Properties of r.f. sputtered cadmium telluride thin films

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CdTe thin films were prepared using r.f. magnetron sputtering in an Ar atmosphere. Substrate temperatures in the range 100–320 °C were used. XRD results showed that the films are amorphous below 200 °C while above 200 °C the films were polycrystalline with cubic structure and grains preferentially oriented along the [1 1 1] crystallographic direction. SEM measurements showed significant enhancement of crystallite size with increase of Tsub or with post-preparation annealing above 400 °C. The 5 K photoluminescence spectrum showed a broad (FWHM ~ 80 meV) band with a maximum at 1.538 eV. This band showed significant narrowing after annealing above 400 °C suggesting that it originates from transitions involving grain boundary defects. The refractive index n was determined from the interference pattern of the optical transmission. The results agree with the values of n calculated using the Jensen theory. The absorption coefficient was determined for photon energies \( h\nu \geq E_g \) (the energy bandgap) from the optical transmission spectra in the absorption region using the Swanevpoel theory. Several direct and indirect allowed optical transitions were identified. It was found that the transitions can be grouped into four main allowed transitions (two direct; \( E_2 \), \( E_3 \) and two indirect; \( E_1 \), \( E_4 \)) whose energy values vary from one sample to another due the quantum size effect associated with small grain size. The main transitions are: \( E_2 \) (1.50–1.77 eV) assigned to \( \Gamma_8 \) valence band (VB) \( \rightarrow \Gamma_6 \) conduction band (CB) transition, \( E_4 \) (1.84–2.05 eV) assigned to \( L_{4,5}(\text{VB}) \rightarrow \Gamma_4 \) transition where \( \Gamma_4 \) is an impurity level at 1.2 eV above the \( \Gamma_6 \) (VB), \( E_3 \) (2.37–2.49 eV) assigned to \( L_{4,5}(\text{VB}) \rightarrow \Gamma_6 \) (CB) transition and \( E_3 \) (2.25–2.55 eV) assigned to \( \Gamma_7 \) (VB) \( \rightarrow \Gamma_4 \) transition. The impurity is attributed to native centers or grain-boundary-related defects.

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1. Introduction

In the past decade, considerable interest has been shown in the study of CdTe due to its importance as a material for optoelectronic applications, particularly in the field of polycrystalline thin-film solar cells. A number of techniques have been used for the preparation of such films [1, 2] and all-thin-film solar cells have been prepared with an efficiency of 15.8% [3] using heterojunctions of the type CdTe/CdS prepared by closed-space sublimation. On the other hand, the cells prepared by r.f. sputtering are relatively less well, studied despite the known importance of r.f. sputtering as a suitable technique for large-scale applications. The efficiency of all-sputtered CdTe/CdS cells has reached 12.4% [4]. A further improvement of the efficiency requires detailed studies of the physical properties of the material in the thin-film form.

The optical properties of CdTe single crystals and thin films have been reported in the literature [5–8]. However, there have been no reports on the refractive index of r.f. sputtered thin films. Also, the optical transitions in this type of films have not been studied in detail. Here, we report on the optical properties of r.f. sputtered CdTe thin films. The refractive index was determined and the experimental values compared with those calculated using the Jensen theory [8] for the refractive index of semiconductors below the bandgap energy. Also, we present a detailed analysis of the optical absorption results, which reveal four main optical transitions (two direct and two indirect) in the energy range 1.50–2.50 eV in this type of films.

2. Experimental

CdTe thin films were prepared using r.f. magnetron, sputtering in an Ar atmosphere. Substrate temperatures between 100 and 320 °C and an r.f. power of 80 W were used. A hot-pressed CdTe target (purity 99.999%) from E-Vac Inc. was used. The sputtering was performed in the chamber of a Edward 306 sputtering system, which uses a planar magnetron source. A base pressure of \( 1.3 \times 10^{-3} \) Pa was reached before admitting pure Ar gas (99.999%) at a pressure of about 0.67 Pa. More details on experimental procedure have been given elsewhere (see, for example, El Akkad et al. [9]).

The film thicknesses were measured using a Tencor Instruments profiler type Alpha-Step 200. Transmission measurements were carried out in the wavelength range
$300 \leq \lambda \leq 3000$ nm using a Cary 5E spectrophotometer. For XRD spectra, an X-ray diffractometer, Siemens D5000, was used.

The luminescence was excited using a CW argon ion laser of intensity 80 mW focused to 1.55 mm$^2$. Lock-in detection was performed, PMT with a GaAs : Cs cathode, spectrally flat up to 850 nm, and a grating monochromator were used.

### 3. Results and discussion

#### 3.1. Structural and luminescence properties

For substrate temperatures $T_s \leq 200 \degree$ C, the XRD pattern (Fig. 1) is featureless indicating that the range of crystallinity of the films is less than a hundred angstroms [10, 11]. These films are likely to have an amorphous nature. For temperatures $T_s \geq 200 \degree$ C, the XRD spectra indicate a cubic CdTe structure with preferential crystalite orientation along the [111] crystallographic direction.

The effect of annealing on the crystallinity of the films is demonstrated in Fig. 2, which shows two SEM pictures for a CdTe film sputter-deposited on a steel substrate at 100 \degree C before and after annealing at 450 \degree C for 15 min. While before annealing no crystallite domains could be observed, the domains grow to a size ranging from 300 to 1000 nm after annealing.

The photoluminescence spectra at 5 K for the film before and after annealing are shown in Fig. 3. Before annealing, a broad band (full width at half maximum FWHM = 80 meV) with a peak at 1.538 eV is observed. This band becomes much narrower (FWHM = 22 meV) with no measurable change in peak position after annealing. The significant narrowing of the band with the growth of grains after annealing suggests that it involves transitions associated with grain-boundary defects.

#### 3.2. Optical properties

##### 3.2.1. Refractive index

The optical transmission was measured in the wavelength range $300 \geq \lambda \geq 3000$ nm. Typical results are shown in Fig. 4. The refractive index $n$ can be calculated from the interference fringes appearing at long wavelengths using the basic equation for those fringes

$$2nd = m\lambda$$

where $m$ is an integer for maxima and half integer for minima. The sample thickness $d$ was measured using the Tencor profiler and was precise to 3%. Fig. 5 shows the experimental values of $n$ as a function of photon energy for some representative samples.

The refractive index $n$ was calculated using the following equation derived theoretically by Jensen [8] for compound semiconductors below the energy band gap.

$$n^2 = 1 + 2C_n[(y_B - y_F) - z(tan^{-1}(y_B/z) - tan^{-1}(y_F/z))]$$

where

$$C_n = \frac{R}{E_0}$$

$R$ being a constant, and $E_0$ the energy band gap (1.46 eV for CdTe single crystals [7]), and

$$z = \left(1 - \frac{hv}{E_0}\right)^{1/2}$$

$$y_B = M(a_o - a)$$

$$y_F = \frac{1}{2} \left(\frac{m_e}{m_i}\right)^{1/2} \lambda_c k_F$$

where $M$ and $a_o$ are constants (for the II–VI compounds $M = 3.46 \pm 0.2 \text{ nm}^{-1}$, $a_o = 1.737 \pm 0.088 \text{ nm}$), and $a$ is the lattice constant. $k_F = (3\pi^2 n_e)^{1/3}$ is the electron wave vector at low carrier concentration $n_e$.

$$\lambda_c = \left(\frac{n^2}{2m_i E_0}\right)^{1/2}$$

$m_e$ is the electron effective mass, $m_i$ the reduced effective mass of electrons and holes (for CdTe $m_i = m_e$).

Fig. 5 shows the calculated values of $n$ as a function of $hv$ (solid line). The values of parameters used are $a_o = 1.825 \text{ nm}$, $M = 3.66 \text{ nm}^{-1}$, $a = 0.641 \text{ nm}$, $y_F = 0.203/E_0^{1/2}$ for $n_e = 10^{15} \text{ cm}^{-3}$ (the calculated value of $n$ does not show significant variation with $y_F$ for values of $n_e$ between $10^{15}$ and $10^{16} \text{ cm}^{-3}$). $C_n = 1.12$ [8]. It is seen in Fig. 4 that, within experimental uncertainty of about 5%, the calculated values of $n$ account fairly well for the observed values.

##### 3.2.2. Absorption coefficient

The absorption coefficient $\alpha$ was calculated from $T$ in the region of the strong absorption ($\lambda \leq 840$ nm) where the interference fringes disappear. In this case, according to Swanepoel [12], the following equation holds for an absorbing film on a transparent substrate,