Ellipsometric characterization of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ thin films in the presence of perturbative fields[†]

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Abstract. Ellipsometric studies in the 1.5 to 5 eV range have been carried out on thin films of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ and exhibit E_0 , E_1 and $E_1 + \Delta_1$ transitions of the cubic semiconductors. The effect on these transitions upon irradiation by HeNe laser light, application of small alternating magnetic fields and the influence of both the fields, applied simultaneously, has been investigated. The observed critical point shifts have been interpreted on the basis of changes in the band structure of these thin films. This has been corroborated by theoretically calculating the effective number of electrons contributing to the transition per atom $-N_{\text{eff}}$.

Keywords. Semimagnetic semiconductors; optical properties.

1. Introduction

$\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ (CMT) alloys come under the general category of diluted magnetic semiconductors (DMS). In these semiconductors the 3d transition metal ions (Mn^{2+} , Fe^{2+} , etc.) substitute the cation sites of the host II–VI lattice (sulphides, selenides and tellurides of Cd, Hg and Zn) with either zinc-blend or wurtzite structure (Furdyna and Kossut 1988). The corresponding changes in the electronic levels are brought about by the intra-atomic exchange and correlation effects (Fazzio *et al* 1984). These correlation effects give rise to several interesting phenomena in DMS which are solely due to the transition metal ion (Gaj *et al* 1978). Thus, DMS exhibit very large g factors (≈ 100), large Faraday rotation ($\approx 10^4$ deg/cm) for small magnetic fields and large Shubnikov-de Hass oscillations for a small change in the temperature (Furdyna and Kossut 1988). In addition, effects such as tunability of the band gap, lattice vibrations and localized electronic and vibrational levels in the forbidden gap are also exhibited, just like the non magnetic ternary semiconductors (Long and Schmidt 1970). Mn has $3d^5 4s^2$ configuration; hence a valency of two (on considering the $3d^5$ levels as part of the core), and exists in the DMS compounds in Mn^{2+} state. In the CMT alloys, the occupied one electron d levels of Mn^{2+} lie within the valence band (Zahorowski and Gilberg 1984; Taniguchi *et al* 1986), their centre being about 2.5 eV below the top of the valence band (Taniguchi *et al* 1986). This leads to the hybridization of the spin up- $3d^5$ levels of Mn with the $5p$ band states of Te. The absorption edge of CdTe occurs at the top of the valence band (Te- $5p$ states) and the bottom of the conduction band (Cd- $5s$ states) at the Γ point ($\mathbf{K} = 0$) of the Brillouin zone (Bell 1977). The ellipsometric spectra of the CMT alloys show transitions which, according to the notation of Cardona and Greenway (1968) for the cubic semiconductors, are labelled as E_0 , $E_0 + \Delta_0$, E_1 and $E_1 + \Delta_1$ inter-band transitions in the Brillouin zone (Muller *et al* 1983; Chandra *et al* 1994). The

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E_0 peak corresponds to the Te 5p-Cd 5s transition while, $E_0 + \Delta_0$ is its spin-orbit component. E_1 and $E_1 + \Delta_1$ are the direct transition and its spin-orbit component along the $\langle 111 \rangle$ direction (Lautenschlager *et al* 1985).

Most of the earlier work reported in literature dealt with bulk DMS alloys. However, in recent years, the emphasis has been on preparing the superlattices and heterostructures of DMS by various techniques, such as molecular beam epitaxy (Nakamura and Nakano 1992), etc. The present study was guided by an active interest in the optical properties of thin DMS films. In this paper we present our results on the ellipsometric measurements of the dielectric function of the CMT thin films in the 1.5 to 5 eV range. The dependence of E_0 , E_1 and $E_1 + \Delta_1$ peak positions on the X values is discussed. The variations in positions of these peaks on application of small alternating magnetic fields, irradiation with HeNe laser beam and the simultaneous application of both, during the measurements are also presented and discussed.

2. Experimental

The films were deposited on Corning 7059 glass substrates, maintained at 350°C, by sublimation from stoichiometric alloys prepared by melt quenching. The composition of the alloys was determined from auger electron spectroscopy (Physical Electronics AES system Model 590A) and corresponded to nearly $X = 1.00, 0.60, 0.50, 0.40, 0.30, 0.25, 0.20 (\pm 0.01)$ in the higher Mn concentration range and $X = 0.10, 0.06, 0.04, 0.02, 0.00 (\pm 0.01)$ in the dilute range. All the films were deposited at a constant rate of 20 Å/sec for a thickness of 1.02 µm, as controlled by a quartz film thickness monitor (Edwards FTM5). In our study, films were deposited at a source to substrate distance of 90 mm and the film composition varied up to 12% from the starting alloy composition (Chandra *et al* 1994). The film compositions were also obtained from the empirical relation $E_g = 1.53 + 1.65X$ (Lautenschlager *et al* 1985), where the band gap energy E_g was derived from the plots of $(\alpha\hbar\omega)^2$ vs $\hbar\omega$, α being the absorption coefficient obtained from the reflectivity (R) and transmittivity (T) data (Chandra *et al*

Figure 1. Variation in X values of the as-deposited $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ films from that of alloy as calculated from Auger spectra and the reflectivity and transmittivity spectra.

1994). An IR-VIS-UV spectrophotometer (model Hitachi 330) has been used for obtaining the R and T data in the 1.5 to 5 eV energy range. Figure 1 shows the composition of the starting alloys and as-deposited films. All the film compositions have been indicated by their respective alloy compositions in the text. A Phillips (CM-12) transmission electron microscope (TEM) was used to study the structure and to detect phase segregation in the films, if any. No segregation of MnTe and CdTe phases was found in the films. The ellipsometric measurements were performed at room temperature in air ambient using a SOPRA-France model ES2G rotating polarizer type spectroscopic ellipsometer in the energy range 1.5 to 5 eV with a sampling period of 0.01 eV. The samples were mounted inside a notch made on one side of the core of a low inductance coil wound electromagnet capable of giving 50 Hz alternating fields up to 15 mTesla, perpendicular to the surface of the film. The other side was fixed onto a flat perspex sheet which could be inserted directly into the sample holder slot of the ellipsometer. A 10 mW HeNe laser light (1.96 eV energy) could also be impinging on the sample surface at normal incidence, simultaneously during the measurements.

3. Results and discussion

The imaginary parts of the dielectric function for some typical compositions in the absence of any external perturbative fields are shown in figure 2. As is evident only the E_1 and $E_1 + \Delta_1$ transitions are clearly visible at 3.52 and 4.08 eV respectively in the ϵ_2 spectra for the pure CdTe films. The start of E_2 transitions at about 5 eV is also indicated. Similarly, the E_0 peak is out of the range of our measurements. However, we have not observed the peak corresponding to $E_0 + \Delta_0$ reported at ≈ 2.5 eV (Cardona and Greenway 1968) for bulk CdTe. Increasing Mn concentration up to $X = 0.06$ leads to small but measurable blue shifts in the E_1 and $E_1 + \Delta_1$ peak positions.

Figure 2. ϵ_2 plots for some typical CMT compositions. The centred symbols have been given only as a guide. The plots have been shifted along y-axis for better representation.

Figure 3. Shifts δE_0 , δE_1 and $\delta(E_1 + \Delta_1)$ as function of X values. (a) Shifts due to Mn concentration only, (b) and (c) shifts in presence of HeNe laser and magnetic field.

For X in the range $0.1 < X \leq 0.6$, E_1 and $E_1 + \Delta_1$ peaks occur almost at the same positions as those for CdTe. The E_0 peak can now be observed. For $X > 0.25$, the E_0 peak is masked by the stronger peaks corresponding to those of MnTe ($X = 1$) at 1.85 and 2.10 eV respectively. These two peaks have been observed in all the films with $X > 0.25$ and occur at the same position irrespective of the changing Mn concentration. The shifts in the peak positions as a function of X are shown in figure 3a, where a linear fit to the E_0 peak shifts yields a slope of 1.757 eV, as opposed to a slope of ≈ 1.3 eV for single crystals of CMT (Lautenschlager *et al* 1985). We observe that the E_1 and $E_1 + \Delta_1$ peaks show a maxima for $X \approx 0.1$ composition film. It may be mentioned here that sufficient time was allowed for irradiation with HeNe laser before measurements and all peak positions were calculated from second derivatives of corresponding ϵ_2 spectra.

Blue shifts in positions of the E_1 and $E_1 + \Delta_1$ peaks in the ϵ_2 spectra have been observed in pure CdTe films on irradiation with a HeNe laser beam. However, almost constant red shifts are observed for the films in the composition range $0.0 < X \leq 0.25$. As the band gaps of the films with $X > 0.25$ are greater than the incident energy, hence no shifts in the peak positions are observed in the higher Mn concentration films. Figure 3b shows the corresponding shifts in the peak positions, for the various compositions studied, under the influence of laser light. Above band gap modulation has also been reported to produce comparable or even larger shifts (≈ 250 meV) in GaAs thin overlayers on GaAs substrates (Xiong *et al* 1993a, b).

No shifts in peak positions in the ϵ_2 spectra of the films with compositions in the dilute range ($X \leq 0.06$) are observed. For the films with $X \geq 0.1$, blue shifts are observed in E_0 and E_1 peaks while the $E_1 + \Delta_1$ peaks show red shift. The magnitude of all the shifts depend on the Mn concentration, the higher the X value, the larger the shift. The shifts in the presence of alternating magnetic field are shown in figure 3c. They occur at much lower magnetic fields (15 mTesla) compared to about 500 mTesla reported for the bulk alloys (Nakahara *et al* 1992). The simultaneous application of both the perturbations does not produce any observable new shifts. For $X \leq 0.25$, the shifts correspond

Table 1. Values of slope parameter b obtained by fitting E_0 peak position to linear equation $E = a + bX$ (O, L and M: unperturbed, laser and magnetic perturbation).

Critical point shifts	O (eV)	L (eV)	M (eV)
δE_0	1.757	-0.020	0.34
δE_1	—	-0.066	0.25
$\delta(E_1 + \Delta_1)$	—	-0.033	-0.06

to those brought about by laser light while, for $X > 0.25$, the shifts are equal to those obtained by the application of the magnetic field alone.

The critical point energy variations in all the three configurations were approximated by linear fitting of the peak shift data shown in figure 3, to the expression $E = a + bX$. The values of the parameter b , which give the slope of the linear fits, are given in table 1 for the various configurations. In figure 3a, blue shifts are observed in E_1 and $E_1 + \Delta_1$ peaks due to presence of Mn, which is contrary to the behaviour observed in the single crystals of CMT (Lautenschlager *et al* 1985). This may be due to the presence of some Mn at interstitial sites in the grains, forming a hexagonal MnTe sublattice intermixed with a cubic $\text{Cd}_{1-X}\text{Mn}_X\text{Te}$ sublattice. With increasing X , the lattice constant of the CMT decreases as $a = 6.486 - 0.148X$ (Furdyna and Kossut 1988), resulting in an increasing mismatch between the $\text{Cd}_{1-X}\text{Mn}_X\text{Te}$ ($a \approx 6 \text{ \AA}$) and MnTe ($a = 4.15 \text{ \AA}$, $c = 6.71 \text{ \AA}$) sublattices ($\approx 33\%$ for $X = 0$ in the x - y plane (Chandra *et al* 1994)). This strain tends to flatten the valence and conduction bands along the $\langle 111 \rangle$ direction, resulting in higher energies for E_1 and $E_1 + \Delta_1$ transitions (Lee *et al* 1992; Chandra *et al* 1994). The band structure of the CMT alloys is just the superposition of the band structures of CdTe and MnTe (Lautenschlager *et al* 1985). In the absence of any external perturbation, the $d\uparrow$ (spin up) and $d\downarrow$ (spin down) states are symmetrically split with respect to the top of the valence band of CdTe (mostly Te $4p$ like), hence the blue shifts in E_0 are caused only by an increase in the band gap of the films due to a decrease in the lattice constant with increasing X (Lautenschlager *et al* 1985). We have also calculated N_{eff} , the effective number of electrons taking part in the transition per atom, from the following sum rule (Greenway and Herbeke 1968)

$$N_{\text{eff}} = 0.766 \frac{M}{\rho} \int_{E_M}^{E_m} E \varepsilon_2(E) dE, \quad (1)$$

where M is the molecular weight, ρ the density in Kg/m^3 , E the energy in eV. It is assumed that all the three components of CMT viz. Cd, Mn and Te, contribute in the ratios of their X values and that the density of the material also follows a linear behaviour. The results of these calculations are shown in figure 4. The maximum contribution is for CdTe which decreases with increasing X up to $X = 0.25$ and then starts to increase again for $X > 0.25$. This indicates that for small X , Mn acts as a substitution impurity site in the CdTe lattice, while for large X , the Mn atoms also act as donor impurity site leading to an increase in N_{eff} . This explains the observation of the peaks corresponding to MnTe in the ε_2 spectra. An increase in N_{eff} in the presence

Figure 4. Effective number of electrons taking part in a transition per atom, N_{eff} , for the various compositions and configurations.

of laser light is observed, indicating that the shifts and broadening are associated with the inter-band transitions.

The absorption of the laser light increases the local temperatures on the surface of the films, leading to an increase in the phonon activity which is reflected in the increased peak width in films with $X < 0.25$. The photogenerated electrons and holes redistribute so as to reduce the internal fields generated due to the electromagnetic interactions at the air-film and the film-substrate interface. This alters the polarization state of the incident probe beam near the critical point energies via the well known Franz-Keldysh effect (Aspnes and Moss 1980) and results in a change in the dielectric function at these points. The shifts in this case depend on the number of carriers generated in CMT thin films which have high resistivity. The number of carriers thus generated is same for all films which results in the constant red shifts in the presence of laser light. It may be pointed out that blue shifts in pure CdTe films are suggestive of a relaxation of the CdTe lattice to a higher crystallinity state on laser annealing.

On the application of alternating magnetic field alone, the field starts interacting with the magnetic moment of the Mn^{2+} ions ($J = 5/2$) in the material. This leads to a Ruderman-Kittel-Kasuya-Yosida (RKKY) like interaction between the conduction band electrons and the magnetic field (Story *et al* 1992) and an internal field is set up in the material which is strongest for the film with highest Mn concentration. Due to the internal field, the valence and conduction bands stretch resulting in an increased energy gap. This redistribution of the bands in the $\mathbf{K}$ space results in the removal of the degeneracy of the Mn 3d bands, reducing the degree of hybridization of these band states with those of the Te-5p valence band states along the $\langle 111 \rangle$ direction, resulting in increased energy for the E_1 peak. The spin-orbit component of the E_1 peak—the $E_1 + \Delta_1$ peak—shows red shifts as the spin-split band is repulsed towards the valence bands of Te resulting in smaller transition energies.

4. Conclusions

We have measured the dielectric function of the $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ thin films of compositions $0 \leq x \leq 0.60$ in the near IR, visible and near UV energy range. Variations in the spectra observed in the presence of a HeNe laser beam, for $x \leq 0.25$ are attributed to the generation of charge carriers under the influence of the incident laser radiation. The variation in the band structure is also obtained in the presence of a small alternating magnetic field, which has been attributed to the change in hybridization levels of the Mn 3d states with those of the 5p valence band states of the Te. All these results are reflected in the N_{eff} data obtained from the ε_2 spectra.

References

- Aspnes D E and Moss T S 1980 *Handbook of semiconductors* (Amsterdam: North-Holland) vol. 2
 Bell R O 1977 *Rev. Phys. Appl.* **12** 391
 Cardona M and Greenway D L 1968 *Phys. Rev.* **131** 98
 Chandra S, Malhotra L K and Rastogi A C 1994 *Thin Solid Films* **238** 167
 Fazzio A, Kaldas M J and Zunger A 1984 *Phys. Rev.* **B30** 3430
 Furdyna J K and Kossut J (eds) 1988 *Semiconductors and semimetals* (Boston: Academic Press) vol. 25
 Gaj J A, Ginter J and Galazka R R 1978 *Phys. Status Solidi* **B89** 655
 Greenway D L and Herbeke G 1968 *Optical properties and band structure of semiconductors* (London: Pergamon Press)
 Lautenschlager P, Logothetidis S, Vina L and Cardona M 1985 *Phys. Rev.* **B32** 3811
 Lee J H, Kim S B, Koo B J, Chung L H, Jung M and Park H L 1992 *Solid State Commun.* **84** 901
 Long D and Schmidt J L 1970 *Semiconductors and semimetals* (Boston: Academic Press) vol. 5
 Muller E, Gebhrat W and Rehwald W 1983 *J. Phys.* **C16** L1141
 Nakahara J, Nouchi T, Arai H, Mogi I, Kido G and Watanabe J 1992 *J. Cryst. Growth* **117** 830
 Nakamura K and Nakano H 1992 *J. Phys. Soc. Jap.* **61** 1390
 Story T, Eggenkamp P J T, Swuste C H W, Swagten H J M and de Jonge W J M 1992 *Phys. Rev.* **B45** 1660
 Taniguchi M, Ley L, Jonson R L, Ghijsen J and Cardona M 1986 *Phys. Rev.* **B33** 1206
 Xiong Yi Ming, Snyder P G and Woolam J A 1993a *J. Vac. Sci. Technol.* **A** (to be published)
 Xiong Yi Ming, Snyder P G and Woolam J A 1993b *Thin Solid Films* **234** 399
 Zahorowski W and Gilberg E 1984 *Solid State Commun.* **52** 921