Journal of Non-Crystalline Solids 355 (2009) 1474–1478

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Characterization of CdTe thin films fabricated by close spaced sublimation technique and a study of Cu doping by ion exchange process

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ARTICLE INFO

Article history:
Received 31 August 2008
Received in revised form 2 May 2009
Available online 11 June 2009

PACS:
71.20.Nr
81.05.Dz
73.61.Ga
61.72.Vv

Keyword:
Films and coatings

ABSTRACT

CdTe thin films were prepared onto water-white glass substrates by the close spaced sublimation technique. The films annealed right after the deposition were then immersed in copper nitrate solution for different periods of time. These films were again annealed at 500 °C for 1 h to ensure the diffusion of copper in the films. The samples were characterized by X-ray diffraction and scanning electron microscopy. The electron microprobe analyzer showed an increase of copper-content in composition. The dc electrical conductivity showed a credible increase with increasing copper-content in the films. With the increase of copper-content, the hole mobility increased systematically. The optical parameters were deduced by fitting the optical transmittance in the wavelength range 300–2500 nm.

1. Introduction

Cadmium Telluride (CdTe) is considered as a promising material for several applications like photovoltaic cells, high performance electro-optic modulators and photorefractive devices [1]. The II–VI materials like CdTe and Hg CdTe etc are critical in wide range of detector technology operating in the infrared, ultraviolet, X-ray and gamma-ray spectrum [2]. Thin films of CdTe can exhibit both n and p type electrical conductivity, which makes it useful for diode technology and field effect transistors [3]. It also exhibits a semi-insulating state [4]. CdTe has a direct band gap of 1.5 eV at room temperature, which is optimum for single junction solar cell efficiency [5]. Britt and Ferekides [6] have reported a CdTe/CdS solar cell with an efficiency of 16.8%. Due to its low sublimation temperature, CdTe polycrystalline films can be prepared by several techniques [7–13]. The close spaced sublimation (CSS) technique is one of the various techniques that have produced encouraging results. The CSS process offers the advantages of simple deposition apparatus and high transport efficiency conducted under low vacuum conditions at moderate temperatures, thus, simplifying scale-up for high-volume continuous processing [14]. The CSS approach can be applied to other congruently subliming chemical systems. The group I elements silver (Ag) and copper (Cu) are known as substitutional acceptors in CdTe. Doping of polycrystalline CdTe thin films is usually achieved using Cu as a *p*-dopant [15]. There have been many reports on CdTe films doped by elements, including Sb, Ag, Cd and Te etc. [16–19]. However, CdTe polycrystalline thin films doping with Cu is problematic [20]. Cu can show high solubility and diffusivity in II–VI compounds at above several hundred degrees centigrade. Cu plays dual role in devices like solar cells; it aids the formation of better ohmic contacts by increasing the *p*-doping of CdTe near/at the back-contact interface and also responsible for the degradation of solar cells [21].

In the present paper, we report physical properties of CdTe thin films deposited by CSS technique and then immersed them in Cu solution by ion exchange process. The effects of immersion time and subsequent heating in vacuum on the crystal structure, optical properties and measurements on the electrical conductivity are presented. To our knowledge this is a novel report on Cu treated CdTe thin films by CSS technique.

2. Experimental

CdTe thin films were deposited onto substrates of water-white glass by CSS technique [8]. The substrates of size 25.4 × 76.2 mm were cleaned for 40 min in extra pure isopropanol bath in ultrasonic cleaner. CdTe powder (99.99% pure 12 mg) of Aldrich chemical company (USA) was used as source material. It was placed

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doi:10.1016/j.jnoncrysol.2009.05.016

in a graphite boat of size 20 × 45 mm, heated by a 1000 W halogen lamp through a temperature controller with K-type thermocouple inserted in the graphite boat. The distance between source and substrate was fixed at about 4 mm. A separate 500 W halogen lamp was used to heat the substrate controlled by another K-type thermocouple. Source and substrate temperatures were kept 500 and 400 ± 5 °C, respectively. The chamber was evacuated down to about 10^{-3} mbar with the help of a rotary pump. The deposition time for each film was fixed at 5 min. After that the source and substrate lamps were switched off for cooling down to 50 °C before opening the chamber. These films were then annealed at 500 ± 5 °C for about 30 min at a pressure of about 10^{-3} mbar. In the next step, the films prepared at the above mentioned deposition parameters, were chemically treated by immersing in low concentrated (1 g/1L) $Cu(NO_3)_2{\cdot}H_2O$ solution for different periods of time as 0, 15 min, 1 h, 3 h and 15 h. The solution was kept at 60 ± 2 °C inside cole-parmer heating bath. The films after immersion in copper nitrate solution were cleaned in distilled water and then dried.

All the films were again annealed at 500 ± 5 °C under pressure of about 10^{-3} mbar for 30 min. Further annealing for extra 30 min was required for maximum diffusion of Cu into the films. This was deduced by comparing the optical transmission spectra. The transmission spectra before and after annealing of as deposited films along with immersed in Cu solution and post immersion annealed samples were recorded by Perkin Elmer Lambda 900 UV/VIS/NIR spectrophotometer alongwith UV WinLab software. These samples are given in Table 1. Finally, all the Cu-treated samples were cut into four pieces for taking different measurements.

The structure of the samples was studied by XRD using Cu–K_α radiation. The microstructure of the samples was observed by scanning electron microscopy (SEM). The elemental composition of Cu, Cd and Te of all the samples were measured with the help of electron microprobe analyzer (EMPA) attached to the SEM. Two pieces of each sample were used to study the electrical properties by two-probe method and Van der Pauw geometry. Thermally evaporated gold was used to ensure quasi-ohmic contact for electrical studies [22]. The dark conductivity as a function of temperature was taken to determine the activation energy of each sample. The temperature range was 40–200 °C under pressure of about 10^{-3} mbar. The film thickness and optical properties such as refractive index, absorption coefficient and optical band gap were measured from the transmission spectra between 300–2500 nm recorded by the spectrophotometer.

Due to the effect of surface roughness on the transmission T of the films, transmission formula [23], which includes the roughness, was used as:

$$T = \frac{(1-\rho)T_{123}U}{1-\rho R_{321}U^2}, \tag{1}$$

$$R_{321} = r_{321}r^*_{321}, \tag{2}$$

$$T_{123} = (n_3/n_1)t_{123}t^*_{123}, \tag{3}$$

$$\rho = [(n_1-n_3)^2 + k_3^2]/[(n_1+n_3)^2 + k_3^2], \tag{4}$$

$$U - 1 = (1-\rho)^2/2T_s + [(1-\rho)^4/4T_s^2 + \rho^2]^{1/2}, \tag{5}$$

Table 1

Cu immersion time, composition, thickness, optical constants and activation energy of as deposited and Cu immersed samples.

Samples with Cu immersion time	Composition at.%			Thickness ± 20 nm	Energy gap ± 0.01 (eV)	E_a ± 0.01 (eV)
	Te	Cd	Cu			
As deposited	52.9	47.1	0	510	1.49	0.76
15 min	52.7	46.1	1.2	480	1.48	0.72
1 h	52.5	43.8	3.7	506	1.48	0.58
3 h	52.3	42.8	4.9	530	1.47	0.56
15 h	31.9	2.1	66.0	~500	1.40	~0.0

where, r_{321} and t_{123} are the amplitudes of the electric field of the wave reflected and transmitted in 321 and 123 directions respectively. T_s is the transmittance of the substrate and for transparent substrate $U = 1$, $k_3 = 0$. The refractive indices of air, film and substrate are n_1, n_2 and n_3, respectively. However, the above formula can not be used for the films where the reduction in transmission is due to both the roughness as well as the internal absorption. In the case of Cu treated films, an approximate formula [23,24] was used.

$$T = \frac{Ax}{B - Cx\cos(\phi) + Dx^2}, \tag{6}$$

where, T is the normal transmittance for the system consisting of a thin film on a transparent substrate surrounded by air (refractive index = 1), and taking into account all multiple reflections at the interface for the case of $k^2 \ll n^2$, which is true for this kind of semiconductor thin films. The other parameters are defined as, $A = 16n^2s$, $B = (n+1)^3(n+s^2)$, $C = 2(n^2-1)(n^2-s^2)$, $D = (n-1)^3(n-s^2)$, $\phi = 4\pi nd/\lambda$, $x = \exp(-\alpha d)$, $k = \alpha\lambda/4\pi$. Here n and s are the refractive indices of the film and the substrate; d and α are thickness and absorption coefficient of the film, respectively and λ is the wavelength. Here n varies with the wavelength as,

$$n = a + \frac{b}{\lambda^2} \tag{7}$$

and polynomial approximation for α as:

$$\alpha = c + \frac{f}{\lambda} + \frac{g}{\lambda^2}, \tag{8}$$

where, a, b, c, g and f are constants obtained from the fitting of the transmission spectra. The fitting parameters c, f, g are good only for transparent region where the values of α are very small and varying slowly with wavelength. In the medium and high absorption regions, exact solution for x of Eq. (6) gives the value for α at every wavelength.

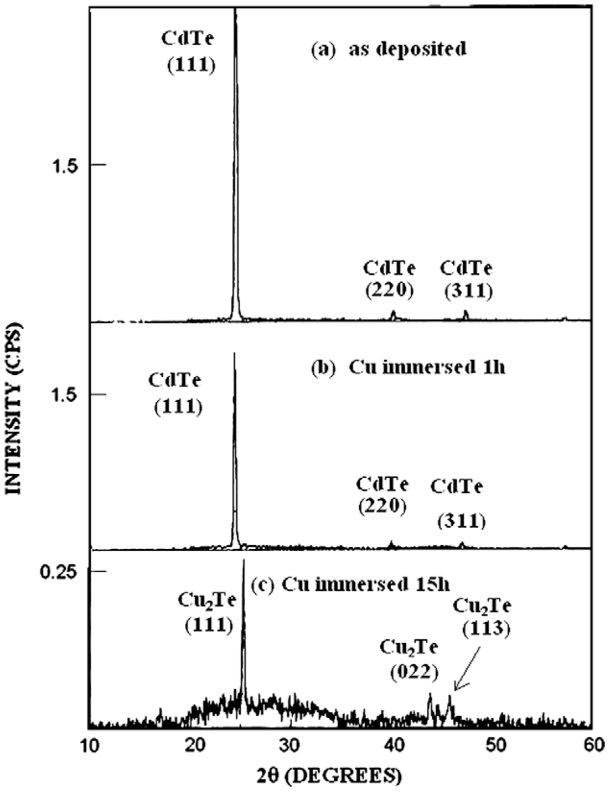

Fig. 1. Indexed XRD pattern of (a) as deposited (b, c) Cu immersed samples for 1 h, 15 h after annealing at 500 °C.