

Crystal growth and reflectivity studies of $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ crystals

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Abstract. Single crystals of $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ were prepared by vertical Bridgman crystal growth method for different concentrations of Mn. Chemical analysis and reflectivity studies were carried out for compositional and band structure properties. Microscopic variation in composition between starting and end compounds was observed from EDAX analysis. Linear dependence of fundamental absorption edge (E_0) as a function of Mn concentration (x) was expressed in terms of a straight line fit and a shift in E_0 towards higher energy was observed in reflectivity spectra of $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$.

Keywords. $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ single crystals; Bridgman method; EDAX.

1. Introduction

A wide class of semiconducting materials is characterized by the random substitution of a fraction of the original atoms by magnetic atoms, known as semi magnetic semiconductors (SMSC) or diluted magnetic semiconductors (DMS) (Furdyna and Kossut 1988). Tunability of lattice parameter and band gap with respect to concentration (x) are the unique properties of DMS. Mn doped II–VI compounds, $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$; $\text{Zn}_{1-x}\text{Mn}_x\text{S}$, $\text{Zn}_{1-x}\text{Mn}_x\text{Se}$ in bulk and thin film form, find potential applications in science and technology. Replacement of the group-II element with Mn leads to significant quantitative changes in the energy gap and optical properties. As Mn is substituted, the energy gap increases and the originally opaque material becomes as transparent as in visible region of electro magnetic spectrum (Furdyna and Kossut 1988). Tunability of lattice parameter and band structure parameters with concentration of Mn is excellent in fabrication of quantum well devices (Furdyna 1986). Distribution of Mn atoms in II–VI lattice exhibits interesting phenomena like negative magneto resistance, giant Faraday rotation and spin-glass behaviour. Nanostructured DMS have revolutionary applications in non-linear optics, fast optical switching and memory devices (Bandarnayake *et al* 1997). Several authors reviewed different growth methods of II–VI DMS (Yodershort 1985; Pajaczkowska 1978).

2. Experimental

Appropriate quantities of ZnTe and freshly synthesized MnTe (99.99% M/s Nuclear Fuel Complex, India) were

taken in a quartz tube of 15 cm length and 0.8 cm inner diameter and were evacuated to 2×10^{-6} Torr pressure with one end conically shaped capillary, known as growth tube. This was inserted in a thick walled quartz tube (protective tube) evacuated to 2×10^{-6} Torr, kept in a vertical furnace ($50 \times 50 \times 70 \text{ cm}^3$ dimensions with a central 70 cm long alumina tube with super Kanthal 16 SWG winding) of temperature gradient ($10^\circ\text{C}/\text{cm}$) and drawn with 6 mm/h pulling rate. Zirconia wool blanket and alumina firebricks were used for thermal insulation. Auto-transformers with thyristor power supplies were used as input power supplies with typical currents in the range 10–30 A. Proportional band integral differential (PID) controller (TTM-300 Toho, Japan) with fuzzy logic controlled programmer and platinum–rhodium thermocouples as temperature sensor, was used for complete temperature programming of the furnace. Temperature of the furnace was maintained at above the melting point of the charge in the growth region and the corresponding temperature profile of the furnace at 1100°C was shown in figure 1. After a great deal of trial and error, best quality crystals of $\text{Zn}_{1-x}\text{Mn}_x\text{Te}$ were obtained by vertical Bridgman method for $x = 0.10, 0.25, 0.45, 0.50$ and 0.60 for different concentrations of Mn and were shown in figure 2. Leitz 12 ME ST optical microscope was used to observe the surface texture and crystalline nature of the crystals. Reflectivity spectra were recorded by using optical Carry 5E-spectrophotometer from 200–2000 nm wavelength range.

3. Chemical analysis

Compositional analysis of the crystals is carried out using EDAX technique. The average composition of the end compounds is within $\pm 5\%$ variation with respect to the target composition. This deviation might be due to in-

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congruent melting and vapourization of charge, in leaving some charge unused (left over) and the deposits formed on the walls of the growth tube. Such chemical gradiency might have occurred due to incongruent melting of charge and temperature fluctuations during the growth of the crystal.

4. Microscopy

Figures 3 and 4 show a uniform cleaved surface of the crystal for $x = 0.10$ and $x = 0.50$ at $100\times$ magnification. From the above micrographs, it is obvious that for lower concentrations of Mn, the crystal surface is uniform while for higher concentrations small circular striations were observed. The crystals of all compositions exhibited single crystalline in nature (Veera Brahmam 2002) and the crystallites in random orientations were also found.

5. Reflectivity studies

Reflectivity spectrum of pure ZnTe at room temperature is recorded in figure 5. 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 transitions represent from the highest valence band (Γ_{15}) to the lowest and second lowest conduction bands, respectively. The values of band gaps and the corresponding transitions of E_0 , E_1 and E_2 are given in table 1. The experimental values are in good agreement with the reported values (Greenway 1963) of ZnTe spectrum. Similarly, figure 6 shows $Zn_{1-x}Mn_xTe$ reflectivity spectra

at RT for all concentrations of Mn between 200 and 2000 nm (i.e. 6.4–0.6 eV) wavelength range. As the content of Mn is increased, the fundamental absorption edge (E_0) is shifted towards higher energy region and finally the spectra are flattened for higher concentrations of Mn. The transition corresponds to E_0 and has been assigned to critical point transition from the spin-orbit split valence band along Λ direction or the transition from the L-point of the Brillouin zone to the lowest spin-orbit split conduction band of $Zn_{1-x}Mn_xTe$.

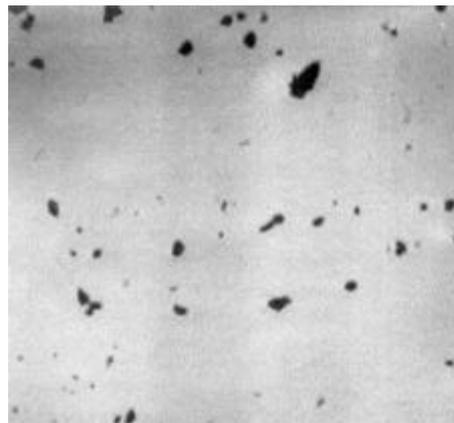


Figure 3. Optical micrograph of $Zn_{1-x}Mn_xTe$ for $x = 0.10$ at $100\times$.



Figure 4. Optical micrograph of $Zn_{1-x}Mn_xTe$ for $x = 0.50$ at $100\times$.

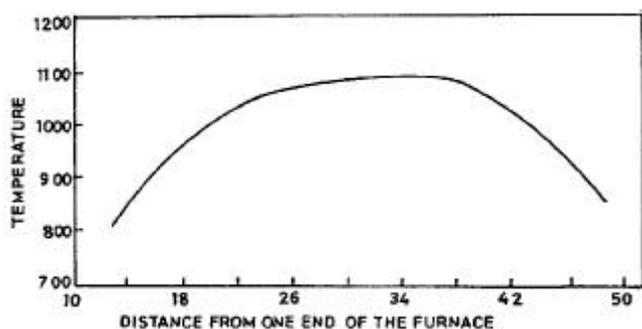


Figure 1. Temperature profile of the furnace at 1100°C .



Figure 2. $Zn_{1-x}Mn_xTe$ crystals for $x = 0.10, 0.25, 0.45, 0.50$ and 0.60 using vertical Bridgman method.

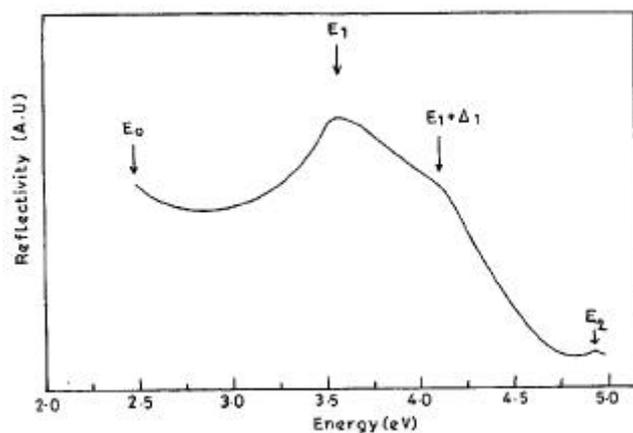


Figure 5. Reflectivity spectrum of pure ZnTe.

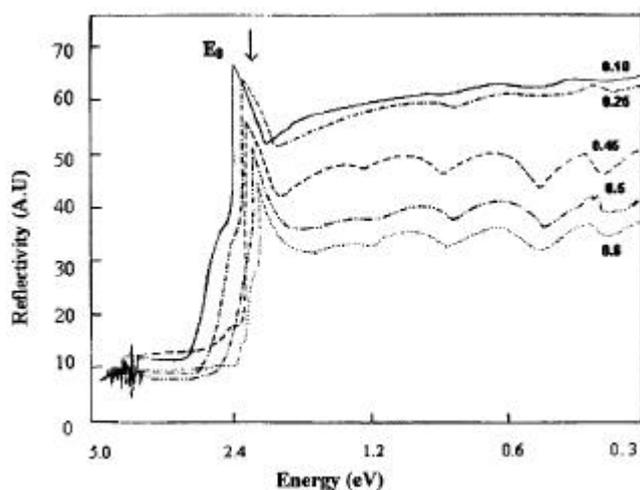


Figure 6. Reflectivity spectra of $Zn_{1-x}Mn_xTe$ for $x = 0.10, 0.25, 0.45, 0.50$ and 0.60 .

spectra with composition (x) can be understood as follows (Kissel *et al* 1987). In $Zn_{1-x}Mn_xTe$ system '3d' states of Mn are split into two groups of sub levels by a strong exchange interaction as spin up states located in the valence band region and the spin down empty states located in the conduction band region. At lower concentration of Mn, the Mn atoms can be considered as impurities and their '3d' states are considered as well localized states and they split further into e and t_2 components by the tetrahedral crystal field and hence a prominent structure of peaks is observed. Increase of Mn concentration forms interaction between 'd' levels of Mn and 'sp' levels of II-VI host lattice. The '3d' levels of Mn hybridize with Te energy levels as well as cation 's' and 'p' levels and hence a further distortion in band structure is likely to occur. As a result of it the spectra are flattened. The shift observed in the spectra is a characteristic property of several Mn doped II-VI systems like HgMnTe (Ken-

Table 1. Band gaps and the corresponding transitions in ZnTe.

Transition	Band gap (eV)	Reported values (Greenway 1963)
$\Gamma_{15}-\Gamma_1$	2.30 (E_0)	2.35
$\Lambda_3-\Lambda_1$	3.60 (E_1)	3.58
	4.12 ($E_1 + \Delta_1$)	4.14
X_5-X_1	4.90 (E_2)	5.41

Table 2. Band gap (E_0) as a function of composition (x) in $Zn_{1-x}Mn_xTe$ crystals.

Composition (x)	Band gap (E_0) (eV)	
	Experimental data	Reported data (Stankiewicz 1988)
0.10	2.34	2.29
0.25	2.42	2.37
0.45	2.50	2.47
0.50	2.55	2.49
0.60	2.69	2.54

deleucicz and Kierzek-Pecold 1978), ZnMnTe, CdMnTe (Kissel *et al* 1987) and $Zn_{1-x}Mn_xTe: N$ (Stifter *et al* 1999). Table 2 shows the linear dependence of fundamental absorption edge (E_0) as a function of Mn concentration (x), and is expressed in terms of a straight line fit, $E_0(x) = 2.271 + 0.631x$. This fit is in agreement within ± 0.02 eV variation to the best-fit reported, $E_0(x) = 2.25 + 0.487x$ (Stankiewicz 1988). This variation sometimes depends upon the quality of the crystals as well as on the preparation of the reflective surface. The transitions remain the same irrespective of the crystal orientation. Hence no anisotropy was observed in the reflection spectra.

6. Conclusions

Single crystals of $Zn_{1-x}Mn_xTe$ were prepared successfully by vertical Bridgman technique for different concentrations of Mn. Microscopic variation in starting and end compound composition was observed due to incongruent melting of charge. Blue shift of fundamental absorption edge as a function of Mn concentration was observed in reflectivity spectra of $Zn_{1-x}Mn_xTe$.

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