Ag doped ZnTe films prepared by closed space sublimation and an ion exchange process

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ABSTRACT

ZnTe thin films were deposited by closed space sublimation (CSS) technique on amorphous glass substrate. The deposited films were immersed in AgNO3 solution for different time periods, then heated in vacuum. The resistivity of the film, immersed for 30 min, was reduced by less than six orders of magnitudes. The films structures were characterized by X-ray diffraction (XRD). Atomic force microscope (AFM) was used to detect the surface morphology of the films. The films thickness, the optical properties, such as refractive index, absorption coefficient and the optical band gap were determined from transmittance spectra in the wavelength range of 400–2500 nm. The dark electrical conductivities of the films were studied as function of temperature to determine the conductivity activation energy.

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1. Introduction

Among II–VI compound semiconductors zinc telluride (ZnTe) is very attractive for optoelectronic device applications in the green spectral range, due to its direct band gap of ~2.26 eV [1–4].

ZnTe thin films were prepared by several techniques including pulsed laser deposition [1], sputtering [5], electron beam [6], electro-deposition [7], isothermal closed space sublimation [8], SILAR method [9], brush plated [2], thermal evaporation [10–12] and CSS [13]. On the other hand, ion exchange process was recently utilized for doping of ZnTe and other II–VI semiconductors by Cu, Ag and In [10,13–22] due to the simplicity and low cost of the method.

One of the most important application of ZnTe is high efficiency stable electrical back contacts for CdTe based solar cells [2,4]. For that low resistive p-type ZnTe is required. Ag as group I element acts as acceptor dopant for II–VI semiconductors [23], which lead to increase in the electrical conductivity of ZnTe.

In this work we deposited ZnTe films by CSS method, which was more common for deposition of CdTe based solar cells, and Ag doping of the films was achieved by an ion exchange process. In this regard the electrical properties of the films were studied. Furthermore the optical, structural and surface morphology of the films were also studied due to its importance in the application of ZnTe in optical devices.

2. Experimental methods

High purity (99.99%) ZnTe fine powder was used as a source material for films deposition on water-white glass substrates (2.5 cm × 5 cm). Before deposition, the substrate was cleaned by distilled H2SO4 solution, then rinsed by distilled water and I.P.A and then dried by dry nitrogen gas. Source material (0.1 g of ZnTe) was put in the graphite boat, to be heated by 500 W quartz lamp. The source and substrate heaters (quartz lamps) were connected to the main through two separate triacs. The gates of the triacs were connected to temperature controllers. The, k-type, thermocouples of the temperature controllers were inserted into the source graphite boat and the graphite substrate supporter. The CSS system, used in our experiment, is shown in Fig. 1. Substrate was fixed at a
distance of about 10 mm from the source of material. The chamber was closed and evacuated, by the help of rotary pump, to \(~1 \times 10^{-2}\) mbar. The substrate and source temperatures were kept at 400 °C and 600 °C, respectively. The time of evaporation was 10 min. The chamber was evacuated for 30 min before starting the source and substrate heating. After deposition, the source heater was turned off, while the substrate remains at the deposition temperature for 30 min. This was to allow the source temperature to cool down, avoiding further deposition at lower substrate temperature. The film remains under vacuum till source temperature reduced to below 100 °C, to avoid the oxidation of the film.

Numbers of films were prepared with similar deposition parameters to study the effect of post treating in AgNO₃ solution. The solution contained 1 g of AgNO₃ in 11 of distilled H₂O. The solution was kept at 60 ± 2 °C. The films were immersed for different time, as listed in Table 1. After immersion the films were cleaned in distilled water and dried by nitrogen gas. Next step was heating the immersed films, in vacuum of \(~10^{-2}\) mbar, at 400 °C for 1 h to ensure the diffusion of Ag into the entire film [10]. Ion exchange process occurs on the films surface, i.e. Ag layer formed above the ZnTe film. So heating the films, at high temperature, cause diffusion of Ag atoms in the entire film. Further studying the Ag doping of ZnTe films, not the properties of Ag layer on ZnTe films.

X-ray diffraction (XRD) patterns, using Cu-Kα radiation, were used to study the structure of the films. The transmission spectra in the range 400–2500 nm were recorded by PerkinElmer, Lambda19, UV-vis–NIR spectrophotometer with UV-WinLab software. The dark electrical DC conductivity, of cut pieces of the films with evaporated Au contact, according to Van der Pauw geometry, was measured as a function of temperature (30–200 °C). The morphology of the films was analyzed by using atomic force microscope (AFM). The composition of the films were detected using electron micro-probe analyzer (EMPA) attached to scanning electron microscope.

### Table 1

<table>
<thead>
<tr>
<th>Film number</th>
<th>Immersion time (min)</th>
<th>Ag ratio (atm.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z₀ (as- deposited)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Z₁</td>
<td>1</td>
<td>1.7</td>
</tr>
<tr>
<td>Z₅</td>
<td>5</td>
<td>8.0</td>
</tr>
<tr>
<td>Z₁₀</td>
<td>30</td>
<td>12.9</td>
</tr>
</tbody>
</table>

### Results and discussions

#### 3.1. Structure and morphology studies

Fig. 2 shows the XRD pattern for as- deposited and immersed films. All the peaks in XRD pattern of as- deposited film was referred to Ag cubic structure of ZnTe, which is the most dominant structure for ZnTe [10,13]. The most dominant peaks in the XRD pattern are corresponding to (1 1 1), (2 2 0) and (3 1 1) direction, other low intensity peaks corresponding to (2 0 0), (2 2 2), (4 0 0), (3 3 1), (4 2 0), (4 2 2) and (5 1 1) were also observed. No peaks related to Ag or Ag compounds were observed in the XRD pattern of the films immersed in AgNO₃ solution for short time (i.e. \(\leq5\) min). This could be due to small amount of Ag in the films, which is below the detection limit [10,15]. However peaks related to monoclinic structure of Ag₂Te appears in the films, which is immersed for longer time (i.e. 30 min).

Due to an ion exchange in AgNO₃ solution different ways of Ag incorporation in ZnTe could be possible. Substitution of Zn²⁺ by Ag¹⁺ since the following interaction is possible [24].

\[
\text{Zn} + 2(\text{Ag}^+ + \epsilon) \rightarrow \text{Zn}^2^+ + 2\epsilon + 2(\text{Ag}),
\]

or incorporation of Ag as interstitial in ZnTe or formation of Ag₂Te.

AFM was used to assess the surface quality of the films. Surface morphology of the films deposited at 400 °C substrate temperatures and immersed in Ag NO₃ solution, for different periods of time, and followed by heat treatment are shown in Fig. 3. The average surface roughness observed by AFM were in the range 16–18 nm, while the average grains size were \(~0.3\) μm and almost the same for all the
films. This indicates that the structure and the films morphology are more depending on the films deposition parameters. It is well known that deposition parameters such as substrate temperature, deposition rate and vacuum have great influence on the films structure and roughness. In our case these parameter were the same for all films. And the only different parameter was post treatment in AgNO3 solution.

The Ag ratio (atom %) in the films (EMPA result) versus the immersion time in AgNO3 solution are listed in Table 1. It shows a non linear behavior i.e. the speed of the silver adsorbance at the film decreases with time and this result is observed for other II–VI semiconductors [10,13,14,16,17,19–22] and this was explained by the fact that ion exchange process takes place on the film surface, which was exposed to the liquid. However, the concentration of silver in these films is much higher than the films prepared by two-source evaporation [10] and immersed in AgNO3 solution. The most probable explanation is the comparative surface roughness of the films (i.e. more area is exposed to the solution).

3.2. Optical analysis

The thickness and refractive index of the films were calculated by fitting the transmission data to the following equation [10,11,25]

$$T = \frac{Ax}{B - Cx \cos(\phi) + Dx^2},$$

where $T$ is the normal transmittance for the system of thin film on transparent substrate surrounding by air (refractive index = 1), and taking all multiple reflection at the interface [11,25] into account, in case of $k^2 \ll n^2$, $A = 16n^2S$, $B = (n+1)(n+s^2)$, $C = 2(n^2 - 1)(n^2 - s^2)$, $D = (n-1)^2(n-s^2)$, $\phi = 4\pi nd/\lambda$, $x = \exp(-\alpha d)$, $k = \alpha \lambda/4\pi$. Here $n$ and $s$ are the refractive indexes of the film and the substrate, $d$ is the thickness of the film and $\alpha$ is the absorption coefficient of the film and $\lambda$ is the wavelength. The refractive index of the substrate $s = 1/T_s + (1/T_s^2 - 1)^{1/2}$, where $T_s$ is the transmission of the substrate.

Here, the refractive index of the films obey the simple classical dispersion relation for a single oscillator centered at wavelength $\lambda_0$ [26] is expressed by

$$n^2 = 1 + \frac{(n_0^2 - 1)\lambda^2}{\lambda^2 - \lambda_0^2},$$

where $n_0$ is the infinite wavelength refractive index. The wavelength dependence of the absorption process is complicated, therefore, if the total absorption coefficient is small, it may be expanded in a Taylor series around the photon energy far from absorption line. If only terms up to second degree are included ($\alpha$ varies slowly with $\lambda$), the relation for $\alpha$ can be written as:

![Fig. 2. XRD pattern of heated the films.](image)

![Fig. 3. AFM image of heated Z0 (up), Z5 (middle) and Z30 (down).](image)
\[ \alpha = c + g/\lambda + f/\lambda^2, \] where \( c, g \) and \( f \) are fitting parameters. The values of \( n \) and \( d \), obtained by fitting of transmittance data to Eq. (1), were used to calculate \( \alpha \) in the high absorption region. The exact solution of Eq. (1) for \( x \) is:

\[
x = \frac{\left\{ C_1 + \frac{4}{\lambda} - \left[ \left( C_1 + \frac{4}{\lambda} \right)^2 - 4BD \right]^{1/2} \right\}}{2D}, \quad \text{where } C_1 = C \cos(\phi).
\]

For allowed transition, \( \alpha \) varies with photon energy (\( hv \)) as the well-known dependence \( ah \sim (hv - E_g)^{\lambda/2} \). Near the absorption edge, the optical energy gap \( E_g \) is obtained by extrapolating \( (\alpha hv)^2 \) against photon energy plot, as shown in Fig. 4. Fig. 5 shows that heating the films in vacuum for 1 h at 400°C, after immersion, improves the transmittance of the films. This attributed to diffusion of silver into the entire film rather than residing on the film surface. The films transmission decreases as the immersion time increases (Fig. 6), as result of increasing the silver concentration in the films. Fig. 7 shows a good fitting of the experimental transmittance data to Eq. (1). The calculated optical results are listed in Table 2. The refractive index of the films increases as the immersion time increases. Higher Ag concentration in the films leads to higher refractive index and decrease of the optical energy gap. This indicates that high doping occurs, which lead to prominent shift in the optical energy gap (Fig. 8).

### 3.3. Electrical conductivity

The room temperature resistivities of the films are listed in Table 3. The resistivity of as deposited film is very high \( \sim 10^9 \) (\( \Omega \cdot m \)) as expected for ZnTe films on amorphous glass substrate [5, 6, 11]. The resistivity of the films is decreased as function of immersion time, in AgNO3 solution. However increase in the resistivity is observed after heating the immersed film in vacuum (Table 3). This is due to that the electrical contacts, used for measuring the resistivity, were on the films surface where the Ag was concentrated after immersion (ion exchange process occurs at the film surface). Ag diffused in the entire film after heating the immersed films. The p-type conductivities of the films were confirmed by the well-known hot probe method. The dark DC electrical conductivity (\( \sigma \)) of the films as function of temperature was studied in the temperature range of 30–200°C. The DC conductivity, in this temperature region, is represented by the following relation [27, 28].

\[
\sigma = \sigma(0) \exp \left[ \frac{-(E_f - E_v)}{kT} \right],
\]

![Fig. 4. Plot of \( \alpha \) vs. photon energy for Z1 and Z5.](image1)

![Fig. 5. Transmittance of Z30 before and after heating at 400°C for 1 h.](image2)

![Fig. 6. Transmittance of immersed and heated films.](image3)

![Fig. 7. Transmission data along with fitting to Eq. (1) of heated Z30.](image4)
Table 2
Table 3 optical results.

| Film number | Thickness (nm) | Refractive index $n = \left(1 + \frac{\sigma^2}{2k^2}ight)^{1/2}$ | Energy gap (eV) |
|-------------|----------------|-------------------------------------------------|-----------------|
| Z0          | 514            | 2.71                                           | 2.24            |
| Z1          | 477            | 2.72                                           | 2.21            |
| Z5          | 386            | 2.75                                           | 2.18            |
| Z30         | 436            | 2.82                                           | 2.16            |

Table 3
Electrical properties of the films.

<table>
<thead>
<tr>
<th>Film number</th>
<th>Immersion time (min)</th>
<th>Room temperature resistivity of immersed films ($\Omega$ cm)</th>
<th>Room temperature resistivity of heated films ($\Omega$ cm)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z0</td>
<td>0</td>
<td>4.5 x 10^8</td>
<td>4.5 x 10^8</td>
<td>0.63</td>
</tr>
<tr>
<td>Z1</td>
<td>1</td>
<td>1400</td>
<td>8.1 x 10^7</td>
<td>0.42</td>
</tr>
<tr>
<td>Z5</td>
<td>5</td>
<td>18.6</td>
<td>5.9 x 10^2</td>
<td>0.25</td>
</tr>
<tr>
<td>Z30</td>
<td>30</td>
<td>0.052</td>
<td>3.54</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Ag-doped ZnTe by two- source evaporation

The value of activation energy decreases as the immersion time increases, as listed in Table 3. The minimum activation energy belongs to the film which is immersed for 30 min. The decrease of the activation energy indicates an increase in Ag concentration and a strong interaction among the impurities (i.e. shift of $E_f$ closer to the valence band). It is obvious, from Table 3 that the conductivity and the activation energy were lower than that reported for films prepared by two- source evaporation. The comparatively rough surfaces of the films allows more area of the ZnTe films to expose to the solution during ion exchange process, which increase the quantity of Ag ions adsorbed at the film surface.

4. Conclusions

ZnTe thin films are prepared by low-cost simple technique (CSS). Low resistive silver doped films was achieved by an ion exchange process (immersion the post prepared films in AgNO₃). All ZnTe films were cubic in structure with [1 1 1] preferred orientation. Small peaks, related to Ag₂Te, appear in the XRD diffraction pattern for of the long time immersed film. The highest conductivity is found to be for the film immersed for 30 min. The surface morphology is almost the same for all films. The films lose their transparency as the immersion time increases. Increase of the films refractive index and shift of optical band gap are also observed. Controlling of immersion time is important parameter to improve the electrical conductivity of the films without drastic change in their optical properties.

References