Study on Structral and Optical Properties of Tin Oxide Thin Films at Different Annealing Temperatures

Zin Mar Win[1], Ohn Mar Swe[2], Phyu Phyu Win[3] Amy Aung[4]

Abstract

Chemical synthesis of SnO_2 was prepared by co-precipitation method .In this preparation, the stannous chloride ($SnCl_2.2H_2O$) will be used as a precursor and ammonia solution as a precipitating agent. The as-synthesized SnO_2 were heated at temperature 500ºC for 1hr.Then SnO_2 thin films on glass substrate were successfully fabricated by using sol-gel and spin coating technique. The films were annealed at temperatures 400ºC, 500ºC and 600ºC for 1 hr. The films were analyzed by X-ray diffraction (XRD) and optical absorption spectroscopy technique. From the XRD analysis, lattice parameters, unit cell volume and crystallite sizes of the samples were calculated Furthermore, the XRD data, dislocation density of the samples were also calculated. The optical characteristics of these films was investigated by using UV- Visible spectrophotometer. From the UV-Visible spectrum, absorption coefficient and the band gap energy of the samples were evaluated.

Keywords: XRD, thin films, UV-Vis, absorption coefficient and band gap energy.

Introduction

Tin oxide (SnO_2) has been intensively investigated because of its rich physical properties and large applications in commercial devices. Recently, nano materials have greatly attracted due to their unique properties, which are different from those of their corresponding bulk state. Semiconductors are one of the most interesting and most useful solids. They have been investigated many times because of their flexibility, electricity and optical features. [Chen Z et al (2003), Liu Y et al (2014)]. SnO_2 is one of these semiconductors. Stoichiometric SnO_2 is a good insulator because it has little carriers in this circumstance, but non-stoichiometric SnO_2 is transparent and conductive because it has many charge carriers in this circumstance. [Suematsu K et al (2014), Wang Y et al (2005)]. Also, it has a direct optical band gap of about (3.8 ~ 4.3 ev) and an indirect band gap of about (2.7 ~ 3.1 ev) with 80% transparency in the visible range. It is suitable for use in gas sensors, solar cell, and optoelectronic devices and photo catalysts in a wide range because it has a wide band gap and unique electronic and optical properties. [Paraguay-Delgado F et al (2005), Geraldo V et al (2003)]. One of the most important parameters of the semiconductor is their energy band gap. This parameter affects many of electrical and optical properties of semiconductors. The energy band gap will be changed according to changes in temperature, pressure and size of the particles. Therefore, this parameter can show new properties of the semiconductor. [Goswami, Y. C et al (2014), Gu F et al (2004)]. There are many different methods to synthesize nanoparticles of SnO_2 such as thermal solvent, micro emulsions, sol-gel, hydrothermal, spray-pyrolysis, and the non-aqueous methods. . Tin dioxide (SnO_2) has been intensively investigated because of its rich physical properties and large applications in commercial devices.

Experimental Procedure

Chemical synthesis of SnO_2 was prepared by co-precipitation method using the stannous chloride ($SnCl_2.2H_2O$) as a precursor, ammonia solution as a precipitating agent. The as-synthesized SnO_2 were heated at temperature 500ºC for 1hr. Then, SnO_2 thin films were grown on glass substrate by using sol-gel and spin coating technique. The glass substrates were ultrasonically cleaned by keeping in ethanol and in the distilled water, for ten minutes,

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respectively. Then the glass substrates were dried. The films deposited on the glass substrates by spin coating technique. In order to prepare the coating solution, firstly SnO_2 thin films by sol-gel process. SnO_2 powder was grounded by agate mortor to obtain the homogeneous and uniform grain size. This powder was heat treated at 500ºC for 1 hr. The crystalline powder, were mixed with 2-methoxyethanol solution by using sol-gel method. And then these pastes were coated on glass substrates and annealed at 400ºC, 500ºC and 600ºC for 1 hr, respectively. These three annealed samples were measured by X-ray diffraction (XRD) and UV-Visible spectroscopy.

Results and Discussion

X-ray Diffraction (XRD)

The crystal structure and crystallite size of prepared films were characterized by X-ray diffraction (Rigaku Multiflex, Japan) with CuK_α source. (λ = 1.54056Å). X-ray diffraction patterns of SnO_2 thin films on glass substrate prepared and being annealed at 400ºC, 500ºC and 600ºC was shown in Figure 1 (a ~ c). It can be noted that these prepared SnO_2 thin films are polycrystalline with tetragonal structure, the polycrystalline film with preferred growth along (110). Other peaks corresponding to the direction (101) (200) (211) and (220) compatible with the standard JCPDS data card. The lattice constant a and c for the tetragonal phase structure were determined by the relation

$$\frac{1}{d^2} = \left(\frac{h^2}{a^2} + \frac{k^2}{a^2}\right) + \left(\frac{l^2}{c^2}\right)$$

where d and (hkl) are interplanar distance and Miller indices, respectively. In order to determine the variation of crystallite size, the size of crystallites oriented along the (110) plane was calculated using Scherrer's formula,

$$L = \frac{0.9\lambda}{\beta \cos\theta}$$

where β, θ, and λ are the broadening of the diffusion line measured at half its maximum intensity in radians, the diffraction angle and the X-ray wavelength respectively. The calculated values of lattice parameters and unit cell volume were given in Table 1.Crystallite size and dislocation density were given in Table 2.Comparative XRD spectra of the SnO_2 thin films annealed at 400ºC,500ºC and 600 ºC were shown in Figure 1(d).

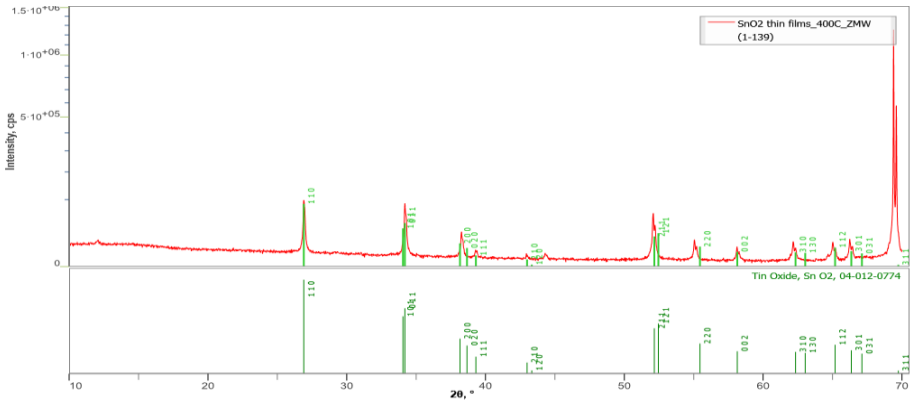

Figure 1(a) XRD pattern of SnO_2 thin films on glass substrate at annealing temperature 400ºC.

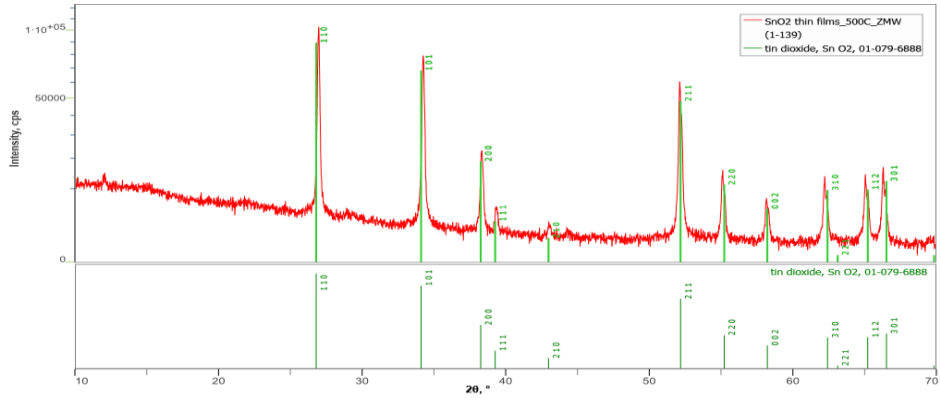

Figure 1(b) XRD pattern of SnO_2 thin films on glass substrate at annealing temperature 500ºC.

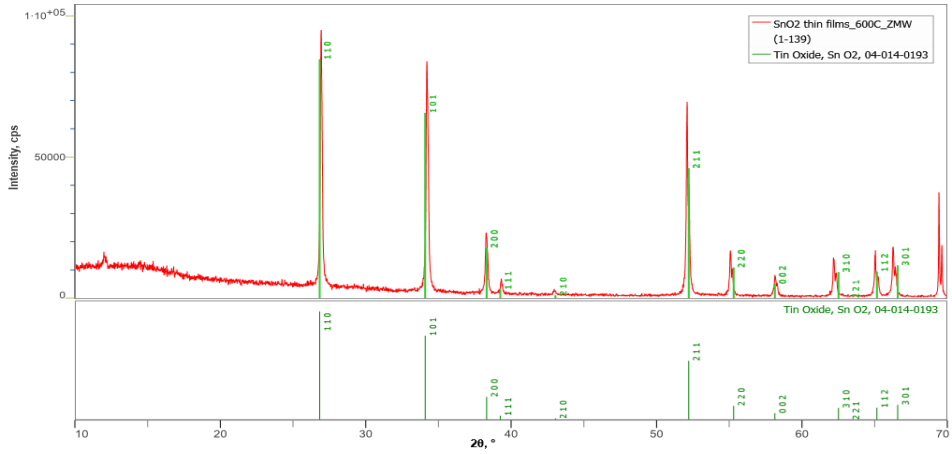

Figure 1(c) XRD pattern of SnO_2 thin films on glass substrate at annealing temperature 600ºC.

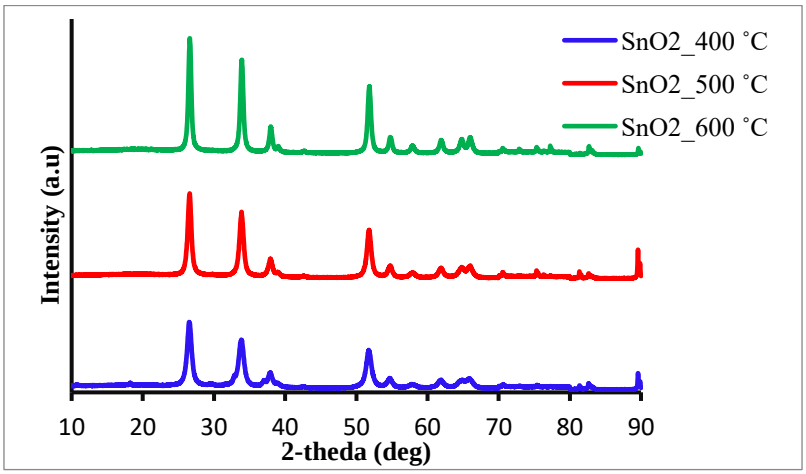

Figure 1(d) Comparative XRD spectra of the SnO_2 thin films at different annealing temperature .

Table 1. Lattice parameters and unit cell volume for SnO_2 thin films on glass substrate at different annealing temperatures.

Temperature (ºC)	Maximum Peak	Lattice Constant "a" (Å)	Lattice Constant "c" (Å)	Unit cell Volume "V" $(nm)^3$
400ºC	(110)	4.7127	3.171	0.0696
500ºC	(110)	4.7011	3.1665	0.0699
600ºC	(110)	4.6944	3.171	0.0698

Table 2. Crystallite size and Dislocation density for SnO_2 thin films on glass substrate at different annealing temperatures.

Temperature (ºC)	Maximum Peak	Crystallite Size "L" (nm)	Dislocation Density "δ" $(m)^{-2}$
400ºC	(110)	84.5477	1.3989×10^{14}
500ºC	(110)	71.3826	1.9625×10^{14}
600ºC	(110)	53.0228	3.5569×10^{14}

Ultraviolet Visible Spectroscopy (UV-Vis)

Optical transmittance spectrum

UV-Visible absorption spectroscopy was widely used tool for checking the optical properties of nanosized particles. The UV-Vis spectra were obtained by using Shimadzu UV-1800 UV-Vis spectrophotometer. UV-Vis spectroscopy was widely used to investigate the optical properties of the particles. UV-Vis spectroscopy was used to estimate the direct band gap of thin films. The optical transmittance of SnO_2 thin films deposited with various annealing temperature was shown in Figure 2 (a ~ c). The transmittance of all samples with nearly 70% transparency in the whole visible region (i.e., above 400 nm).

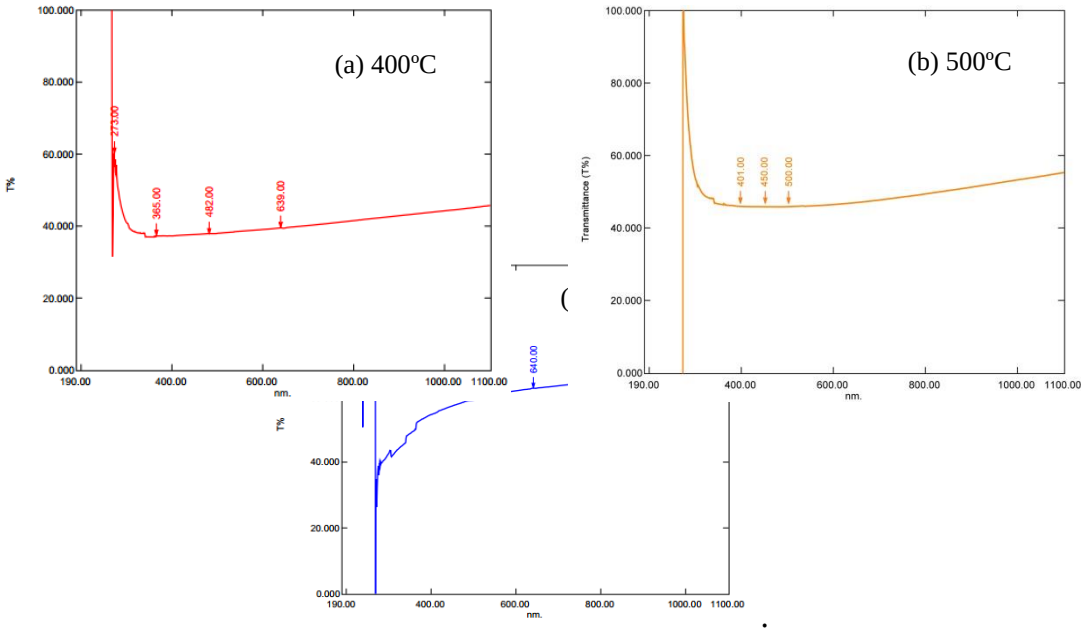

Figure (2) Variation of transmittance with wavelength of SnO_2 thin films at different annealing temperatures.

The absorption coefficient (α)

The UV- visible spectroscopy were carried out for the optical characterization. The band gap values of thin films were calculated from the UV-Visible absorption data. The absorption coefficient (α) has been calculated from equation.

$$\alpha = 2.303\ A/t$$

where α is the absorption coefficient, A is the absorbance, and t is the thickness of film. The UV-Vis absorbance spectrum of thin films at different annealing temperatures was shown in Figure 3(a ~ c).

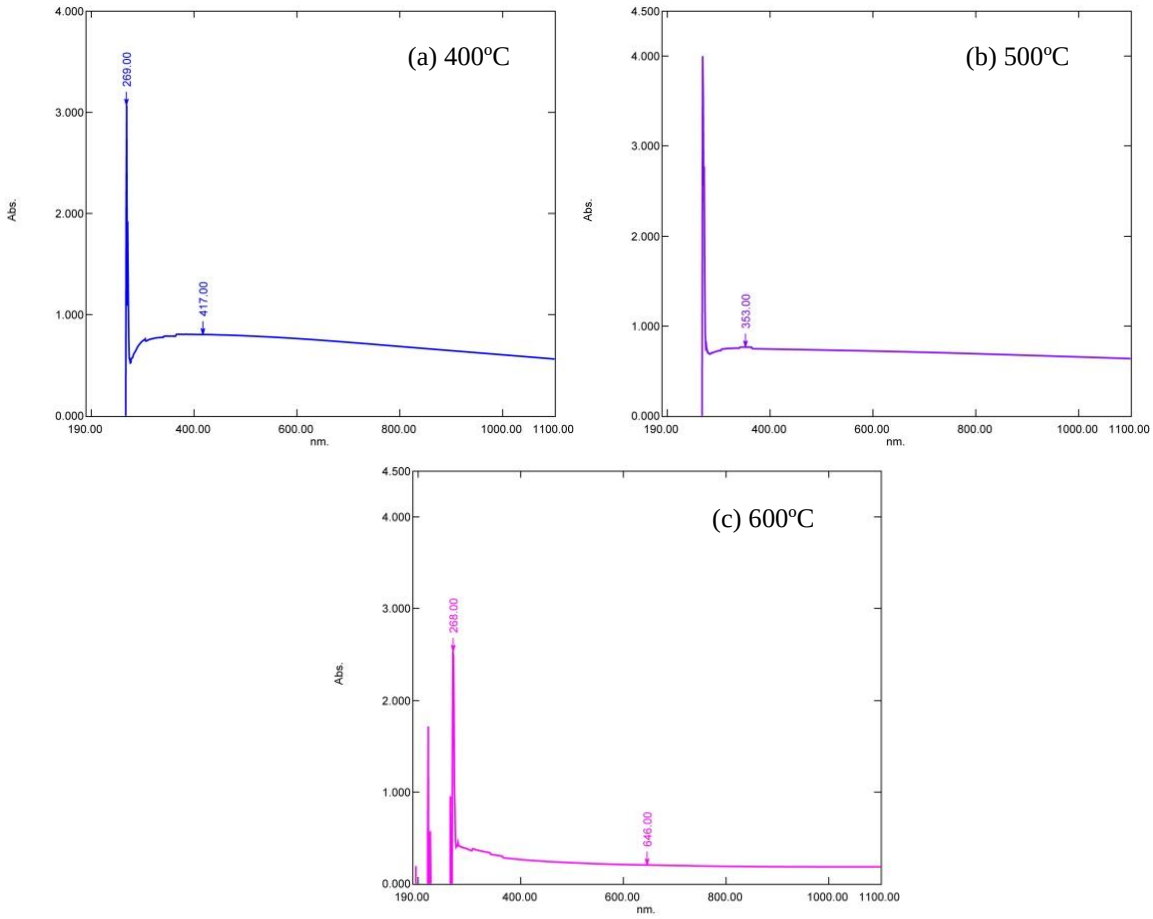

Figure 3 The UV-Vis absorbance spectrum of thin films at different annealing temperatures.

Optical energy band gap

The optical band gap energy (E_g) of the semiconductor was calculated from Tauc relation. The band gaps of these thin films were calculated from the formula

$$\alpha h\nu = A\ (h\nu - E_g)^{½}$$

where α = absorption coefficient, h = Plank's constant, ν = frequency of incident light, E_g = optical energy of the material. The E_g can be determined by extrapolations of the linear portion of the curve to the hν axis. Where A is constant, hν is the photon energy and E_g is the optical band gap. The relationship between $(\alpha h\nu)^2$ and photon energy (hν) for the SnO_2 thin films was shown in Figure 4 (a ~ c). It was observed that by increasing the annealing temperature, the band gap of the films was found to increase from 3.77 eV to 4 eV. The value of the energy band gap for each sample was shown in Table 3.

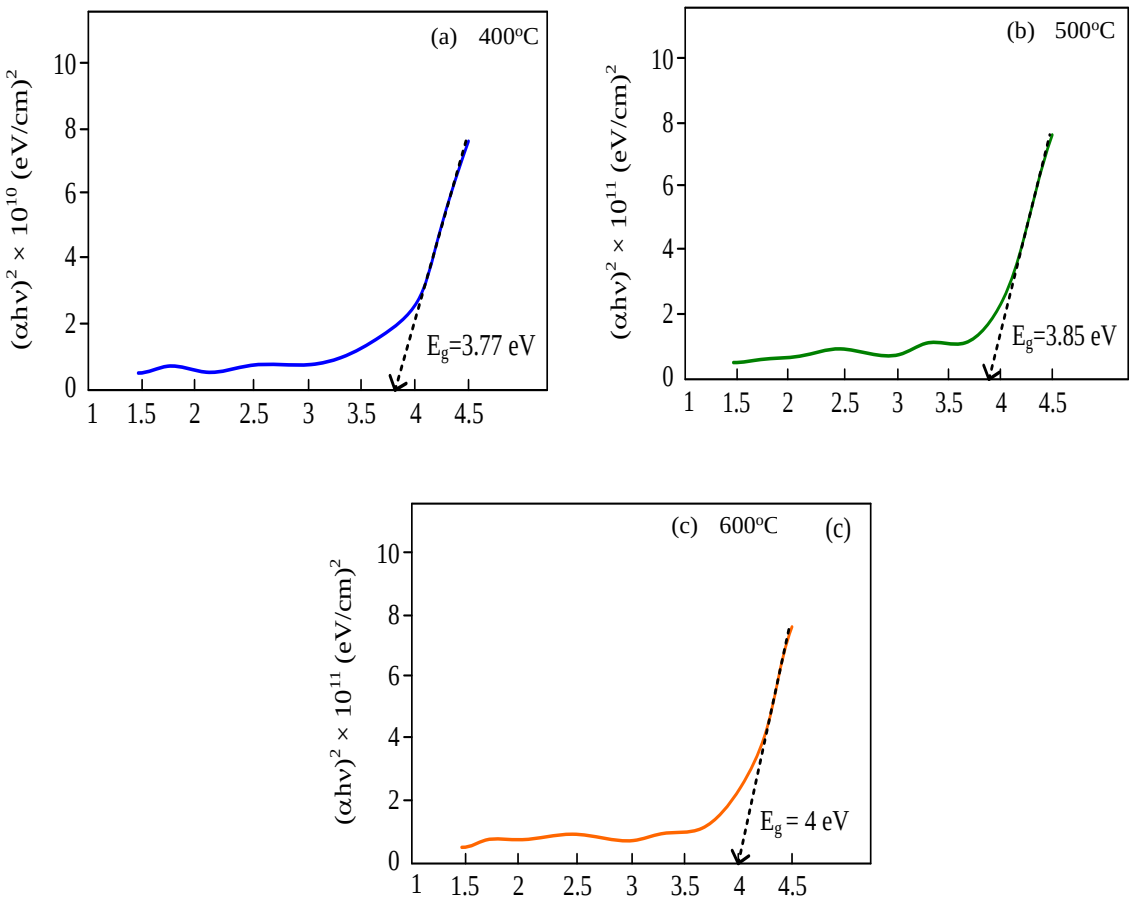

Figure 4 $(\alpha h\nu)^2$ versus photon energy of SnO_2 thin films at different annealing temperatures.

Table 3. Energy band gaps of SnO_2 thin films at different annealed temperatures.

Temperature (ºC)	Energy band Gap E_g (eV)
400ºC	3.77 eV
500ºC	3.85 eV
600ºC	4.00 eV

Conclusion

SnO_2 thin films were deposited on glass substrate by using sol-gel and spin coating technique. The structural and optical properties of the films were studied as a function of annealing temperature. The structural by XRD analysis was showed that all the samples were polycrystalline with tetragonal structure. The X-rays measurements, the lattice constant were a = b = 4.7Å and c = 3.17Å. It was also observed that these films at different annealing temperature did not change the lattice parameters. The optical transmittance of thin films was measured and the optical band gap E_g values of the films were obtained in the range of 3.77eV~ 4.00eV, using Tauc relation. The results showed that, SnO_2 thin films exhibited a promising application for solar cell fabrication.

Acknowledgements

The authors would like to acknowledge Professor Dr Tin Maung Htun, University of Yangon, for his permitting and encouragement for this work. We would like to thank Professor Dr Yin Maung Maung, Head of Department of Physics, University of Yangon, for his kind permission to carry out this work.

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