{1-x}Co_xTe$ crystals grown by vertical Bridgman technique with x = 0.001, 0.004 and 0.008. Such decrease in band gap energies with 'Co' content has also been reported by some other authors [13,14] also in similar other II–VI DMS. The present linear dependence of band gap (E_g) on x is expressed by a straight line fit of the form:

$$E_0(x) = 1.487 - 4.947x \,(\text{eV}) \tag{1}$$

This is in good agreement with the best fit.

$$E_0(x) = 1.48 - 4.23x \,(\text{eV}) \tag{2}$$

reported earlier by Kim et al. [12]. This variation is dependent on the quality of the crystals and the preparation of the reflective surfaces. The electronic configuration of Co^{2+} ion is $3d^7$ so that, the ground state of the free Co^{2+} ion is ⁴F and the first excited state is ⁴P. The lowest energy term ⁴F splits into an upper ⁴T₁ orbital triplet, a middle ⁴T₂ orbital triplet and a lower ⁴A₂ orbital singlet ground state under a crystal potential of tetrahedral symmetry (T_d). Introduction of spin-orbital coupling shifts ⁴A₂ level, which becomes Γ_8 state. The orbital triplet ⁴T₁ and ⁴T₂ are split according to $\Gamma_6 + \Gamma_7 + 2\Gamma_8$ [7]. Sugano et al. [15] have shown band positions of each of the above-mentioned transitions.

The reflectivity spectra for the present samples of $Cd_{1-x}Co_xTe$ of all compositions exhibit broad bands around 5300 and 11,100 cm⁻¹ due to ${}^{4}A_{2} \rightarrow {}^{4}T_{1}$ (F) and ${}^{4}A_{2} \rightarrow {}^{4}T_{1}$ (P) transitions, respectively. These are shown in Fig. 7. Hommerich et al. [16] have observed the same type of transitions at \sim 5347 cm⁻¹ (1870 nm) due to ${}^{4}A_{2} \rightarrow {}^{4}T_{1}$ (F) transition and at \sim 11,111 cm⁻¹(900 nm) due to ${}^{4}A_{2} \rightarrow {}^{4}T_{1}$ (P) transition. Similar types of bands were also observed by Kim et al. [7] at room temperature. Therefore it is concluded that when cobalt ions are incorporated in CdTe lattice, the Cobalt ions enter the lat-



Fig. 7. Reflectance spectra of $Cd_{1-x}Co_xTe$ crystals with wave number.

tice substitutionally in place of divalent metal ions and the site symmetry is tetrahedral.

3.4. Electrical studies

All the samples exhibited 'p' type conductivity as revealed by the "hot probe test". Electrical resistance measurements were carried out using the two probe technique on samples of dimensions $4 \text{ mm} \times 3 \text{ mm} \times 2 \text{ mm}$ cut from the as-grown boules of $Cd_{1-x}Co_xTe$ in the temperature range 190–450 K. Keithley 2000 DMM along with scanner cord facility was used to measure the resistance of the crystals. The measuring instruments were integrated to a computer through RS 232 cables. The scanner chord of the instrument scanned the data in required intervals of time/temperature and stored the data in ASCII files. At room temperature, the resistivities of the present $Cd_{1-x}Co_xTe$ samples were in the range 1–4 M Ω -cm. Fig. 8 shows the variation of resistivity ' ρ ' with temperature '*T*' for samples of all compositions studied. A decrease in resistivity is observed with increase



Fig. 8. Variation of electrical resistivity with temperature of $Cd_{1-x}Co_xTe$ crystals.



Fig. 9. Variation of resistivity with Co concentration at 300 K.

in temperature showing semiconducting behaviour. Further the resistivity showed a definite decrease with increasing Co concentration. Fig. 9 shows the variation of resistivity with Co concentration at room temperature. There are no reports on electrical studies of $Cd_{1-x}Co_xTe$ system for comparison. Ueda et al. [17] measured the temperature dependence of resistivity of Co doped ZnO samples and observed semiconducting behaviour. The resistance measured by Ko and Blamire [18] for x = 0.04 and 0.06 of $Cd_{1-x}Cr_xTe$ in the temperature range 77–320 K also exhibited semiconducting behaviour. Saito et al. [19] also observed similar semiconducting nature in Cr doped ZnTe with x = 0.035.

The decrease in resistivity with increasing Co concentration in the present samples can be explained as follows. The magnetic impurity'd' states in DMS generally appear near the Fermi level (here Co is magnetic impurity in CdTe). The states may exhibit splitting resulting in high spin configuration of 'd' electrons. These impurity states undergo hybridization with 'p' states. The 'd' states of Co split under the influence of tetrahedral crystal field of CdTe. This results in lower doublet eg state and a higher energy t_{2g} state. This doublet hybridizes with 'p' orbital of the valence band further splitting into t-bonding and t-antibonding states. The t-bonding states participate in the bonding and hence are localized. However, the antibonding states have higher energy level and contain itinerant electrons. The energy of bonding states lies in the close vicinity of the conduction band. Hence with the increase in temperature the electrons in the impurity states jump into the conduction band on thermal activation. This explains the observed decrease in resistivity with increase of temperature that is the semiconducting behaviour in $Cd_{1-x}Co_x$ Te samples (Fig. 8). Also since CdTe is a semiconductor by itself and small dopant concentrations which is the case in the present samples may not affect the semiconducting nature of the host CdTe which is a wide bandgap material. Upon increase in Co concentration more number of electrons are promoted to conduction band, resulting in further decrease in resistivity. This explains the observed decrease in resistivity with increase in Co content (Fig. 9).



Fig. 10. Plots of $\ln \sigma$ vs. 1/T of $Cd_{1-x}Co_xTe$ crystals.

For the as-grown crystals of all compositions of $Cd_{1-x}Co_xTe$, the activation energies are obtained from the slopes of the ln σ versus 1/T plots shown in Fig. 10.The activation energies of all the crystals lie in the range 36–81 meV and no regular variation is found with composition. This could be due to unknown defect state structure and slight stoichiometric deviations in the Cd_{1-x}Co_xTe crystals.

4. Conclusions

The reflectivity spectra exhibited a regular shift in the fundamental absorption edge (E_0) with composition x. The band gap energy of $Cd_{1-x}Co_xTe$ samples decreased with composition x. The reflectivity spectra for the present samples of $Cd_{1-x}Co_xTe$ of all compositions exhibit broad bands at 5300 and 11,100 cm⁻¹ due to ${}^{4}A_{2} \rightarrow {}^{4}T_{1}$ (F) and ${}^{4}A_{2} \rightarrow {}^{4}T_{1}$ (P) transitions, respectively. Hot probe test revealed that all the samples of $Cd_{1-x}Co_xTe$ exhibited p-type conductivity. Temperature dependence of resistivity revealed semiconducting behaviour of the samples. The activation energies of all the crystals lie in the range 36–81 meV and no regular variation is found with composition.

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