Characteristics of electron beam evaporated nanocrystalline SnO$_2$ thin films annealed in air

Abdul Faheem Khan$^a$, Mazhar Mehmood$^{a,*}$, Muhammad Aslam$^a$, Muhammad Ashraf$^b$

$^a$ National Centre for Nanotechnology & Department of Chemical and Materials Engineering, Pakistan Institute of Engineering and Applied Sciences (PIEAS), Islamabad 45650, Pakistan
$^b$ Optics Lab. Nilore, Islamabad, Pakistan

**A R T I C L E   I N F O**

Article history:
Received 29 September 2009
Received in revised form 14 October 2009
Accepted 16 October 2009
Available online 24 October 2009

Keywords:
Nanocrystalline SnO$_2$ thin films
Quantum confinement
Raman spectroscopy
Band gap energy
FTIR spectroscopy
Electrical resistivity

**A B S T R A C T**

Tin oxide (SnO$_2$) thin films (about 200 nm thick) have been deposited by electron beam evaporation followed by annealing in air at 350–550 °C for two hours. Optical, electrical and structural properties were studied as a function of annealing temperature. The as-deposited film is amorphous, while all other annealed films are crystalline (having tetragonal structure). XRD suggest that the films are composed of nanoparticles of 5–10 nm. Raman analysis and optical measurements suggest quantum confinement effects that are enhanced with annealing temperature. For instance, Raman peaks of the as-deposited nanoparticles of 5–10 nm. Raman analysis and optical measurements suggest quantum confinement effects are enhanced with annealing temperature. Two orders of magnitude decrease in resistivity is observed after annealing at 350–400 °C due to structural ordering and crystallization. The resistivity, however, increases slightly with annealing temperature above 400 °C, possibly due to improvement in stoichiometry and associated decrease in charge carrier density.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Nanostructured semiconducting oxides have attracted considerable interest due to their unique physical properties caused by quantum confinement effects. Among such semiconductors, tin oxide (SnO$_2$) seems to be a good candidate for the solar cell applications (e.g., as a window material) because of its wide band gap (3.6 eV) at room temperature [1–5]. It has also been employed in a wide range of applications including solid state gas sensors, liquid crystal displays, transparent conducting electrodes, infrared reflectors, plasma display panels (PDPs), transistors, etc. [6–10]. In addition, SnO$_2$ is useful as a hard film material for applications requiring high refractive and reflective properties. SnO$_2$ thin films have been prepared by various techniques such as RF-magnetron sputtering [1,11,12], electron beam evaporation [13], sol–gel coating [14], chemical vapor deposition [15], etc. Various characteristics of these SnO$_2$ films have been observed to change by altering the preparation technique and environment. For example, electrical properties of such films depend upon oxygen vacancies, adsorbed gases [16], film thickness, microstructure, deposition conditions such as substrate temperature, rate and temperature of deposition [17], etc. Earlier studies on rfsputtered SnO$_2$ films by Khan et al. [1] have shown very small variations in band gap energy and multiphase structure (SnO$_2 +$ SnO) with annealing temperature up to 500 °C. In addition, RMS roughness and electrical resistivity have demonstrated opposite trend with annealing [2]. In this paper structural, optical and electrical properties of electron beam evaporated nanocrystalline SnO$_2$ thin films have been investigated in pre- and post-thermal annealed (in air over the temperature range of 350–550 °C) conditions using X-ray diffraction (XRD), Raman spectroscopy, Fourier transform infra-red spectroscopy (FTIR), transmission spectroscopy, impedance spectroscopy (IS), and atomic force microscopy (AFM).

2. Experimental

SnO$_2$ thin films were deposited using electron beam evaporation of SnO$_2$ powder (99.9%) as a starting material onto BK7 glass substrates using tungsten crucible. The system was pumped to a base pressure of less than $10^{-5}$ mbar before deposition and O$_2$ was injected into the chamber during evaporation at a partial pressure below $2 \times 10^{-5}$ mbar. The substrate was set at a temperature of 300 °C and at a distance of 35 cm from the source and rotated at 30 RPM during deposition to obtain uniform and homogeneous films. The deposition parameters were optimized to reduce the film roughness. Thickness of film and rate of its deposition were
controlled with the help of an in situ quartz crystal thickness monitor. Intended thickness of the film was about 200 nm and the deposition rate was set as 0.45 nm s\(^{-1}\). However, the thickness estimated by ellipsometry and transmittance data is found to be 240 ± 10 and 280 ± 10 nm, respectively. We consider that the thickness of 240 nm, as determined by ellipsometry, may be more reliable.

These films were then annealed in air at various temperatures ranging from 350 to 550 °C with a step of 50 °C for a fixed time of 2 h. Structure of these films was determined by recording X-ray diffraction patterns at room temperature using Bruker D8 Discover diffractometer equipped with Cu K\(_\alpha\) radiations. The Raman spectra were obtained at room temperature using confocal mode of Micro-

Fig. 1. X-ray diffraction patterns of SnO\(_2\) thin films, as-deposited (a) and annealed for 2 h at 350 °C (b), 400 °C (c), 450 °C (d), 500 °C (e), 550 °C (f).

Fig. 2. Plots of volume of the unit cell (curve 1) and particle size (curve 2) as a function of annealing temperature (\(T_A\)) for SnO\(_2\) thin films.

Fig. 3. AFM image (100 nm × 100 nm) showing the surface morphology of SnO\(_2\) thin films, as-deposited (a) and annealed at 350 °C for 2 h (b).
Raman-Spectrometer (MST-1000A, DongWoo Optron Co. LTD., South Korea) under excitation with HeCd laser beam at 442 nm. Optical transmittance and reflectance of the as-deposited and annealed films were recorded at room temperature by a Perkin Elmer UV/VIS/NIR Lambda 19 spectrophotometer in the wavelength range 200–3000 nm. FTIR transmission spectra were recorded at room temperature on a NICOLET 6700, Thermo Electron Co. USA in the range of 400–2000 cm⁻¹. Impedance spectroscopic measurements were made at room temperature using Alpha-A High Performance Frequency Analyzer, Novocontrol Technologies, Germany in the frequency range of 0.1 Hz–1 MHz. Silver paint electrodes were used at a separation of about 40 mm on 50 mm wide films. The contacts were allowed to dry for 24 h in open air before making measurements. DC electrical resistivity was measured having an approximate radius of curvature of 10 nm.

3. Results and discussion

SnO₂ thin films deposited on BK7 glass substrates are physically stable. Cracks and blisters are not found even after annealing up to 550 °C. Fig. 1 shows typical XRD patterns of the as-deposited and annealed SnO₂ films. Broad halo in the XRD pattern of as-deposited film depicts its amorphous nature. On the other hand, all annealed films are polycrystalline with tetragonal structure (P42/mmm (1 3 6)) [19]. Crystallinity of the films seems to improve with the rise of annealing temperature. X-ray diffraction peaks are broad signifying that the present films are composed of small nanoparticles [1,2]. The average particle size as estimated by Scherrer formula [2] is in the range of 5–10 nm and demonstrates an increase with annealing temperature as clear from Fig. 2. Furthermore, X-ray diffraction peaks shift towards lower 2θ angles with annealing temperature (Fig. 1) suggesting an increase in lattice parameters, and consequently, the unit cell volume (Fig. 2). It is also noticed that the unit cell volume of annealed films is smaller than that for bulk SnO₂ (0.0724 nm³).

Two and three-dimensional AFM images of the as-deposited and 350 °C annealed SnO₂ films are shown in Fig. 3. It can be seen that the as-deposited film is amorphous (Fig. 3a) while annealed film is crystalline (Fig. 3b). The asperities and depressions on the surface of crystalline film are of the order of 5–10 nm wide. Furthermore, RMS roughness of the as-deposited film is about 4 nm. While on annealing it reduces to about 0.4 nm representing smooth surface and uniform growth. This is also confirmed from the height scales of 2D AFM images (Fig. 3). Generally the electron beam evaporated films are rough but in present case, films are smooth enough due to optimization of the deposition conditions such as distance between target and substrate. Moreover, smoothness of the present films can also be related with the orderedness caused by annealing [20].

SnO₂ is known to have six atoms per unit cell (space group D₄h₄) giving 18 vibrations modes. Among these modes 2 are IR active (A₂, E_u) and 4 are Raman active (E_g, A₁g, B₁g, B₂g) [21]. The microstructure, shape, size and defects can affect the intensity and shape of IR and Raman peaks. Fig. 4 shows Raman spectra of the as-deposited and annealed SnO₂ films. Three peaks are visible in the spectrum of as-deposited film at about 472.7, 631.0, 773.2 cm⁻¹ which can be assigned to SnO₂ optical phonons [1,22]. It is clear from Fig. 4 that these peaks are blue-shifted as compared to those for bulk SnO₂ (474.0, 632.0, 776.0 cm⁻¹) [22], suggesting quantum confinement effects. These peaks show more blue shift on annealing at higher temperatures, possibly due to enhanced quantum confinement effects. Intensity of the Raman peaks increases with an increase in annealing temperature due to improvement in the structural order. The asymmetry observed in the Raman peaks may be due to small size of nanoparticles and structural defects [23,24].

In order to examine the vibration modes on the surface of SnO₂ films, FTIR analysis have been performed on the as-deposited and annealed SnO₂ thin films, as-deposited (a) and annealed for 2 h at 350 °C (b), 400 °C (c), 450 °C (d), 500 °C (e), 550 °C (f).
annealed films at room temperature and results are plotted in Fig. 5. Three peaks are visible in the spectra at about 655, 790, 985 cm$^{-1}$ for the as-deposited and all annealed films. The peak at 655 cm$^{-1}$ can be assigned to O–Sn–O and 790 cm$^{-1}$ to Sn–O–Sn stretching vibrations, while the peak at 985 cm$^{-1}$ is due to lattice vibrations. Popescu and Verduraz [25] have seen these peaks for SnO$_2$ powder at 665, 770 and 960 cm$^{-1}$, respectively; their peaks were comparatively narrower in comparison with our FTIR spectra. This may be due to amorphous and nanocrystalline nature of our films. The shape of the FTIR spectra and the positions of the peaks have been shown to vary with the synthesis routes and particle size [26].

Fig. 6 shows plot of transmittance of the as-deposited and annealed SnO$_2$ films at different temperatures as a function of wavelength. The behavior of transmittance for the as-deposited and annealed films is almost similar in the wavelength range of 300–3000 nm with a slight shift in the peak position towards lower wavelengths. The blunt and slow decrease at wavelength below 500 nm is probably due to the absorption edge, which can also manifest the amorphous nature of the as-deposited film, while the annealed films show some sharp decrease compared with the as-deposited film, which demonstrates crystalline nature of these films along with some amorphous phase. Any variation in transmittance caused by annealing may be related with non-stoichiometry, improvement in the structural order, removal of residual stresses and defects formed during film deposition.

Fig. 7 shows plot of $(\alpha h\nu)^2$ as a function of photon energy, $h\nu$, to determine the band gap. Band gap energy, $E_{\text{opt}}$, estimated from Fig. 7 is shown in Fig. 8 as a function of annealing temperature. The band gap of as-deposited SnO$_2$ film is 3.61 eV. It shows substantial rise to 4.15 eV for the film annealed at 350 °C and increases further at higher annealing temperatures to 4.22 eV. These $E_{\text{opt}}$ values are almost in agreement with those of Lee [26]. The low value of $E_{\text{opt}}$ for the as-deposited film as compared with the crystalline films may be attributed to band tailing caused by disorderedness [27]. Since amorphous semiconductors have band tails inside the energy gap, transition of band tails to the...
extended states can happen below the absorption edge of the crystallized state [27]. $E_{\text{opt}}$ values increase slightly with an increase in annealing temperature due to improved structure [1] and/or enhanced quantum confinement.

Fig. 9 shows reflectance, $R$, of the as-deposited and annealed films as a function of wavelength. As-deposited and annealed films show almost similar trends in a wide range of wavelength with a slight shift of peaks towards lower wavelengths. Refractive index, $n$, can be determined from the reflectance data using the relation [1,28]:

$$n = \sqrt{\frac{1 + \sqrt{R}}{1 - \sqrt{R}}}$$  \hspace{1cm} (1)

The refractive index (calculated using Eq. (1)) of as-deposited and annealed films is shown in Fig. 10 as a function of wavelength. Fig. 10 shows an oscillatory behavior of refractive index (from $n_{\text{min}} = 1.25$ to $n_{\text{max}} = 2.30$) in the UV, visible and near IR regions. Fig. 11 is a plot of refractive index at $\lambda = 589$ nm, as a function of annealing temperature ($T_A$). The refractive index measured at $\lambda = 589$ nm is found to increase from 1.35 to 1.88 showing oscillatory behavior due to fringing effect. The values of refractive index are close to early reported values [1]. In order to establish a relation between refractive index, $n$ ($\lambda = 589$ nm), and optical band gap energy $E_{\text{opt}}$, a graph has been plotted as shown in Fig. 12. An
approximately linear relation is observed as given below:

$$n = 0.5954 + 0.3086E_{opt}$$

(2)

Fig. 13 shows a plot of electrical resistivity ($\rho$) as a function of annealing temperature. Resistivity first decreases rapidly from 4.4 m$\Omega$-cm (for as-deposited film) up to an annealing temperature of 400 °C. Further annealing causes resistivity to increase slowly from 0.039 m$\Omega$-cm (at 400 °C) to 0.483 m$\Omega$-cm at 550 °C. It can be seen in Fig. 1(a and b) that the as-deposited amorphous film becomes polycrystalline at 350 °C. Therefore, the substantial decrease in resistivity observed at 350 °C is due to orderedness/crystallization of the film. Lee et al. [27] have shown that resistivity of SnO$_2$ based thin films depends on mobility and density of charge carriers out of which the former increases with crystallinity and structural ordering and the latter increases with oxide ion vacancies or excess metal ions, i.e. non-stoichiometry of SnO$_2$ phase. Annealing the SnO$_2$ films in air is expected to lower the oxide ion deficiency or improve the stoichiometry. Accordingly, initial decrease in resistivity of the films with annealing temperature up to 350 °C is related with the improvement in crystallinity, as mentioned above, and an increase in resistivity above 400 °C is due to decrease in oxide ion vacancies and associated charge carrier density.

Typical complex impedance spectrum ($Z'$ plotted against $Z''$) for the as-deposited SnO$_2$ film recorded at room temperature is shown in Fig. 14. Such IS plots for all annealed films show single semicircles (not shown here) analogous to that of as-deposited film. Measured data is well fitted with simulated curve using an equivalent RC parallel circuit (shown as inset of Fig. 14). The intercept on the real impedance axis ($Z'$) in the fitted Nyquist plot (Fig. 14) gives dc resistance. Optimum (best-fitted) value of the capacitance, $C_1$, is found to be approximately same for all the films and is about 50 pF. On the other hand, optimum value of the resistance, $R_1$, first decreases sharply (from $10^{10}$ Ω to $2 \times 10^4$ Ω) and then increases gradually to $5 \times 10^8$ Ω with rise of annealing temperature as shown in Fig. 15. The behavior of dc resistance obtained from IS measurements (Fig. 15) and dc resistivity (Fig. 13) are almost in agreement. Measured resistances and capacitances may be attributed to grain boundaries of nanocrystals [29,30]. The sudden fall of dc resistance (Fig. 15) seems to be a consequence of orderedness/crystallization of the film, whereas the rise of resistance may be related with the reduction of carrier density through trapping of electrons at grain boundaries by adsorbed oxygens [29] during annealing in air.

4. Conclusions

The electron beam evaporated SnO$_2$ thin films are amorphous in nature and show crystallization at annealing temperature of 350 °C and above. The post-thermal annealing shows greater tendency to affect the structural, optical and electrical properties of SnO$_2$ thin films which are composed of nanoparticles of size 5–10 nm. Optimization of the deposition parameters is useful to obtain smooth films. Due to quantum confinement effects band gap energy of SnO$_2$ rises from 3.61 eV for amorphous film to 4.22 eV for nanocrystalline films. As a consequence such SnO$_2$ films can be useful as a window material for solar cell applications. Raman spectra of SnO$_2$ films are blue-shifted with annealing temperature indicating nanostructure and quantum confinement effects. Electrical resistivity of present films falls abruptly on crystallization but rises gradually due to improvement in stoichiometry. Impedance spectroscopic results also show the similar behavior.

Acknowledgement

Authors are thankful to Higher Education Commission (HEC), Government of Pakistan, for financial support.

References
