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Intentionally incorporated defect and its consequences in oxide thin film through Radio Frequency Magnetron Sputtering Technique

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Abstract : Radio Frequency Magnetron Sputtering Technique has been employed to prepare metal oxide thin film of ZnO and CdO. The films were deposited in such condition that some point defects like oxygen vacancies have been intentionally incorporated. The defects appeared with significant modification in the properties of the thin films. The prepared films were characterized by studying with X-ray diffraction study, X-ray photo-electron spectroscopic measurement, optical transmittance measurement, and electrical study. The electrical properties are found to change profoundly with the defect concentration. Consequently the optical properties also have been changed.

Keywords: RF sputtering; thin film; point defect.

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1. Introduction

Theoretical and experimental investigations as well as fundamental research in Physics with defects in nano-scale materials are interesting field to the researchers. Defect plays a significant role in Nano Science and Technology particularly when it is controllable. Defect appears with some excellent quantum mechanical phenomena in Nano scale as well as in control of different properties of Nano materials. In the past decade, photonic crystals have attracted a lot of attention in theory and potential applications. Recently, there has been much interest in the propagation of elastic or acoustic waves in phononic crystals (PCs). The existence of a complete phononic bandgap (PBG) has been confirmed

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theoretically and experimentally. Zhao *et al* [1] had studied the effect of point defects and characteristics of multi-point defect modes in phononic crystals. Kuleyev *et al* [2] had reported the quasi-transverse ultrasound absorption in cubic crystals due to point defects.

Radio Frequency Magnetron Sputtering is a very useful technique [3] to introduce defect and its control in thin film. Point defects like Frenkel defects and Schottky defects can easily be incorporated in metal oxide thin film. Particularly in metal oxide thin films defects may be incorporated by introducing oxygen vacancy or excess oxygen. This type of defect is more effective than doping with external foreign elements. In this article we have reported the effect of point defects in the form of oxygen vacancies in ZnO and CdO thin film. These point defects were introduced intentionally in the films during their preparation by Radio Frequency Magnetron sputtering technique. Such defects can produce excess charge carriers in the films thereby significantly improving the electrical properties of the film along with remarkable modification in their optical properties. More importantly these films could be used for excellent hetero junction formation and can be used for device fabrication like solar cell, development of nano electronics, and optoelectronic devices, also as excellent field emission material for preparing flat panel displays.

2. Experimental

2.1. Target preparation and film deposition :

The films of ZnO and CdO have been prepared through Radio Frequency magnetron sputtering Technique. The Target materials for sputtering have been made by using pure ZnO and CdO powder. Glass substrates were cleaned at first by mild soap solution then washed thoroughly in deionized water and also in boiling water. The silicon substrates were immersed in 20% HF solution for five minutes in order to remove the surface oxide layers. Finally, these were washed in deionized water and cleaned by alcohol in an ultrasonic cleaner. The RF sputtering unit was evacuated to 10^{-6} mbar by a rotary pump and a diffusion pump. The films of CdO and ZnO were deposited with RF forward power of 120W and 200V self bias D.C. voltage in pressure of 0.1 mbar. The oxygen vacancies were introduced by controlling the oxygen to argon partial gas pressure during film deposition.

2.2 Characterization :

Structural characterization was done by X-ray diffraction (XRD, Bruker, D-8 Advance) studies using the CuK$_\alpha$ radiation (λ = 1.5406 A^0). The surface morphology of the films was studied by an atomic force microscope (AFM, NT-MDT, Solver Pro) in contact mode. The bonding configuration and the compositional analysis of the films were carried out by x-ray photoelectron spectroscopy (XPS). UV-Vis-NIR spectrophotometric measurements were performed by using a spectrophotometer (Shimadzu UV-3101PC) in the wavelength region of λ = 300 nm to 800 nm at room temperature.

3. Result and discussions

3.1. Structural and Morphological Characterizations :

The structural analyses of the thin film of ZnO and CdO show that the crystallinity has been decreased with the increasing number of defect locations. The X- ray diffraction pattern of different defect incorporated CdO thin films have been shown in Figure 1. The XRD pattern reveals that the films are polycrystalline in nature. Different peaks in the XRD pattern appeared at 2θ values 33.09^0, 38.54^0, and 55.28^0 and were assigned to the reflections from (111), (200), (220) planes of FCC CdO [4]. The relatively stronger intensity of the peak at $2\theta = 33.09^0$ indicates a preferential (111) orientation of the films. Similar property was observed for ZnO thin film. The characteristic peaks in the XRD pattern appeared at 2θ values 32.0^0, 34.0^0, and 36.0^0 and were assigned to the reflections from (101), (002), and (100) planes of hexagonal ZnO.

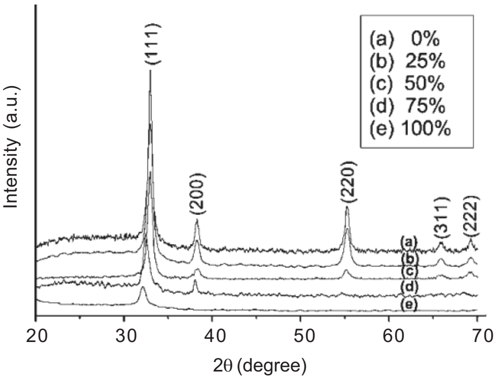

Figure 1. X-ray diffraction pattern of CdO thin film with different oxygen partial pressure.

A typical AFM image of ZnO thin film is shown in Figure 2. AFM study shows that all the films have a uniform surface morphology over the whole film.

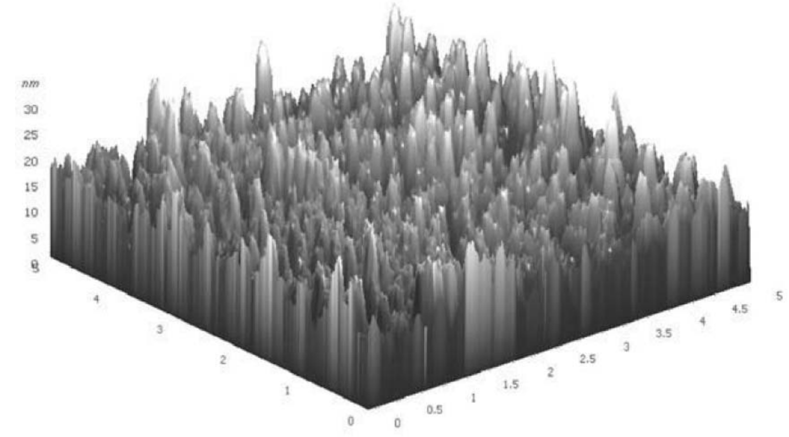

Figure 2. AFM image of ZnO Thin film.

3.2. *Compositional Analysis* :

Compositional information of the films was obtained by studying the XPS spectrum (Figure 3), which shows that the film deposited with higher oxygen partial pressure has lower oxygen vacancy. The binding energies corresponding to the peaks Cd $3D_{3/2,}$ O 1S, and Cd 3S as obtained from XPS analysis are 411 eV, 532 eV, and 770 eV, respectively. The C $1S_{1/2}$ peak at 284.46 eV appeared due to some surface contamination. For ZnO thin film the binding energies corresponding to the peaks Zn $2P_{3/2,}$ O 1S as obtained from XPS analysis are 1021.38 eV, 532 eV respectively.

3.3. Electrical Characterizations :

All the films showed good electrical conductivity particularly the CdO thin films with oxygen vacancy are of very high electrical conductivity. The electrical conductivity increases due to point defects arisen from oxygen deficiency related centers. Oxygen vacancy produces excess charge carriers in the film which contributes to the increase in electrical conductivity of the film. The metal interstitials and oxygen deficiencies in the lattice lead to crystal defect, and the defect chemistry plays an important role for the increase in n-type conductivity of the CdO thin film. The approximate defect reaction for the CdO thin films may be represented by the following equation:

$$Cd = Cd^{N} + V_{O}^{++} + 2e^{-} \tag{1}$$

where Cd^N, V_O, and e denote lattice cadmium, oxygen vacancy and electron, respectively. Superscripts N, '+' and '_' denote effective neutral, positive and negative charge states, respectively. Similarly in case of ZnO also these defects produces excess charge carriers and enhances the electrical conductivity but with very large number of oxygen vacancies the crystallinity decreases as a result the mobility decreases thus the effective electrical conductivity decreases again. The electrical conductivities are illustrated in Figure 4.

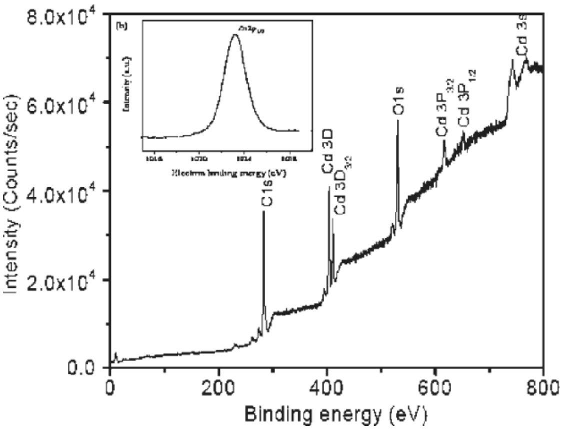

Figure 3. XPS spectra of CdO thin film and core level spectra of Zn $2P_{3/2}$ in ZnO thin film (inset).

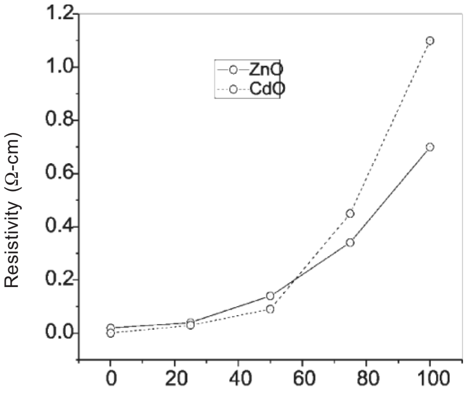

Figure 4. Electrical resistivity plot of ZnO and CdO thin film with oxygen partial pressure.

3.4. Optical characterizations :

Optical properties were studied from the transmittance spectra and found to have transmittance of more than 75% in the visible range for all the films of CdO and ZnO. The optical band gap also was found to respond profoundly with the defect concentrations. As the number of oxygen vacancy increases the number of charge carrier increases as a result the optical band gap increases due to Burstein- Moss effect [5,6]. Assuming that the Fermi surface is spherical, the following well-known equation is derived for the Burstein–Moss effect.

$$E_g = E_g^0 + \Delta E_g^{BM} \tag{2}$$

where the BM shift is given by

$$\Delta E_g^{BM} = \frac{\hbar^2}{2m_{vc}^*}(3\pi^2 n_e)^{2/3} \tag{3}$$

where E_g^0, m_v^*, m_c^*, m_{vc}^*, n_e are the intrinsic band gap of an undoped semiconductor, the valence-band effective mass, the conduction-band effective mass, the reduced effective mass and carrier concentration, respectively.

4. Conclusions

Incorporation of point defects in the form of oxygen vacancy or metal interstitials have been successfully done through RF sputtering. These defects may play a significant role to make the metal oxide thin films more functional. Their electrical optical properties were found to improve and can be controlled.

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