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# CHARACTERIZATIONS OF $SnO_2$ THIN FILMS PREPARED USING SOL-GEL METHOD

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## ABSTRACT

The aim of this project is to investigate the effect of annealing process on the structural, morphological and optical properties on $SnO_2$ thin film. A chloride-based inorganic sol-gel route was used for preparing pure $SnO_2$ sol. $SnCl_4$ as a precursor was first reacted with propanol and then the resulting compound was hydrolyzed. The obtained sols were used for depositing thin films by spin coating technique or for preparing powder by solvent evaporation at 100°C followed by annealing at 500°C and 600°C for 4 hours. Structural investigation using XRD revealed that unannealed $SnO_2$ powder exhibited an amorphous structure while the crystalline peaks of $SnO_2$ powder at both 500°C and 600°C corresponds to the tetragonal crystallographic structure (*cassiterite*). The annealed $SnO_2$ film showed rough surface with porous structure and small grains. However, no grain boundary observed in as-deposited $SnO_2$ thin film. TEM analysis showed that the crystallized $SnO_2$ particles exist as round grains with size varies between 15-50 nm range. The optical measurement revealed the annealing process significantly reduced the optical band gap, $E_g$ with from 3.93 eV in as-deposited film to 3.86 eV after annealing.

## INTRODUCTION

Tin dioxide, $SnO_2$ is an *n*-type semiconductor material, largely used as a transparent conductive layer or in the fabrication of gas sensor devices [1]. It has been prepared by a wide range of techniques, such as spray pyrolysis [2], chemical vapor deposition [3], evaporation [4], and sputtering [5]. More recently, the sol gel process offered a promising alternative technique for the preparation of $SnO_2$, both in the form of monoliths and the thin films. The advantages of sol gel processing with respect to other routes are the low processing temperatures, the possibility of chemically tailoring the starting solutions, resulting in new compositions, better control of the final microstructure and the easy deposition of the films. Two different approaches are generally used in the sol gel synthesis of $SnO_2$. The first consist of the hydrolysis of a tin alkoxide with low values of the $H_2O$:Sn molar ratio to avoid precipitation in the sol [6]. This procedure has the advantage of minimizing the impurities in the final material,

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but the high cost of the precursors and the short-term stability of the sols against the increase of viscosity make this type approach inconvenient. For this reason, sol-gel preparation of $SnO_2$ is more commonly achieved through the hydrolysis of inexpensive precursors, such as $SnCl_2$ or $SnCl_4$ [7]. Initially, a precipitate is obtained by treating the precursors with an alkaline solution. Then the precipitate, best described as hydrous $SnO_2$, is peptized, resulting in a $SnO_2$ sol. In the present work, a different route was used for the preparation of $SnO_2$ thin films. $SnCl_4$ was used for the precursors, but it was modified through reaction with alcohol before hydrolysis [8]. In this way, sols were obtained with long-term stability against gelation. The above considerations make it important to study the structural, morphological and optical properties of $SnO_2$ thin film.

## EXPERIMENTAL PROCEDURES

Pure $SnO_2$ sols were prepared starting from anhydrous $SnCl_4$, water, propanol ($C_3H_7OH$), and isopropanol ($2\text{-}C_3H_7OH$) in the following molar ratios: $SnCl_4$:$H_2O$:$C_3H_7OH$:$2\text{-}C_3H_7OH$= 1:9:9:6. Initially, $SnCl_4$ was dropped into two-thirds of the total amount of $C_3H_7OH$. After an exothermic reaction, the solution was allowed to cool down. The one-third of the total water dissolved in the remaining $C_3H_7OH$ was added dropwise to it for prehydrolysis of the tin precursors, followed by 1 hr stirring. The prepared sol was then mixed with a solution of the remaining amount of $H_2O$ dissolved in the prescribed amount of $2\text{-}C_3H_7OH$, followed by 1 hr of further stirring. The whole preparation of $SnO_2$ solution is shown in Figure 1.

For the purpose of producing $SnO_2$ thin film, the sample was prepared by spin coating the preceding solution at 3000 rpm for 30 s onto glass substrate. A few drops of glucupone was added into the solution to act as surfactant. After spinning, the coating was dried at 80°C for 10 mins. This procedure was repeated 3 times to ensure good coverage of the substrate. After the final drying, the thin film was annealed using slow heating rate (1°C/min) at 600°C in air and then allowed to cool to room temperature. To produce a crystalline powder, the $SnO_2$ sols was evaporated at 100°C to dryness followed by annealing at 500°C and 600°C for 4 hours. The crystal structure of $SnO_2$ powder were determined using Bruker D8 Advance X-ray diffaractometer with Cu Kα (λ=1.5406 Å) in the scanning angles between 20°-60°. For the surface morphology and estimation of the film thickness, Zeiss (Gemini) FE-SEM unit was employed. TEM images were obtained with Philips TEM unit while for optical measurement were recorded using Shimadzu UV-Vis-Spectrophotometer model no. 160A.

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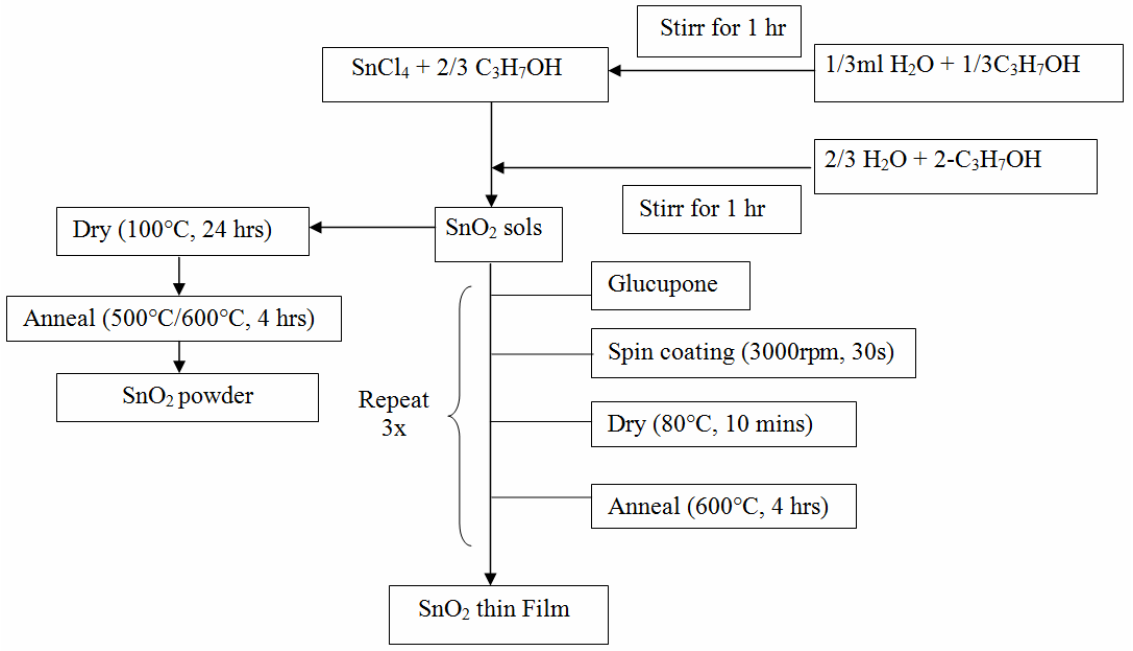


Figure 1: The preparation of $SnO_2$ thin films and powder.

## RESULTS AND DISCUSSION

### *General*

With the previously described procedure, clear and homogenous $SnO_2$ sols were obtained. $SnO_2$ sols after dryness 24 hrs appeared in dark colour but formed in yellow pale powder after annealing at 500°C and 600°C.

According to Epifani et al (2001), thin films deposited from sols with low $H_2O$:Sn molar ratio generally exhibited poor adhesion to the substrate. They suggested that this could be improved by increasing the $H_2O$:Sn molar ratio. For this reason, films were prepared from the sols with $H_2O$:Sn molar ratio of 9. Initial deposition trials showed that $SnO_2$ thin films exhibited poor adhesion to either glass or Si wafer substrate. The introduction of few drops of glucupone to act as surfactant improved the adhesion properties of $SnO_2$ onto glass substrate. However, similar problem remained when $SnO_2$ deposited onto Si wafer.

### *XRD Analysis*

Figure 2 shows the XRD diffractogram of $SnO_2$ at 3 different conditions as-deposited, annealed at 500°C and 600°C. The as-deposited $SnO_2$ powder showed an amorphous structure. By comparison, annealed $SnO_2$ powder at both 500°C and 600°C showed the presence of crystalline peaks correspond to the tetragonal crystallographic structure *(cassiterite)*. Furthermore, x-ray diffractogram for sample annealed at 600°C also

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showed a clean, low background and high peak to background ratio. By comparison, the presence of small unknown crystalline phase peaks (labelled as *) were observed in sample annealed at 500°C, indicated lower $SnO_2$ purity. Moreover, the crystalline $SnO_2$ peaks of sample annealed at 600°C have smaller FWHM value, a clear evidence of larger crystallite size and better $SnO_2$ crystallization process compared to sample annealed at 500°C.

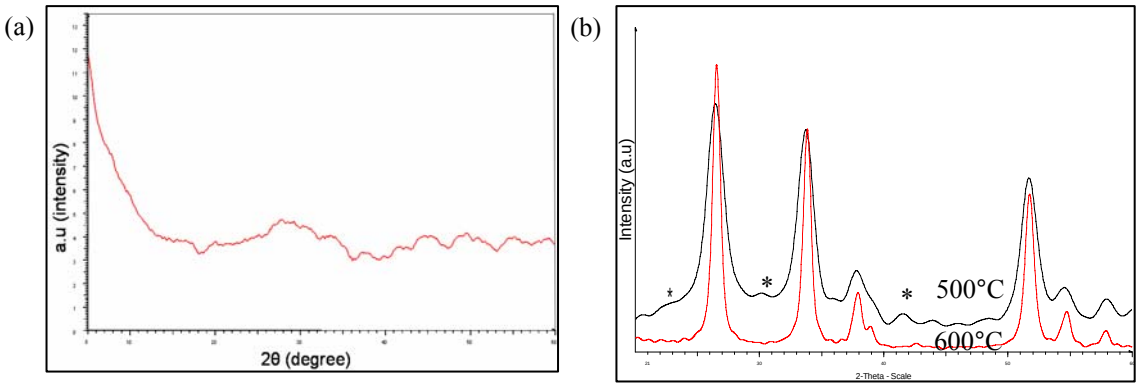


Figure 2: XRD Diffractogram (a) unannealed powder and (b) $SnO_2$ powder annealed at 500°C and 600°C - * Unknown phase

*TEM Image*

TEM analysis revealed that the annealed $SnO_2$ particles tend to form agglomeration in big cluster with bad dispersion (Figure 3). Detailed examination showed that the crystalline $SnO_2$ particles exist as spherical grains with size varies between 15 to 50 nm.

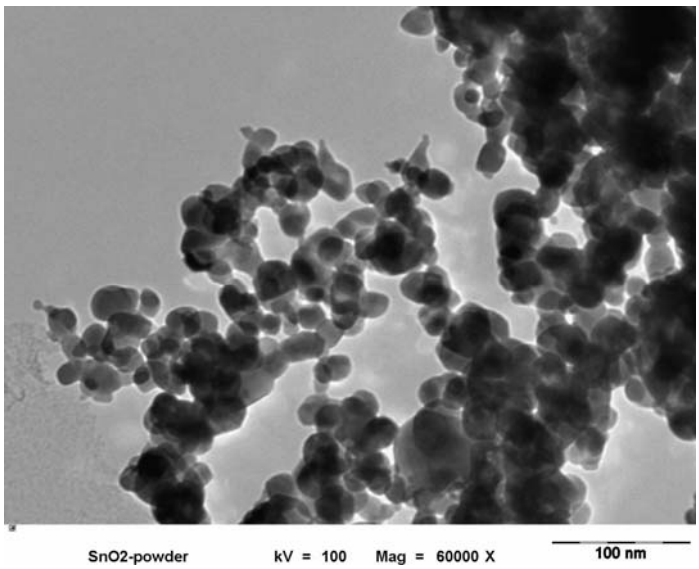


Figure 3: TEM image of annealed $SnO_2$ powder

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### *SEM Analysis*

SEM micrographs for as-deposited and annealed $SnO_2$ thin film are presented in Figure 4. It was found that as-deposited film has no grain boundary, another indicator of amorphous film. The film surface was observed relatively smoother (compared to annealed film) although large non uniform craters were clearly soon. These craters were formed due to the evaporation of solvent during slow drying process. Cross sectional image showed that the film thickness is approximately 90 nm. By comparison, the annealed film exhibited open porous structure with spherical, nanosize grains, which resulted in higher surface roughness in the film. The formation of pores were resulted from decomposition of hydrolyzed and condensed tin alkoxide in the film during annealing process. The film thickness was significantly increased from ~ 90nm (as-deposited film) to approximately 300 nm in annealed film.

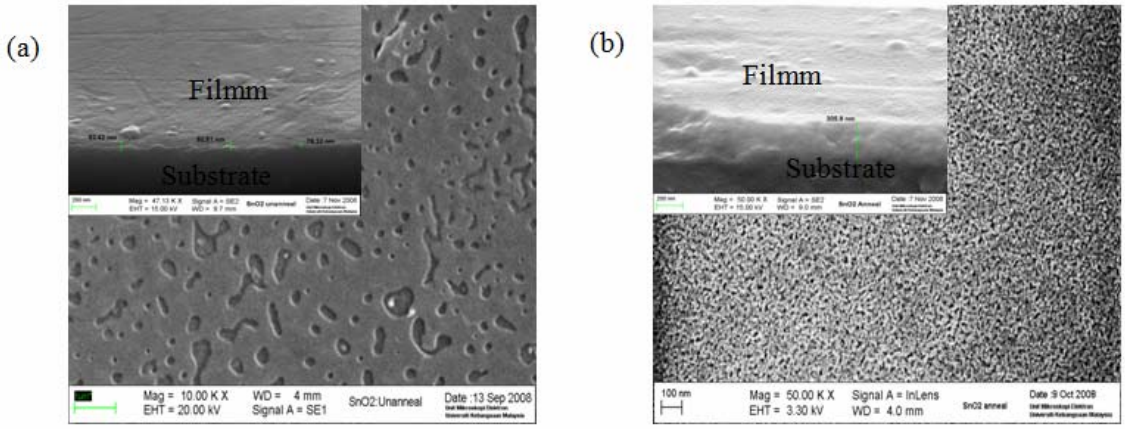


Figure 4: Scanning electron micrograph of (a) $SnO_2$ as-deposited thin film (b) $SnO_2$ annealed thin film and inset shows the cross-sectional view of both films.

### *Optical measurement*

The optical transmittance in the wavelength range 0.25 μm - 0.8 μm for the as-deposited and annealed $SnO_2$ thin film were also investigated. A transmission of 85% was measured in the visible region of the solar spectrum for as-deposited $SnO_2$ but increased significantly to 97% for annealed $SnO_2$ (Figure 5). The transmittance percentage of as-deposited $SnO_2$ film is somewhat higher as compared with reported values [10]. The higher transmittance percentage may be due to different approach in preparation of the film. The increment of the transmittance of annealed $SnO_2$ film contributed by the reduction in the hydroxide accumulation along grain boundary and formation of porous thin film structure. Moreover, high transmittance in the visible region is one of the crystalline $SnO_2$ characteristics.

Significant change was found in optical band gap ($E_g$) at room temperature between as-deposited and annealed films. It was observed that the optical band gap was decreased from 3.93 eV (as-deposited film) to 3.86 eV after annealing. A difference of 0.07 eV

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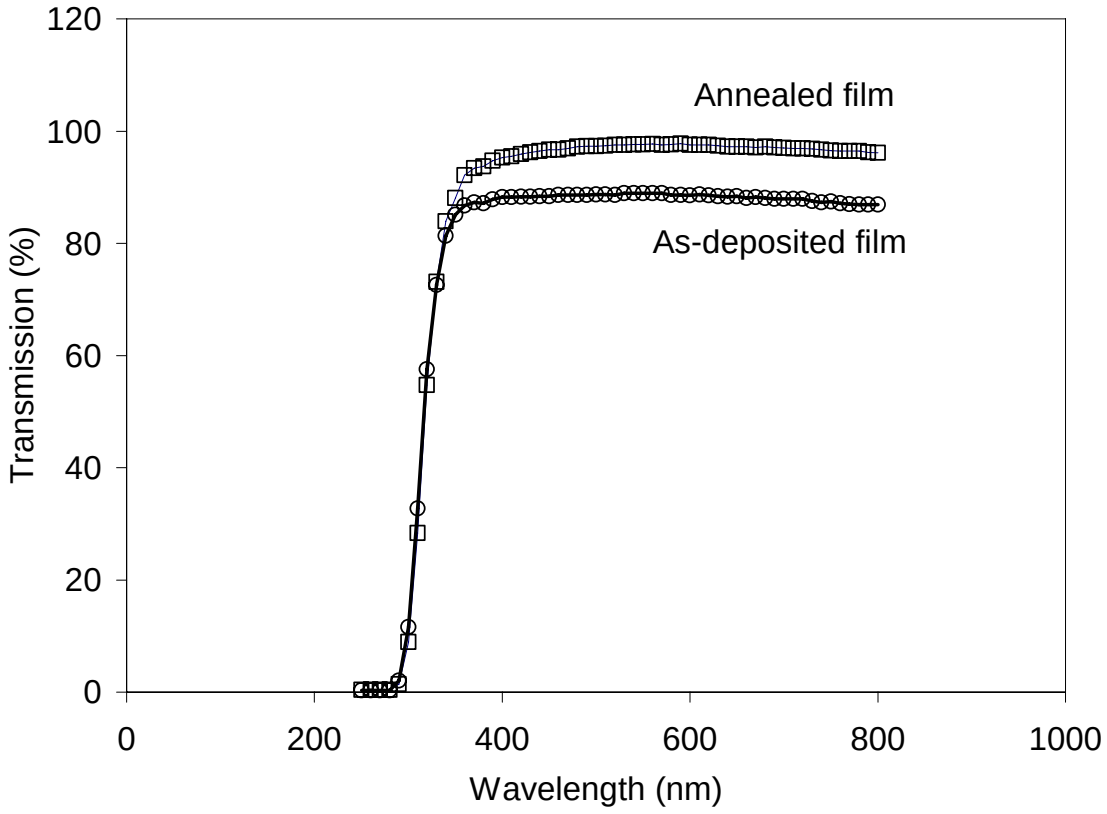
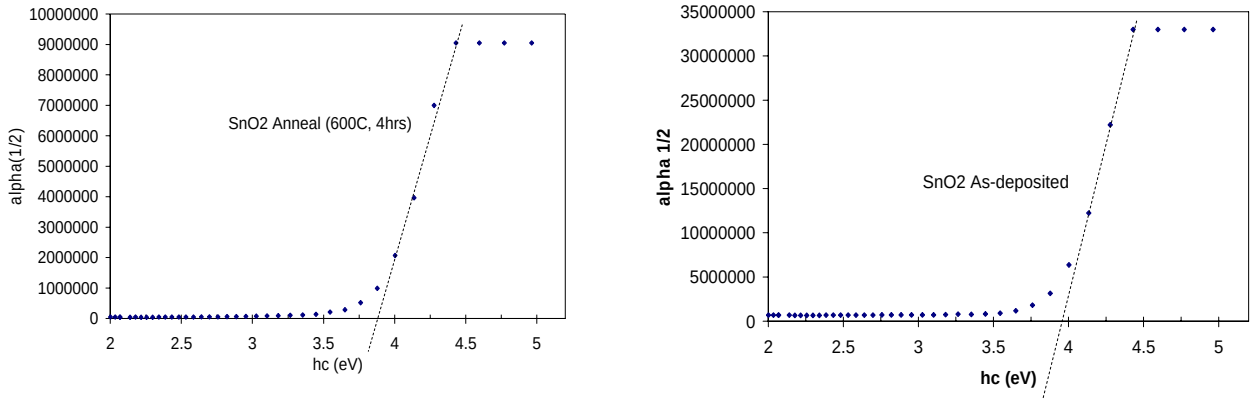
between these films is attributed to the agglomeration of nanocrystallites (in amourphous film) into relatively larger crystallites in annealed film as evidence from x-ray diffractogram. This value however is ~10% higher compared to previously reported value [10].




(a)




(b)

**Figure 5**. (a) Transmittance of $SnO_2$ thin film anneal and as-deposited (b) Square root of the product absorption coefficient and photon energy versus photon energy for both $SnO_2$ thin films

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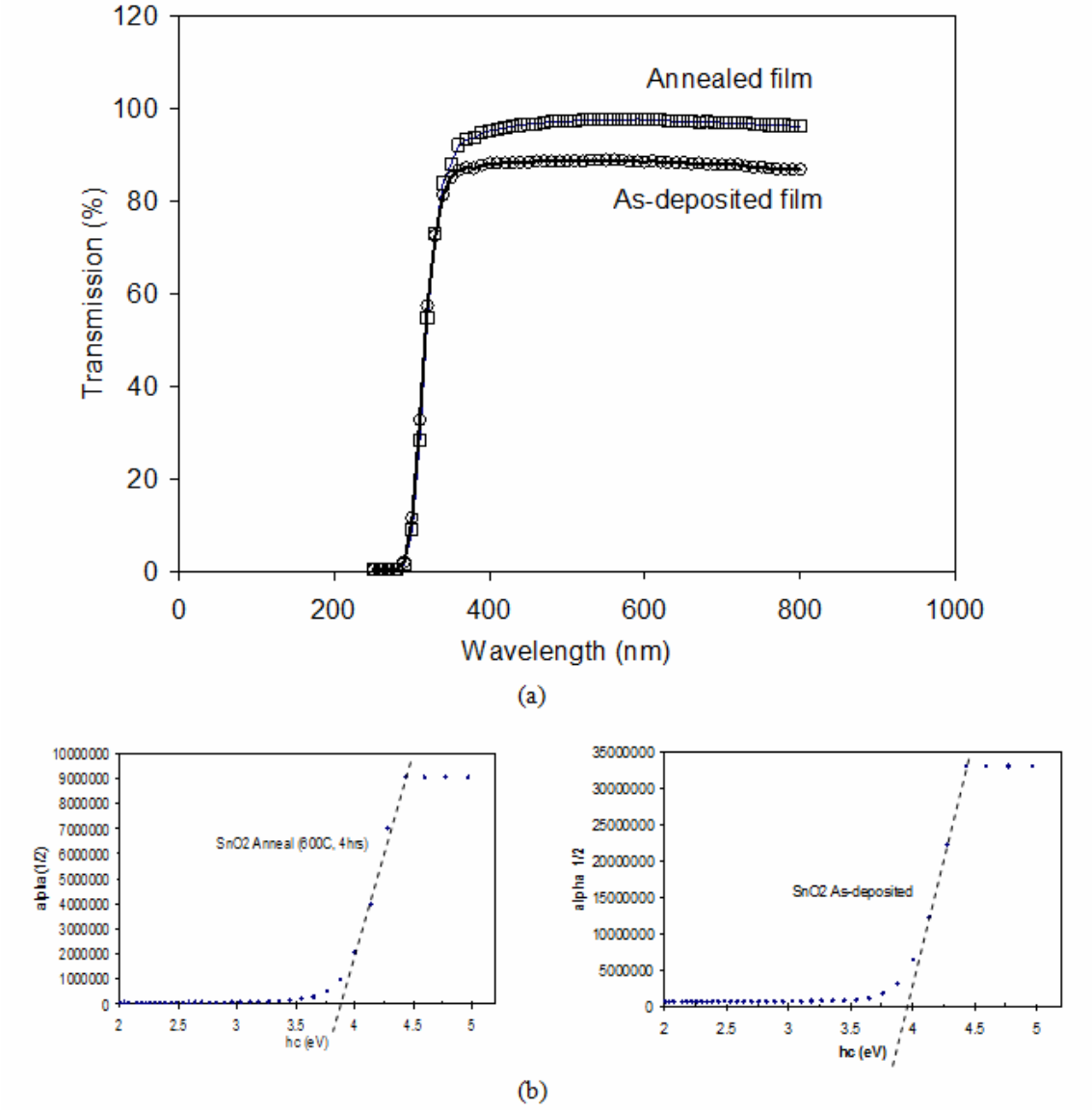


## CONCLUSION

Sol gel method with $SnCl_4$ as precursor is the simple and low cost for preparation of $SnO_2$ thin film. Annealing process significantly altered the microstructure and morphology of the $SnO_2$ film. The optical band gap observed decreased from 3.93 eV (as-deposited film) to 3.86 eV after annealing.

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