# Deposition of Some Transparent Conducting Oxide Thin Films by a Simple Spray Pyrolysis Technique and Their Characterizations for Optoelectronic Applications

J. Podder and T. Hossain

***Abstract:*** In this study, spray pyrolysis method has been employed for the deposition of some transparent oxide thin films like ZnO, CdO and $SnO_2$ onto glass substrate under atmospheric pressure using zinc acetate, cadmium acetate and tin chloride precursors at relatively low temperature around 200~350°C. Films of various thicknesses have been obtained by varying the deposition time and concentrations, while all other deposition parameters such as spray rate, carrier gas pressure and distance between spray nozzle to substrate were kept constant. Surface morphology, structural and optical properties of the as-deposited thin films has been studied by Scanning Electron Microscopy (SEM) attached with an EDX, XRD and UV visible spectroscopy.The elemental composition of the samples studied by EDX reveals that the as-deposited films are homogeneous and stoichiometric. The SEM micrograph shows uniform deposition and scattered nano fiber around the nucleation centers of the ZnO film and small crystallites and agglomeration of the grain particles for pure cadmium oxide and tin oxide samples. The optical band gaps of the ZnO, CdO and $SnO_2$ thin films were found to be around 3.4 eV, 2.53 eV and 3.75 eV respectively. The obtained experimental results also discuss the suitability of these films as transparent and conducting window materials in optoelectronics applications.

***Keywords:*** Transparent conducting oxide films, Spray pyrolysis, XRD, EDX, SEM and UV-visible spectroscopy, bang gap.

## I. INTRODUCTION

In recent years transparent conducting oxide thin films is given much attention to the researchers due to their wide range of applications in solid state devices such as solar cells, flat panel displays, gas sensors and electro-chromic devices. ZnO, CdO and $SnO_2$ have transparency in the visible region of the electromagnetic spectrum and show n-type conductivity. Due to its high exciton binding energy (60 meV) and its wide band gap (3.3eV), ZnO is currently considered as one of the most promising materials for use in optoelectronic devices operating at blue and ultraviolet wavelengths [1]. On the other hand CdO has a direct band gap of 2.5 eV. Much more attention has been paid to the study of the electrical and optical properties of CdO thin films [2-6]. $SnO_2$ thin films are of great interest due to its unique attractive properties like high optical transmittance, uniformity, non-toxicity, good electrical, low resistivity, chemical inertness, stability to heat treatment, mechanical hardness, piezoelectric behavior and its low cost [7-9]. Different types of methods have been reported for the preparation of these films such as electrodeposition, molecular beam epitaxy, sol-

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gel process and spray pyrolysis [10-14]. Among the various methods spray pyrolysis deposition (SPD) technique provides a simple root of synthesizing thin films because of its simplicity, low cost experimental setup. In addition, this technique could be used for the production of large-area thin film deposition without any high vacuum system. In considering the importance of these materials in the field of optoelectronic devices, particularly for solar cells, we have synthesized both undoped ZnO, CdO with various molar concentrations and Cu doped $SnO_2$ films using a simple and locally fabricated spray pyrolysis system relatively at low temperature and report the results of surface morphology, structural and optical properties of as-deposited thin films.

## II. EXPERIMENTAL

In the present work, thin films have been deposited on glass substrate by a home-made spray pyrolysis unit. We prepare 0.1 M aqueous solution of zinc acetate/cadmium acetate/tin chloride as the precursor of the film. The pH of the solution was measured to be around 6.0. The solution was sprayed on pre-cleaned commercial glass substrate. Glass substrates were ultrasonically cleaned by deionized water, acetone and methanol before the experiment. The substrate temperature was maintained within 200~350±5°C during the deposition. The normalized distance between the spray nozzle and substrate was fixed at 25 cm. The pressure of the carrier air gas was kept constant at 1 bar. The spray rate of solution was maintained at 0.2 ml $min^{-1}$ throughout the experiment. The solution was sprayed onto the substrate with a constant deposition time of 10 minutes.

The possible chemical reaction that takes place on the heated substrate to produce ZnO, CdO and $SnO_2$ thin film may be as follows: when the droplets of the solution reach the heated substrate, chemical reaction of the zinc acetate water solution takes place under stimulated temperature and provides the formation of film. The expected chemical reactions are given below:

$$\text{(a)}\ Zn(CH_3COO)_2.2H_2O \xrightarrow[\text{deposited to}]{200^\circ C} ZnO + CO_2 + CH_4 + Steam$$

$$\text{(b)}\quad Cd\,(COOCH_3)_2.2H_2O \xrightarrow{350^o C} CdO + CO_2 + CH_4 + steam$$

$$\text{(c)}\quad SnCl_2.2H_2O \rightarrow SnO_2\downarrow + H_2O\ \text{(steam)} + 2HCl$$

$$SnCl_2.2H_2O + Cu\,(NO_3)_2.3H_2O \rightarrow SnO_2{:}\,Cu \downarrow + xN_yO_z + wO_2 + HCl + H_2O\ \text{(steam)}$$

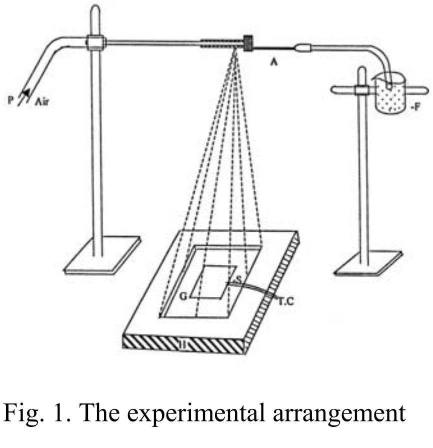
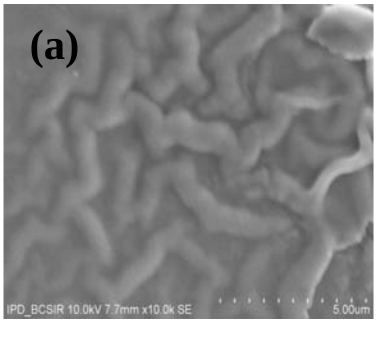


Fig. 1. The experimental arrangement



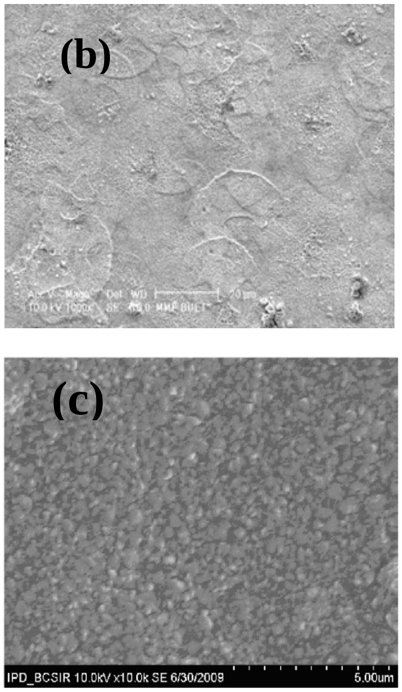


Fig.2. SEM micrograph of (a) ZnO, (b) CdO, (c) $SnO_2$ thin film.

## CHARACTERIZATION

A HITACHI S-3400N model Scanning Electron Microscope (SEM) attached with an EDX was used to observe the surface properties and to study the sample stoichiometry of the films. The optical transmission spectra for as-deposited thin films were obtained in the visible region (300-1100nm) using UV-VIS spectrophotometer (Model: UV-1201V, Shimazdu). The observed transmittance data were corrected relative to optically identical uncoated glass substrate. The thickness of the films was determined by using data pack in a UV-1201V spectrophotometer. A Philips PW3040 X'Pert PRO X-ray diffractometer was used to characterize the materials and to determine the lattice parameters. The monochromatic (using Ni filter) CuKα radiation was used whose primary beam power was 40 kV and 30 mA. All the data of the samples were analyzed by using computer software "X'PERT HIGHSCORE" from which structural parameters was determined.

## III. RESULTS AND DISCUSSIONS

### *Surface Morphology*

Surface morphological characterization of the ZnO, CdO and $SnO_2$ films was performed by SEM. Fig. 2 shows SEM images for all the films. As seen in Fig. 2 (a), nano fiber structure appears on the surface of the pure ZnO film. The SEM micrograph of CdO show that a polycrystalline structure with a well defined circular grain and grain boundaries (2b) and small crystallites and agglomeration of the grain particles for pure tin oxide samples (2c).

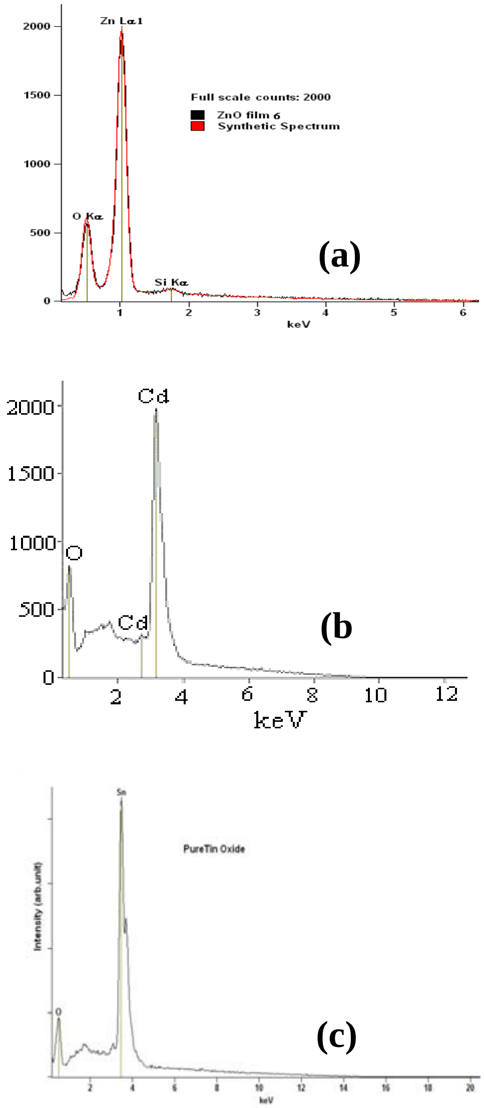


Fig.3 EDX micrograph of ZnO, (b) CdO, (c) $SnO_2$ thin film.

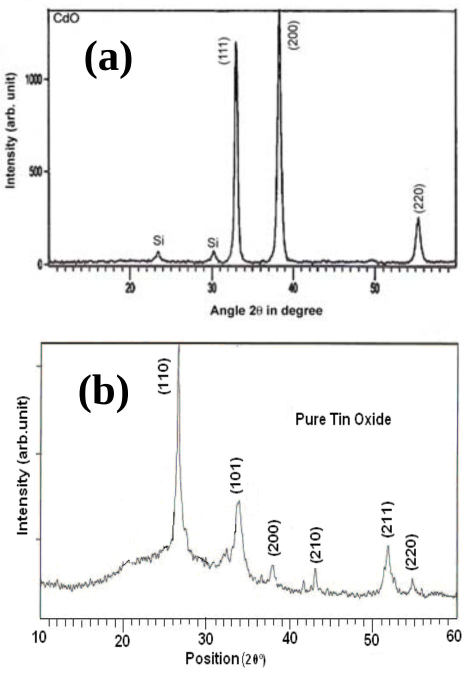


Fig.4. (a) X-ray diffraction patterns of CdO thin film, (b) for $SnO_2$ thin film

The quantitative analysis of the as-deposited ZnO, CdO ande $SnO_2$ films was carried out by EDX and the spectrums are shown in Fig. 3. The strong peaks corresponding to Zn, Cd, The strong peaks corresponding to Zn, Cd, Sn and O were found in the Sn and O were found in the spectrum and confirm the high purity of the thin film.

X-ray diffraction has been taken on as-deposited CdO and $SnO_2$ thin film and the spectrum obtained is shown in Fig.4. Spectrum shows well defined peaks, which indicates that the films are polycrystalline consisting of single phase CdO. The structure was found to be cubic and the value of a is 4.65Å. Strong characteristic peaks at $2\theta = 32.90°$, $38.24^0$ corresponding to (111) and (200) respectively along with weaker reflection at $2\theta = 55.24^0$ were observed in the spectrum and this is also in good agreement with the reported value. The X-ray diffractogram of as deposited $SnO_2$ sample is shown in Fig. 4 (b). Using the $d_{hkl}$ (interplanar distance) values, their corresponding <hkl> values have been identified as (110), (101), (200), (210), (211), and (220) for pure $SnO_2$ films which indicate the tetragonal structure of $SnO_2$. The value of lattice constants a=b=4.7522 and c=3.1804.

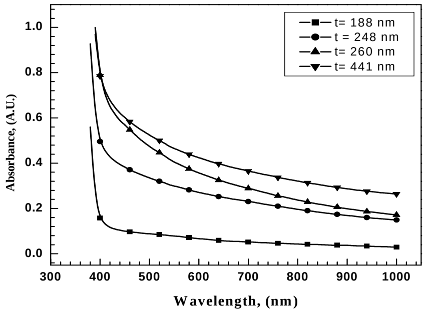


Fig. 5 Variation of absorbance as a function of wavelength for different thicknesses of ZnO films

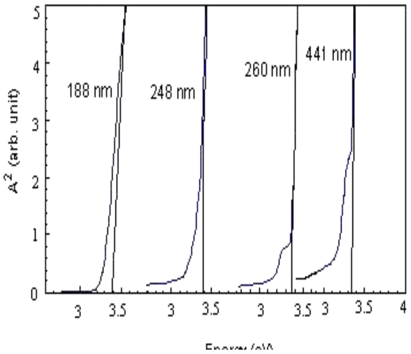


Fig. 6 Plots of $A^2$ vs photon energy (hν) for ZnO thin film.

OPTICAL PROPERTIES

The absorbance spectra of the films were measured to investigate their optical properties. These spectra reveal that films grown under the same parametric conditions have low absorbance in the visible /near infrared region from ~ 450 nm to 1000 nm. However, absorbance is high in the ultraviolet region. Figure shows that absorption increases with the thickness of the film. Plots of $A^2$ versus the photon energy (hν) are shown in Figure 6 in order to achieve the band gap for ZnO films. The band gap of the films varied between 3.31 eV to 3.40 eV and the band gap also decreases with the increase of the film thickness from 180 nm to 441 nm. The decrease of band gap with the increase of film thickness implies that ZnO is an n-type semiconductor. This decrease of band gap may be attributed to the presence of unstructured defects, which increase the density of localized states in the band gap and consequently decrease the energy gap.

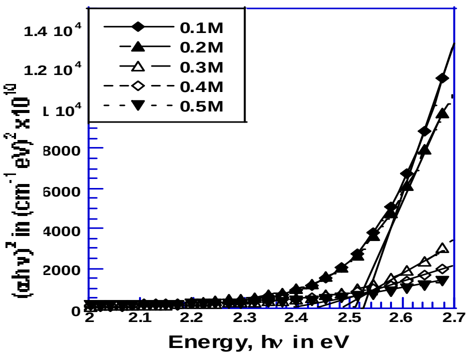


Fig. 7 Variation of $(\alpha h\nu)^2$ with photon energy for CdO films of different molarity.

Plots of $(\alpha h\nu)^2$ versus hν are shown in Fig. 7. The direct band gap energy of CdO has been obtained from the intercept of the straight line drawn from $(\alpha h\nu)^2$ versus hν curve on the energy axis which indicates that the direct band gap decreases with increase of molar concentration of the precursor material. From figure it is seen that the energy gap decrease slightly with increase of molar concentration. The direct optical band gap *Eg* was determined by fitting the transmittance data to the equation, $\alpha h\nu = B(h\nu - Eg)^{1/2}$. The optical band gap is 3.75 eV for pure tin oxide films. The lowest optical band gap was found to be 3.5 eV for 4 wt. % Cu doping. Again the band gap increases with the increase of Cu concentration. The variations of band gap for as-deposited $SnO_2$ thin films with Cu doping are shown in Fig. 8.

## IV. CONCLUSIONS

From the above studies it is shown that spray pyrolysis is a useful technique for the preparation of ZnO, CdO and $SnO_2$ thin films with good stoichiometric ratio. SEM micrograph shows uniform and nano fiber structures around the nucleation center for ZnO films and exhibit clear grains and grain boundary formation for CdO and $SnO_2$ films. The energy band gaps of the as deposited thin films are found in good agreement with the reported values. The X-ray diffraction patterns indicate that the films are polycrystalline in nature. The optical results show the suitability of these thin films as optical window material for photovoltaic applications. In conclusion, we can state that the spray pyrolysis could be a good and convenient method for the preparation of suitable thin films for scientific studies and technological applications.

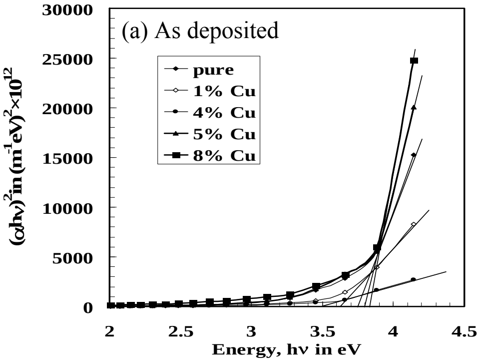


Fig. 8 Optical band gap for as deposited films

## ACKNOWLEDGEMENT

The authors are thankful to M. R. Islam, Lecturer, Dept. of Physics, BUET, M .M. Islam, S.O. AEC, Dhaka and S. S. Roy, Lecturer, Dwarika Paul Mohila Degree College, Sreemongal for their generous help to this work.

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