Full Length Research Paper

Effect of the annealing temperature on the structure and optical properties of Cd$_{1-x}$Mn$_x$Te thin films

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The ternary systems of Cd$_{1-x}$Mn$_x$Te were synthesized by direct fusion technique. Thin films of these compounds were prepared by electron beam gun under vacuum of 10$^{-5}$ Torr. The structural properties of these compounds in thin film forms were investigated by X-ray diffraction. It was found that materials crystallize in the zinc-blende form. The optical constants (absorption coefficient and band gap) of the thin films were determined by measurements of reflectance and transmittance in the wavelength region from 500 to 2500 nm. Analysis of the optical absorption spectra revealed the existence of one direct energy gaps. The energy gaps increase as the Mn concentration increases and the annealing temperature decreases. It is observed that as the Mn content ($x$) increases, the conductivity decreases.

Key words: Structure, optical properties, dilute magnetic semiconductor, Cd$_{1-x}$Mn$_x$Te thin films.

INTRODUCTION

Cd$_{1-x}$Mn$_x$Te crystal is a class of semiconducting material formed by randomly substituting a fraction of the cations in a compound semiconductor with magnetic ions (Furdna, 1982; Furdyna, 1988). This ternary system is a diluted magnetic semiconductor and is known for their interesting magneto-optical properties due to the Sp-d exchange interaction between the mobile spins of the conduction electron and localized spins of the magnetic elements.

This system has been investigated for a long time due to the high spin of Mn and relatively high solubility of manganese in II - VI compounds which are distributed in a random way in the cation sublattice of the crystals which exhibits interesting phenomena like negative magneto resistance, giant Faraday rotation and spin-glass behavior.

Caraman et al. (2006) reported that Cd$_{1-x}$Mn$_x$Te solid solutions crystallize based on the CdTe zinc-blende lattice in a wide concentration range; the lattice parameter, $a$, decreases linearly with concentration $x$, up to $x = 0.8$. For $x \leq 0.7$, Cd$_{1-x}$Mn$_x$Te has the cubic, zinc-blende ( sphalerite) structure (Pajaczowska, 1978), with a smaller lattice parameter (Bottka et al., 1981) the larger the Mn content, whereas MnTe has the hexagonal NiAs structure (Wyckoff, 1967) at ambient conditions.

Furdyna et al. (1985) reviewed the properties and application of II - VI DMS extensively. In the present work the aim is to investigate the effect of the annealing on the structure and the optical properties of the ternary system Cd$_{1-x}$Mn$_x$Te thin films.

EXPERIMENTAL

Cd$_{1-x}$Mn$_x$Te compounds were synthesized by direct fusion method. High purity (99.999%) mixtures of the constituent element (Cd, Mn, and Te) in stoichiometric portions (obtained from Aldrich chemical Co.). The mixture of each composition was taken in a graphitized silica tube evacuated at a pressure of (10$^{-5}$ Torr). The evacuated tube was then placed into a furnace whose temperature was raised in steps to 1100°C for 3 days. During the synthesis the molten material was shaken to ensure homogeneity. Then the temperature of the furnace was cooled to 900°C and kept at this temperature for one week and then cooled to room temperature.

Thin films of the compound were prepared by electron beam gun from molybdenum boat under vacuum of 1.3 mPa (10$^{-5}$ Torr). The thickness of the films was measured using an optical multibeam interferometer. Cd$_{1-x}$Mn$_x$Te thin films are annealed at 100 and 200°C in vacuum (10$^{-3}$ Torr) for 2 h. The crystal structures of the prepared compounds in both powder and thin film forms were investigated by the X-ray diffractometer Philips (Diano Cooperation U.S.A.). The composition of the bulk samples and the corresponding thin films were determined by energy dispersive X-ray analysis. The
Figure 1. X-ray powder diffractograms of Cd$_{1-x}$Mn$_x$Te, 0.05 $\leq x \leq$ 0.2.

Figure 2. X-ray diffraction pattern of representative curve Cd$_{0.8}$Mn$_{0.2}$Te, as deposited and annealed at 100 and 200°C.

RESULTS AND DISCUSSION

The composition of the materials was determined by energy dispersive X-ray analysis (EDAX). It was found that the composition of the prepared samples has approximately the stoichiometric composition. The X-ray diffraction patterns of the Cd$_{1-x}$Mn$_x$Te powder are shown in Figure 1. The XRD patterns of the Cd$_{0.8}$Mn$_{0.2}$Te as deposited and annealed thin films at 100 and 200°C for 2 h are shown in Figure 2 as representative data for all compositions.

No evidence to the existence of more than one phase in the prepared material, the as deposited and annealed thin films is polycrystalline in nature. Both Cd$_{1-x}$Mn$_x$Te in powder and thin films forms have a zinc-blende crystal structure phase. It is clear from the figure that the peak intensity and the half amplitude peak width, increased appreciably with increasing annealing temperature which gave information about the degree of crystallinity for the crystalline plane (111).

Optical properties

To investigate the effect of the annealing temperature on the energy gap of the prepared samples, the transmittance $T$ and the reflectance $R$ at normal incidence in the spectral range (500 - 2500 nm) were measured for thin film of thickness 250 nm, subjected to different annealing temperatures (100 and 200°C) as represented in Figures 3 and 4).
The absorption coefficient ($\alpha$) for Cd$_{1-x}$Mn$_x$Te thin films as-deposited and the heat-treated films were calculated from the transmission ($T$) and reflection ($R$) data using the relation:

$$ T = (1-R)^2 \exp(-\alpha t) / (1-R^2) \exp(-2\alpha t) $$

where $t$ is the film thickness.

Figure 5 represents the variation of the calculated absorption coefficient ($\alpha$) vs. photon energy ($h\nu$) for Cd$_{1-x}$Mn$_x$Te thin film, as deposited and annealed at 100 and 200°C.

The absorption coefficient data for the thin films were analyzed in terms of the relation (Moss, 1957; Kasmorski et al., 1977; Paukove, 1971):

$$ \alpha = B (h\nu - E_g)^p $$

Where $p$ determines the type of transition, being 1/2 for allowed direct transition.

Figure 6 shows the variation of $(\alpha h\nu)^2$ with the photon energy $h\nu$ for the as-deposited and annealed Cd$_{1-x}$Mn$_x$Te. It is clear from this figures that $(\alpha h\nu)^2$ varies linearly with $h\nu$ indicating a direct optical transition. The zero absorption intercepts (extrapolations) of these plots (straight lines) on the energy axis gives the direct energy gap. The band-gap energy decreases with increasing the
Table 1. The values of the optical band gaps of Cd$_{1-x}$Mn$_x$Te films at room temperature and annealed at 100 and 200°C.

<table>
<thead>
<tr>
<th>Composition, x</th>
<th>Eg as deposited</th>
<th>Eg Annealed at 100°C</th>
<th>Eg Annealed at 200°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>1.545</td>
<td>1.52</td>
<td>1.51</td>
</tr>
<tr>
<td>0.1</td>
<td>1.666</td>
<td>1.642</td>
<td>1.634</td>
</tr>
<tr>
<td>0.15</td>
<td>1.741</td>
<td>1.729</td>
<td>1.718</td>
</tr>
<tr>
<td>0.2</td>
<td>1.78</td>
<td>1.775</td>
<td>1.769</td>
</tr>
</tbody>
</table>

Also, it is clear from table (1) that the direct energy gap increases by increasing the Mn content (x) in the compound. The increase of the energy gap with increasing x may be due to the decrease of the lattice constant with increasing Mn concentration. The decrease in the lattice constant with Mn concentration shows strongly that the Mn ions are incorporated into the host Cd site substitutionly (Hwang et al., 2007).

The most accurate method for determining the energy band structure of semiconductors is one based on investigating the spectral distribution of both the refractive index n and the absorption index k. Figures 7 and 8 shows the spectral variation at n and k for the as-deposited and annealed Cd$_{1-x}$Mn$_x$Te thin films with wave length at different annealing temperatures (100 and 200°C).

It is clear from these curves that, both n and k increase with increasing the annealing temperature, which can be attributed to the degree of the crystallinity which increase by increasing the annealing temperature. Also the variation of the refractive index with annealing temperature is related to the change in the lattice parameters. So it can be suggested that the lattice parameter may decrease as a result of increasing the temperature of annealing, which may be the reason for the observed decrease in the values obtained for the energy gap, Eg, by increasing the annealing temperature. This, in turn, would require more detailed study to determine the change of the lattice parameters with annealing temperatures.

### Electrical properties

The electrical conductivity $\sigma$ was measured at room temperature for Cd$_{1-x}$Mn$_x$Te (x = 0.05, 0.1, 0.15 and 0.2) as a function of Mn content by the conventional four-probe method. The electrical conductivity $\sigma$ was calculated from the relation:

$$\sigma = \frac{V}{I} \frac{A}{L} \text{ (} \Omega \text{.cm)}$$

where A is the cross-sectional area, L is the length between the potential probes, V is the measured voltage and I is the measured current. Figure 9 shows the composition dependence of conductivity $\sigma$ at room temperature 300 K. It is observed that as the Mn content
Also, the optical absorption spectra revealed that the existence of one direct energy gap for Cd$_{1-x}$Mn$_x$Te thin films. It can be concluded that the energy gaps decrease with increasing the annealing temperature and increase with increasing the Mn content. It was found that the electrical conductivity decreases as the Mn content increases.

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