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REGULAR ARTICLE

Effect of Annealing on the Physical Properties of Chemically Synthesized Nanocrystalline SnO_2 Thin Films

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This study investigates the effect of annealing on the physical properties of the chemically synthesized nanocrystalline SnO_2 thin films deposited onto glass substrate at room temperature. SnO_2 thin films were annealed for 2 h in an oxygen environment at different annealing temperature. From X-ray diffraction study it was observed that as-deposited SnO_2 film and films annealed at 300 °C and 400 °C exhibited amorphous nature, while SnO_2 films annealed at 500 °C exhibits orthorhombic crystal structure. SEM results demonstrates that morphology of SnO_2 thin films are determined by the annealing temperature. The optical band gap of the prepared nanocrystalline SnO_2 thin films found in the range of 3.28 eV to 2.79 eV depending upon the annealing temperature. Finally, as a result of the analysis, we can say that the physical properties of SnO_2 thin films can be modified by thermal annealing.

Keywords: Thin film, Chemical synthesis, XRD, SEM, EDAX, Optical absorption spectra.

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1. INTRODUCTION

Tin oxide (SnO_2) is one of the most important member of the transparent conductive oxide (TCO) semiconductor family, whose basic features includes *n*-type conductivity, wide band gap (3.6 eV) at room temperature, excellent optical transparency and high electrical conductivity, chemical stability and good reproducibility [1-3]. With the large exciton binding energy, SnO_2 is considerably attractive for different applications such as Li-ion batteries, Perovskite solar cell, solid state gas sensors, optoelectronic devices, transparent conducting electrodes, transistors etc. [4-6]. For these applications, conductive layers of SnO_2 possessing suitable optical and electrical properties could be fabricated on amorphous or metal substrates. Thus, investigation of the physical properties of SnO_2 thin films attain great importance. Over the past few decades, many methods have been developed for the fabrication of thin films of SnO_2 namely, pulsed laser deposition [7], reactive thermal evaporation [8], RF-magnetron sputtering [9], atomic layer deposition [10], electron beam evaporation [6] spray pyrolysis technique [11], dip coating method [12], spin coating [3], SILAR [13], sol-gel technique [14] and chemical bath deposition (CBD) [17] etc.

Recently among these methods, CBD method has appeared as a promising technique for fabrication of SnO_2 thin films. CBD method has many advantages over other deposition methods which includes simple experimental set-up, low temperature process, cost effective, suitable for small to large area deposition and no need of conducting substrate etc. [16, 17]. The physico-chemical properties of thin films prepared by CBD can be controlled by varying the deposition parameters such as pH of the precursor solutions, complexing agent, bath temperature, deposition time, solution concentration, and nature of substrate etc. [18]. Considering these advantages, in this paper, we have reporting the fabrication of nanocrystalline SnO_2 thin films using CBD method at room temperature. The effect of annealing temperature on the structural, surface morphology, optoelectronic properties were investigated in detail.

2. EXPERIMETAL DETAILS

2.1 Deposition of SnO_2 Thin Films at Room Temperature

Analytical-grade tin chloride dihydrate ($SnCl_2.2H_2O$) (Supplied by Merck Life Science Private Limited, Vikhroli (East) Mumbai), urea ($CO(NH_2)_2$), sodium hydroxide (NaOH) (Supplied by Merck Specialties Pvt. Ltd. Worli, Mumbai) were used as precursors in the experiments. Glass Substrate was used for deposition of nanocrystalline SnO_2 film. Double distilled water (DDW) (Supplied by Merck Life Science Private Limited, Vikhroli (East) Mumbai) was used as a solvent and glass micro-slides was used as a substrate. Before deposition glass micro-slides were cleaned with labolene and chromic acid followed by rinsing with DDW and finally, treated with ultrasonic waves in ultrasonicator for 30 min.

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Synthesis of SnO_2 thin films is based on immersion of the well cleaned substrates in an alkaline bath of a complexed tin salt at room temperature (27 °C). 1 M $CO(NH_2)_2$ solution was added slowly to a solution of 0.5 M $SnCl_2.2H_2O$ under vigorous stirring at room temperature for 30 min. The bath was prepared by adding 1 M NaOH to the bath containing mixture of $SnCl_2.2H_2O$ and $CO(NH_2)_2$ with constant stirring for 30 min, which resulted in the formation of white precipitate of $Sn(OH)_2$. This precipitate was dissolved by further addition of NaOH with the formation of clear solution having a resultant pH ~ 12. The solution was stirred for another 30 min and then transferred into another beaker of 100 ml containing cleaned glass micro-slide, clamped vertically into it. The bath was kept at room temperature (27 °C) for 48 hrs for the deposition of SnO_2 thin film. After the deposition, the substrate coated with SnO_2 thin films was taken out, washed with DDW and dried in air. The as-deposited SnO_2 films were annealed at various temperatures for 2 h and used for further characterizations.

2.2 Characterization of SnO_2 Thin Films

X-ray diffraction (XRD) measurements were performed on a Bruker AXS, Germany (D8 Advanced) diffractometer in the scanning range 20°-80° (2θ) using CuKα radiations with wavelength 1.5405 Å. The surface morphology and composition was studied by scanning electron microscopy (SEM) and energy dispersive analysis by X-rays (EDAX) using JEOL-JSM 6360, respectively. The optical properties of as-deposited and annealed SnO_2 films were investigated by estimating the optical absorbance as a function of wavelength ranging from 300-800 nm was measured using a JASCO UV-Vis spectrometer (V-630). The resistivity of the SnO_2 thin films was determined by the standard two-probe method.

3. RESULTS AND DISCUSSION

3.1 Structural Analysis

The effect of annealing temperature on the structural quality of chemically synthesized SnO_2 thin films was studied and demonstrated in Fig. 1; Fig. 1(a-d) represents the XRD patterns of as-deposited and post annealed SnO_2 thin films for 2 h in air at different annealing temperatures. It shows that as-deposited and annealed SnO_2 thin films (until the annealing temperature reaches to 400 °C) are amorphous in nature. This might be attributed due to the substrate was not heated during deposition and the thermal energy was not sufficient for the chemical species to promote the crystallization of tin oxide [19]. However, SnO_2 thin films annealed at 500 °C have crystalline in nature having orientations of (112), (006) and (206) planes corresponding to $2\theta \approx 26.93^o$, 33.84^o and 51.84^o, respectively. These peaks are attributed to orthorhombic structure which coincides with JCPDS No. 78-1063 of SnO_2 structure. There is no peak was observed for impurities or any other phases of tin oxide in the XRD pattern.

3.2 Surface Morphology Analysis

The surface morphology and elemental composition of SnO_2 thin film samples were investigated with scanning electron microscopy (SEM) using JEOL-JSM 6360 attached with energy dispersive analysis by X-rays

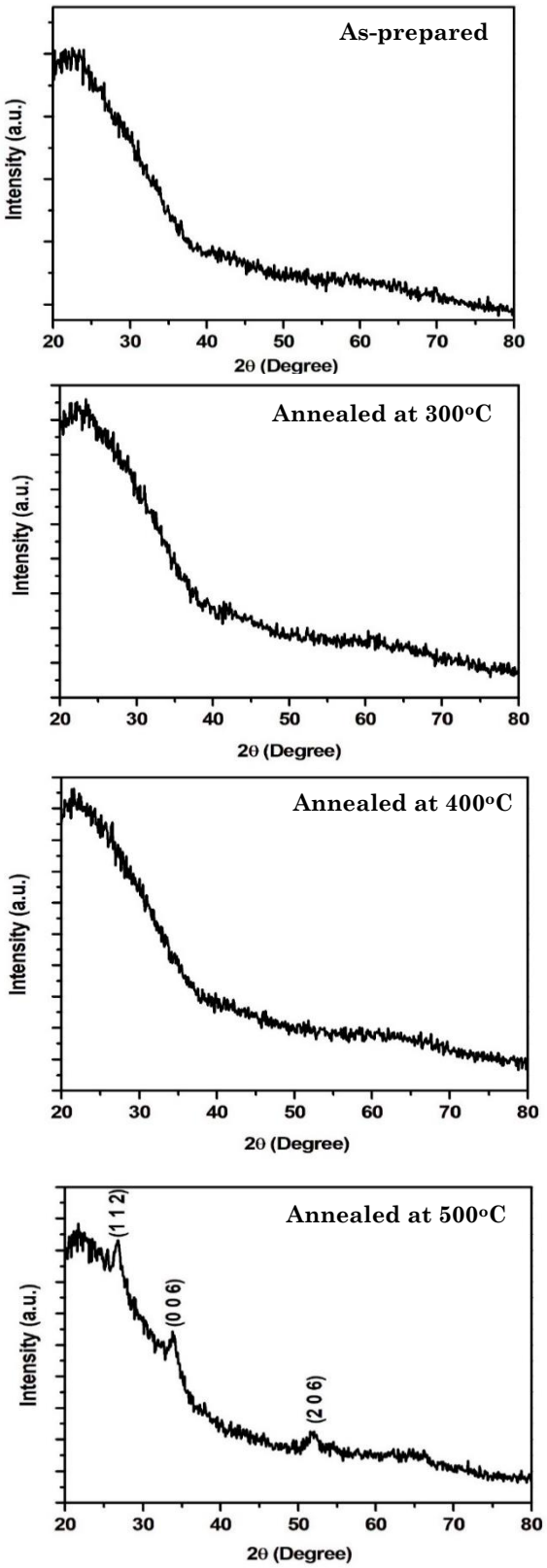

Fig. 1 – X-ray diffraction patterns of chemically synthesized nanocrystalline SnO_2 thin films (as-prepared and annealed at different temperatures)

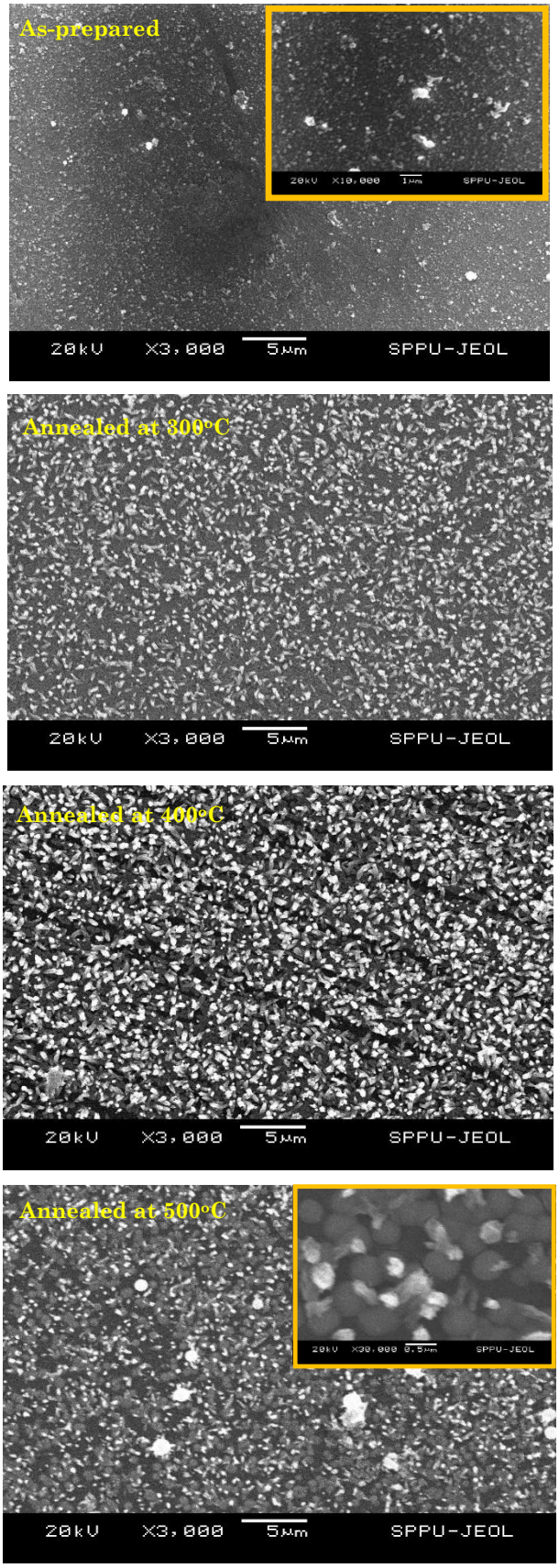

Fig. 2 – SEM images of chemically synthesized nanocrystalline SnO_2 thin films (as-prepared and annealed at different temperatures)

(EDAX). Fig. 2 clearly indicates that the microstructure and morphology of chemically deposited SnO_2 thin films are significantly affected by annealing temperature. For as-deposited SnO_2 films, surface looks smooth and uniform with a granular surface microstructure. The grains are almost spherical in shape and its shape is greatly changed to needle-like microstructure with the increase in annealing temperature. However, for SnO_2 sample annealed at 500 °C, some large crystallites of irregular size along with needle-like particles were nucleated without any cracks.

SnO_2 thin films was subjected to EDAX measurement in order to identify and differentiate the chemical composition of the material deposited on the substrate surface. EDAX spectra of chemically synthesized as-prepared SnO_2 thin films is depicted in Fig. 3. It is clearly revealing that the prepared films contain two elemental components of Sn at 3.7 keV and 4.4 keV and O at 0.5 keV. The presence of these elements indicates the formation of SnO_2. The average atomic percentage of Sn:O was 1:99, which shows the deposited film is rich in oxygen.

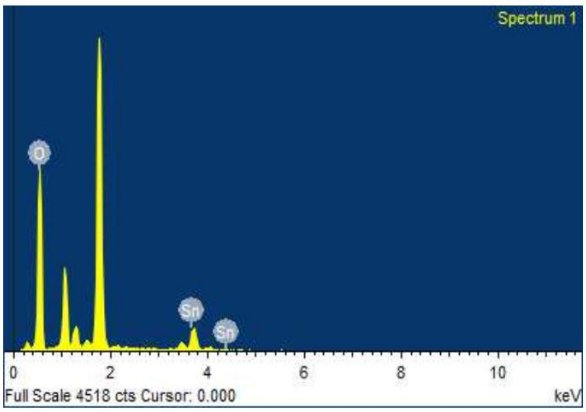

Fig. 3 – EDAX spectra of chemically synthesized as-prepared SnO_2 thin films

3.3 Optical Analysis

In order to study the optical behavior of the deposited nanocrystalline SnO_2 films, optical absorbance measurement was made in the wavelength range of 300-800 nm using UV-Vis spectroscopy. As can be seen in the Fig. 4, the measured absorbance of SnO_2 films increases with increasing annealing temperature, which correlates with the results obtained in XRD and SEM studies.

SnO_2 is considered as a material owing to direct band gap energy [3], hence the optical band gap energy of the films was determined using the following equation [20],

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

where α is the absorption coefficient, A is a constant, $h\nu$ is the incident photon energy, E_g is optical bandgap of the material.

Fig. 5 shows the typical plot of $(\alpha h\nu)^2$ versus $(h\nu)$ for as-deposited and annealed SnO_2 thin films deposited using chemical method. The extrapolation of the straight line of $(\alpha h\nu)^2$ to the $(h\nu)$ axis gives the band gap of the material. Calculated value of optical band gap was found to be about 3.28 eV for as-deposited SnO_2 films and

3.22 eV and 2.79 eV for SnO_2 films annealed at 300 °C and 500 °C. The reported value of the band gap is in good agreement with the value reported previously [3]. This decrease in bandgap causes a strong red shift in the optical spectra, which might be due to the crystallization after annealing the thin films.

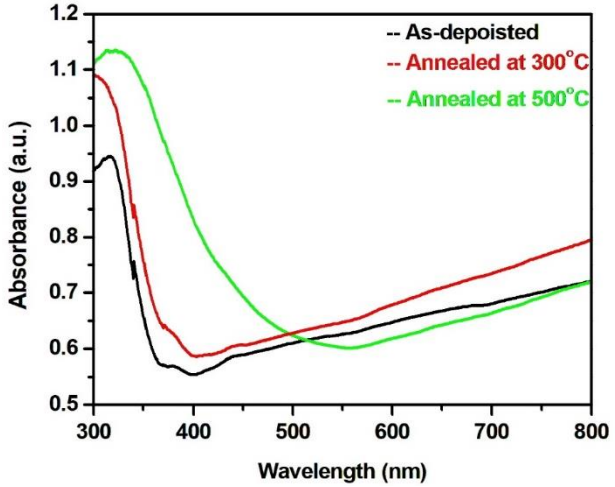

Fig. 4 – Absorbance spectra of chemically synthesized nanocrystalline SnO_2 thin films (as-prepared and annealed at different temperatures)

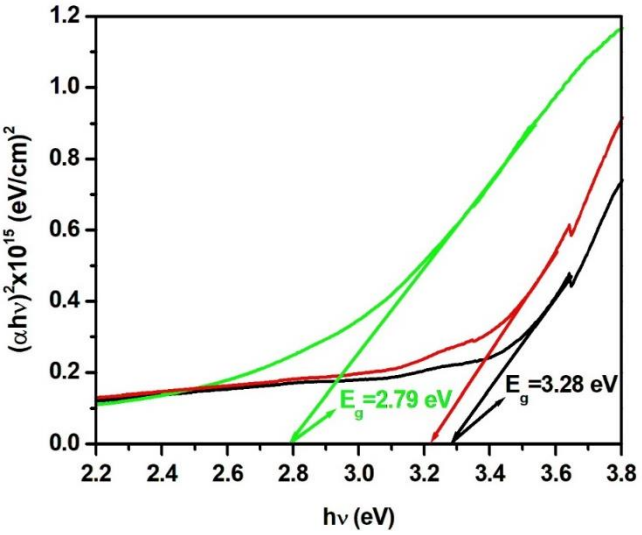

Fig. 5 – Typical plot of $(\alpha h\nu)^2$ versus hν for chemically synthesized nanocrystalline SnO_2 thin films (as-prepared and annealed at different temperatures)

3.4 Electrical Analysis

Fig. 6 shows the variation of log ρ versus the inverse of absolute temperature (1000/*T*) for the nanocrystalline SnO_2 thin films. Standard two-point probe method of dark resistivity measurement shows the semiconducting nature of the deposited films as resistivity of the films decreases with increase in temperature.

Electrical resistivity measured by using conventional dc two probe method was found to be of the order of 1.88×10^2 Ω·cm for the as-deposited SnO_2 thin films and is well agreed with the value earlier reported [10]. Electrical resistivity was found to be decreased to 1.19×10^2 Ω·cm and 0.36×10^2 Ω·cm for SnO_2 thin films annealed at 300 °C and 500 °C, respectively.

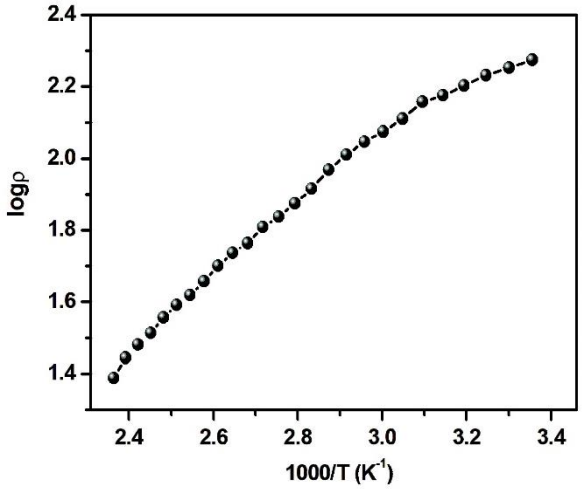

Fig. 6 – Variation of dark electrical (log ρ) with temperature for nanocrystalline SnO_2 thin films deposited by chemical method

4. CONCLUSION

Effect of annealing temperature on the physical properties of chemically synthesized nanocrystalline SnO_2 thin films deposited at room temperature were studied. Increasing the annealing temperature caused the transformation of amorphous phase to orthorhombic phase has been observed from XRD study. Significant change in the morphology was found after annealing the SnO_2 thin films. The red shift in the absorption edge may be attributable to a decrease in optical band gap energy after annealing the film, which may have correlated with the XRD analysis. The electrical resistivity decreased from 1.88×10^2 Ω·cm to 0.36×10^2 Ω·cm after annealing. Consequently, it can be indicated that the annealing temperature play an important role on the characteristics properties of SnO_2 thin films and chemically deposited SnO_2 thin films are useful for optoelectronic applications.

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Вплив термовідпалювання на фізичні властивості хімічно синтезованих нанокристалічних тонких плівок SnO_2

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У цій роботі досліджується вплив відпалу на фізичні властивості хімічно синтезованих нанокристалічних тонких плівок SnO_2, нанесених на скляну підкладку при кімнатній температурі. Тонкі плівки SnO_2 відпалювали протягом 2 год в середовищі кисню при різних температурах відпалу. За допомогою методу рентгенівського мікроаналізу було виявлено, що осаджена плівка SnO_2 і плівки, відпалені при 300 °C і 400 °C, демонструють аморфну природу, тоді як плівки SnO_2, відпалені при 500 °C, демонструють орторомбічну кристалічну структуру. Результати СЕМ показують, що морфологія тонких плівок SnO_2 визначається температурою відпалу. Оптична ширина забороненої зони отриманих нанокристалічних тонких плівок SnO_2 знаходилася в діапазоні від 3,28 еВ до 2,79 еВ залежно від температури відпалу. У результаті аналізу можна сказати, що фізичні властивості тонких плівок SnO_2 можна модифікувати термічним відпалом.

Ключові слова: Тонка плівка, Хімічний синтез, XRD, SEM, EDAX, Спектри оптичного поглинання.