

Swift heavy ion induced modification of CdO thin film: Optical and structural studies

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Abstract— Thin films of cadmium oxide (CdO) were deposited on glass substrate using the sol-gel method by spin coating technique. These prepared films were irradiated by MeV ions of Br and Ni at same fluence 3×10^{12} ions/cm². The structural properties were studied using X-ray diffraction and it shows that the average crystallite size of CdO films is observed to decrease by the irradiation. The atomic force microscopy (AFM) study of the films shows that the roughness of the films varies with different fluence. The maximum transmittance is observed to be 90 % in the visible region for Ni ion. It is also shown that the band gap of CdO is varied using the swift heavy ion irradiation.

Index Terms— CdO thin film, Swift heavy ion, sol-gel, X-ray diffraction, UV-visible spectroscopy

1 INTRODUCTION

Cadmium oxide (CdO) is one of the transparent conducting oxides TCOs that have both, wide band gap and high electrical conductivity. These features play an important role in the high electric conductivity of transparent conducting oxides (TCOs) [1-2]. We have pointed out that these are necessary conditions in the search for new TCOs. Studies of the structural and optical properties of CdO thin films and single crystals have been reported in the literature [3]. Various techniques, including activated reactive evaporation, solution growth, spray pyrolysis, dc sputtering, MOCVD [4-6] etc., have been employed to deposit CdO thin films. To our knowledge, all of the thin films reported in the literature are either polycrystalline or amorphous. On the other hand, CdO single crystals have been grown by chemical transport reaction and vapor phase reaction [7].

Cadmium oxide is attracting tremendous attention due to its interesting properties like direct band gap of 2.3 eV and n-type semiconductor under the nonstoichiometric condition of interstitial Cd or oxygen vacancies [8]. The crystal structure is a rocksalt type, which can be regarded as the densest structure of CdO6 octahedral. Therefore, it is necessary to analyze the electronic structure of CdO in order to understand many TCOs containing Cd as a central cation. It is widely used in the application like the preparation of cadmium coated baths and manufacture of paint pigments [9-10].

Modification of properties of thin films by high energy particles (electron, proton), g-rays and swift heavy ion (SHI) irradiation has gained much attention in recent years. The irradiation of materials with energetic ions leads to the creation of a wide variety of defect state in the materials system, which changes the structural, optical and electrical transport properties of the materials. These changes are strongly dependent on mass of the incident ions, irradiation energy and fluence. The irradiation may cause ionization or excitation, and possibly displacement of atoms from their sites in the lattice of the materials.

SHI are very useful for modification of the properties of the films, foil and surface of bulk solids. Penetrates deep in to the materials and produce a long and narrow disorder zone along its trajectory. The information about this process is stored in

the resulting damage such as size, shape and structure of defects.

When a swift heavy ion (SHI) penetrates a solid, it is slowed down via two processes: (i) direct transfer of energy to target atoms through elastic collisions (Nuclear Energy Loss) range in KeV and (ii) electronic excitation and ionization of target atoms or inelastic collisions (Electronic Energy Loss) range in MeV. The latter is more dominant in the case of SHI. If the thickness of the targeted medium is sufficiently smaller than the range of the projectile ion, then the energy deposition is mainly due to electronic energy loss. This energy deposition leads to production of defects and heat in the material [11-12]. Earlier works showed the structural and micro structural phase transformation due to irradiation using high energy heavy ions in thin films Cadmium oxide (CdO) is a promising transparent conducting oxide (TCO) that exhibits metal-like charge transport behavior with an exceptionally large carrier mobility and good optical transparency in the visible region. Further, CdO films find wide applications in solar cells, photovoltaic electrodes and window deicers [13]. In this paper we report the effect of SHI irradiation with Br, Ni ions on structural and optical properties of spin-coating deposited CdO thin films.

2 EXPERIMENTAL

Detailed Cadmium oxide thin films were deposited on glass substrate by sol-gel method using spin coating technique. Cadmium acetate [Cd (CH₃COO) 2 2H₂O] (purity 99.9%) (Merck Extra pure chemical Ind. Ltd, India) was used as a precursor of cadmium. 2-methoxy ethanol and monoethanolamine [MEA] (Merck India) used as a solvent and stabilizer respectively. The Cadmium precursor solution was prepared by dissolving cadmium acetate in 2-methoxy ethanol for one molarity [14-15]. The sol was warmed at 60°C with constant stirring using a magnetic stirrer for 3 hours. The resultant sol was very clear and transparent and was kept in an air tight beaker for 72 hours before film deposition. The glass slides were used as substrates and they were first cleaned with detergent, ultrasonic bath and then with isopropyl alcohol and

acetone. The substrates were dried at 50 °C for 2 h. A few drops of the sol was spin coated on pre-cleaned glass slides at spinning speed of 3000 rpm and spinning time of 30 second in ambient condition. After deposition, the films were dried in air at 230°C for 10 min over hot plate to evaporate the solvent and remove organic residuals. The procedures from coating to drying were repeated 14 times until the desired thickness. The films were annealing in air at 400°C for one hour in microprocessor controlled furnace.

The annealed films were irradiated with 100 MeV Ni⁷⁺ and 80 MeV Br⁶⁻ ions using the 15UD Pelletron Accelerator facility at Inter University Accelerator Centre (IUAC), New Delhi. Electronic energy loss (Se) of Ni and Br ions in the ZnO is 21.67 KeV/nm, 12.65 KeV/nm and 24.63 KeV/nm, while nuclear energy loss (Sn) is 0.105, 0.049 KeV/nm and 0.044 KeV/nm as estimated from SRIM simulations [16]. The focused ion beam was scanned over an area of 1 cm² with the fluence of 3×10¹²ions/cm² and the beam current was kept constant 1 pA (particles nanoampere). The modifications of the properties are expected mainly due to the electronic excitation induced by SHI, as the range of the ions is much larger than the film thickness. Crystalline nature of the ZnO films was confirmed by PAN alytical X’pert PRO diffractometer using the CuKα radiation having a wavelength of 1.5140°A. The band gap of ZnO films were measured by optical transmittance using a Shimadzu Solid Spec 3700 double beam spectrophotometer.

3 RESULT AND DISCUSSION

3.1 X-RAY DIFFRACTION STUDIES

The structural properties modification induced by SHI irradiation can be explained by total energy deposited in electron excitation and ionization in the film by energetic ions. The impart energy of the incoming ions at higher fluence may result in overlapping of tracks in these film of cause lattice disordering inside the large grains. The structural analysis of pristine and 80 MeV Br or 100 MeV Ni ion irradiated films was carried out using GAXRD technique. The strong two diffraction (Fig. 1) peaks ((111) and (200)) with cubic structure of CdO (JCPDS card No. 79-0597) are observed in pristine and irradiated films. It indicates that most of the grains in CdO. From Fig. 1, it is observed that intensity of diffraction peaks increases for the films irradiated with the fluence of 3×10¹² ions/cm². The increase of peak intensity is due to augmentation in crystallinity of the CdO film. The structural modification induced by SHI irradiation can be explained by total energy deposited in electronic excitations or ionizations in the films by energetic ions. The imparted energy of the incoming ions in these films at higher fluence may result in overlapping of tracks to cause lattice disordering inside large grains.

The crystallite size (D) is calculated using the equation [17]

$$D = K \lambda / \beta \cos \theta \quad (1)$$

Where, K is polarization factor, λ is wavelength of CuKα line (1.5406°A) and β is the full width half maximum (FWHM) and θ is the Bragg diffraction angle. The crystallite size of CdO is

observed 10.5 ±0.6 and 6.89± 1.0 nm for pristine and irradiated films. The crystallite size is decreased from 10.5±0.6 to 4.69±1.0 nm. When the film was irradiated with the fluence of 3×10¹²

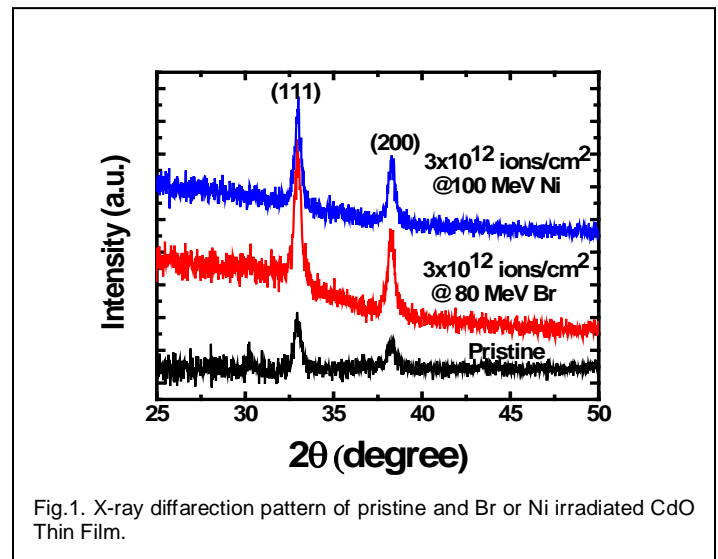


Fig.1. X-ray diffraction pattern of pristine and Br or Ni irradiated CdO Thin Film.

ions/cm².

The value of crystallite size for different fluence is shown in

TABLE 1

Ion fluence (ions/cm ²)	(111)				(200)				Band gap (eV)
	2θ	FWHM	a	D	2θ	FWHM	a	D	
CdO Pristine	32.93	0.7800	4.70	11.3	38.22	0.8000	4.70	10.5	2.68±0.01
3×10 ¹² @ 80 MeV Br	32.97	1.1800	4.69	7.2	38.26	1.1200	4.69	7.1	2.50±0.01
3×10 ¹² @100 MeV Ni	32.98	1.1800	4.69	7.2	38.27	1.2200	4.69	6.8	2.43±0.01

table.

Table -1 The 2 θ (degree), the FWHM (degree), the lattice constant a (Å) and the average crystallite size D (nm) of CdO thin

TABLE 2

Properties	CdO	
	Bulk	Thin film
Lattice Parameter 'a'	4.6958 Å	4.7068 Å
Band gap	2.34 eV	2.68 eV
Transmittance	84 %	90 %

films Br and Ni ions irradiated at same fluence.

Table -2 Comparisons of the bulk and thin film CdO.

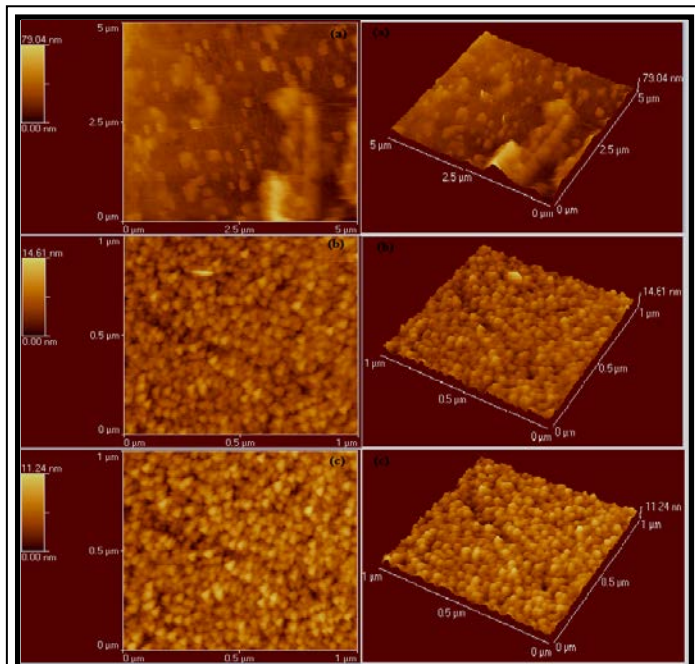


Fig.2. Atomic force microscopy micrographs of (a) As-deposited, (b) Br irradiated (c) Ni irradiated CdO films

3.2 SURFACE MORPHOLOGY

The surface topography of the pristine and irradiated CdO films was studied using Atomic Force Microscopy (AFM) in the tapping mode. Fig. 2 shows the two and three dimensional micrograph in $1 \times 1 \mu\text{m}^2$ of CdO films. The root mean square (rms) roughness of CdO films was decreased from 14.97 to 9.22 nm after irradiation. The grain size of CdO film is decreased from 67 to 29 nm after irradiation. The energetic heavy ions provide sufficient energy for promoting the sputtering from the surface of the grains that leads to reduction in the grain size of CdO films. Such drastic change in the size and shape of the grains at higher fluence is attributed to the high density of electronic excitations induced by SHI irradiation under multiple ion impacts in the near surface region [18]. Kumaravel et.al [19] has also reported increased in grain size with increase in roughness of films due to the increase of density and size of metal particles on the surfaces of the films.

3.3 OPTICAL PROPERTIES

The UV-visible absorption spectra of CdO thin film with 3×10^{12} fluence are shown in Fig. 3 although the wavelength of our spectrometer is limited by the light source, the absorption band of the CdO thin film have been shows a blue shift due to the quantum confinement of the excitons present in the sample compare with bulk CdO quantum dots. This optical phenomenon indicates that these thin films show the quantum size effect [20].

Transmittance measurements were carried out in 300-1000 nm

range of spectrum (fig. 4). Figure 4 shows the transmittance curves of CdO film with 3×10^{12} fluence. The samples showed high and constant transparency higher than 87% in the visible range. Maximum transmittance was found to be 90% for Ni ions as shown in Fig. 4. Increase in transmittance from 87–90% has been observed with ion irradiation. Increase in transmittance can be explained with the help of relation

$$I = I_0 e^{-\alpha d} \quad (2)$$

Where, α is the absorption coefficient and d is the film thickness. Optical absorption coefficient (α) is calculated using [21]

$$\alpha = 1/d \ln (1/T) \quad (3)$$

Where, T is the transmittance of the film and d is the thickness of film.

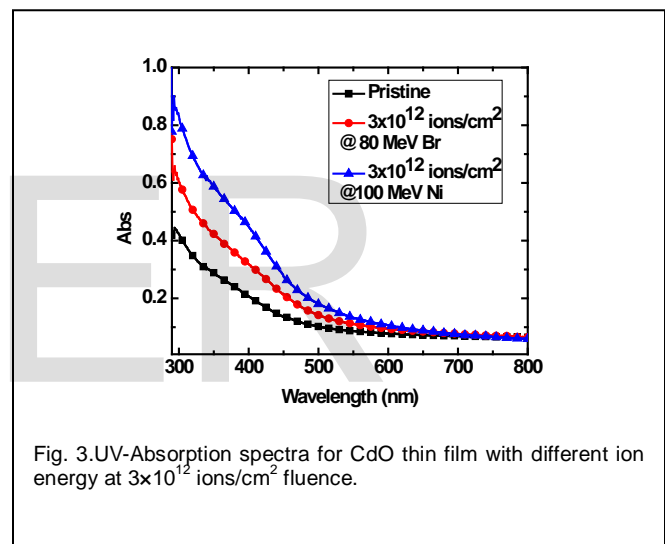


Fig. 3. UV-Absorption spectra for CdO thin film with different ion energy at 3×10^{12} ions/cm² fluence.

It is evident from the figure that absorption increases with Ni ion fluence. This may be due to the irradiation induced defect creation like antisite oxygen and oxygen vacancies in the film.

The optical absorption edge was analyzed by the following relationship [22],

$$\alpha h\nu = A(h\nu - E_g)^{1/2}$$

Where A is a constant, $h\nu$ is the photon energy and E_g is the optical band gap. Shows the plots of $[(\alpha h\nu)^2$ versus $h\nu$]. Theoretical band gap values were calculated from this plot and were found to be about 2.68 ± 0.01 eV, 2.50 ± 0.01 eV and 2.43 ± 0.01 eV for as pristine and Br, Ni irradiated at 3×10^{12} fluence. The optical band gaps of the film decreased with the ions fluence. This result can be attributed to the thermally induced defects which increase dramatically. The values of the band gaps are in agreement with the values reported in the literature for CdO.

The decrease in the band gap energy due to the high energy irradiation induced lattice damage which creates defect energy

levels below the conduction band and hence the band gap is decreases (Soundeswarn et al., 2005). And also lattice damage is proportional to irradiation fluence and hence due to band tailing effects band gap decreases with ion fluence. The Ni irradiation induces band tailing effects, which gravely affect properties of most of the optoelectronic devices.

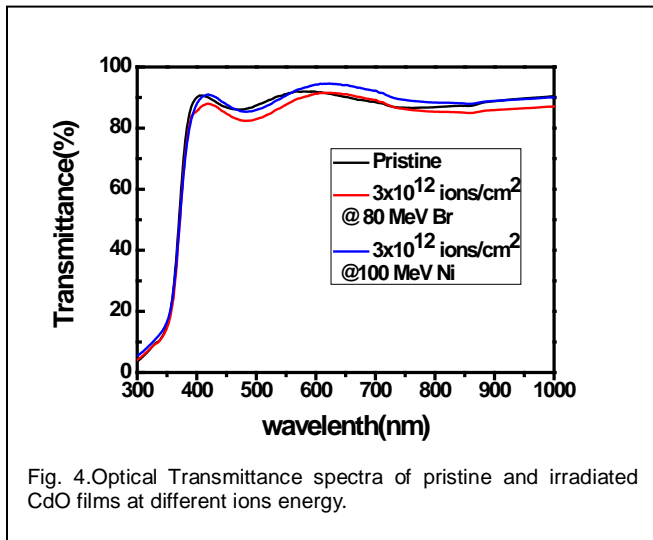


Fig. 4. Optical Transmittance spectra of pristine and irradiated CdO films at different ions energy.

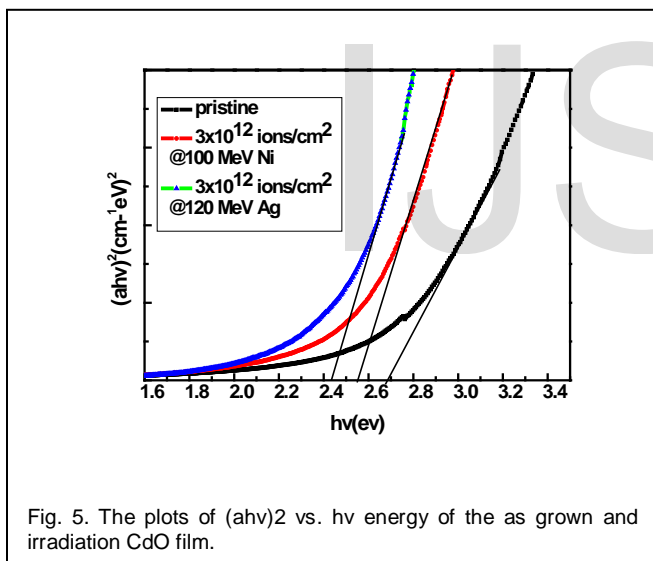


Fig. 5. The plots of $(ahv)^2$ vs. hv energy of the as grown and irradiation CdO film.

We calculated the ion range, S_e and S_n of the Br and Ni ions in CdO matrix using the Stopping and Range of Ions in Matter (SRIM) and Transport of Ions in Matter (TRIM) software. The S_e and S_n energy loss of Br and Ni ion beam in CdO is presented in Figure 6(a). In the Fig. 6(a), we have plotted Incident Ion Energy versus stopping Power of the Br and Ni ions in CdO. In the Fig. 6(b), we have plotted depth versus S_n and S_e of the Ni ions in CdO. It is clear from the Fig.6 that ions lose most of their energy by the electronic energy loss process and the nuclear energy loss process dominant in the low energy regime. The range of 80 MeV Br and 100 MeV Ni ions in CdO target is about to 12 μm , thus all the ions are expected to pass through the film thickness (~ 300 nm) deep into the substrate. Therefore, the observed irradiation effects are to be analyzed as consequences of ion irradiation induced electronic energy

transfer and not due to the implantation of ions in the film material. In the present case, the Sn and Se of 80 MeV Br and

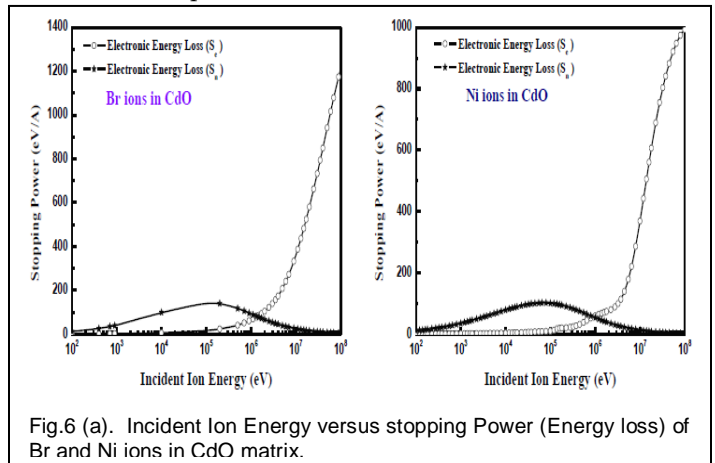


Fig.6 (a). Incident Ion Energy versus stopping Power (Energy loss) of Br and Ni ions in CdO matrix.

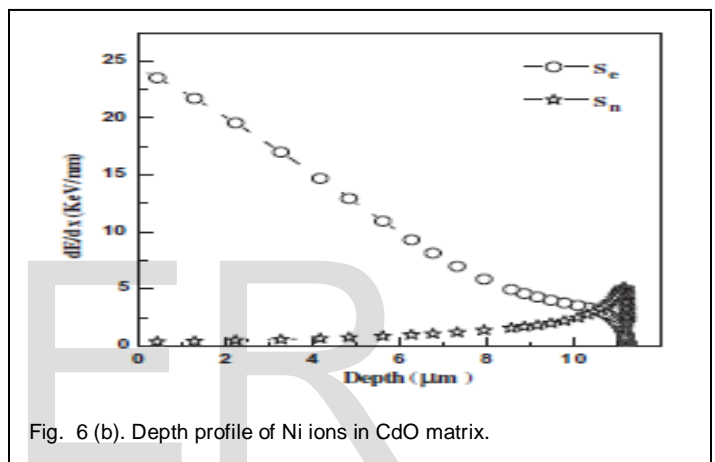


Fig. 6 (b). Depth profile of Ni ions in CdO matrix.

100 MeV Ni ions in CdO are ~ 0.37 keV/nm and ~ 27.6 keV/nm, respectively (calculated by SRIM).

It is known that, to displace Cd and O atoms from their proper lattice sites or to produce Schottky and/or Frenkel pairs in the CdO lattice ~ 0.017 keV energy is required [23]. Therefore, the energy deposited by elastic process ($S_n = 0.37$ keV/nm), is sufficient to displace Cd and O pairs in Cadmium oxide lattice. A theoretical model was proposed, by Szenes, to find out the S_e and the radius of the latent track or molten zone due to SHI irradiation of oxide materials.

We have used the following equations to calculate the S_e and track radius for the Cadmium oxide, irradiated by 80 MeV Br and 100 MeV Ni beam. We conclude that the irradiation of CdO, by the 80 MeV Br⁶⁺ and 100 MeV Ni⁷⁺ ions, can create extensive disorder along the ion path and hence should suppress the crystalline volume fraction with increasing irradiation fluence.

CONCLUSION

We have investigated modifications of structural and optical properties of highly c-axis oriented CdO thin films were deposited by sol-gel spin coating technique with 80 MeV Br and 100 MeV Ni ions irradiation. We have observed the modifications of the intensity of XRD, surface morphology and

Bandgap by ion irradiation. XRD result reveals that at crystalline size are decreases with irradiation ions fluence. The transparency of CdO is change after irradiation and the systematic reduction in the optical band gap is observed with Ni ion fluence, which is associated with Ni ion induced defects leading to the production of localized states near the band edges and in the energy gap of CdO. The observed modification in structural and optical properties was understood in the term of thermal spike model.

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