Thermal Annealing Effect of Strontium Stannate Thin Film Grown by an RF Magnetron Sputtering

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***Abstract*—Strontium Stannate ($SrSnO_3$ or SSO) thin films were deposited on the ITO substrate using an RF magnetron sputtering method. Thermal annealing has been treated to the samples by 400°C, 600°C and 800°C using a furnace. Structure evolution has been observed by X-Ray diffraction (XRD), atomic force microscopy (AFM) and ultraviolet visible (UV-VIS). A decrease full width at half maximum (FWHM) at (002) peak observed. The amplitude's reduction from 0.472 to 0.354 for as deposited and as annealed sample, respectively, indicating an improvement of crystallite size by 30%. Furthermore, an absorbed wavelength by transmittance exhibited at 380 nm and 600 nm. The energy bandgap of the annealed thin film at 400°C, 600°C and 800°C were 3.33 eV, 3.28 eV and 3.20 eV, respectively.**

Keywords*—*$SrSnO_3$, Thermal annealing, RF magnetron sputtering, energy bandgap.

I. Introduction

Strontium Stannate (SrSnO3) has been emerged as a semiconductor material that can potentially be used in wide range of optoelectronics application. The $SrSnO_3$ is also known as SSO perovskite, can be used in photovoltaic cells, light emitting diode (LED), near infra-red (NIR) emission, photo catalysis, photo sensor, power electronics and double layer transistor [1]. As perovskite is an alkaline-earth material, where an SSO crystal structure has the ABX_3 formula in SnO_3 or stannate base beside barium stannate ($BaSnO_3$) and calsium stannate ($CaSnO_3$). Along with attractive new perovskite transparent conductive oxide (TCO), SSO typically has wide bandgap over 3 eV, low resistance as low as 10^{-5} $\Omega.cm^{-1}$ and transmittance around 90% [2].

Various synthesis techniques of SSO perovskite in previous research has been reported such as thermal evaporation, mechanical grinding, co-precipitation, modified Pechini method, hydrothermal, solid state reaction and sol-gel process [3]–[5]. Muthukutty et. al. have concluded that co-precipitation was a simple, fast and handy technique to prepare the uniform structure in the range of nanometer to micron[1]. Despite using synthesis mentioned above, dry-processed RF magnetron sputtering has been considered as an effective and relatively simple technique for preparing SSO film. The sputtering equipment has been a high-priced tool due to system's complexity in conducting plasma circumstance for ion plating to substrate. Meanwhile, to improve the morphology of semiconductor material thin film, thermal treatment or annealing widely applied as typical method [6]. Gul et. al. have demonstrated annealing treatment of sol-gel processed SSO thin film[7].

In this paper, SSO thin film were deposited on an ITO glass substrate using an RF magnetron sputtering from an $SrSnO_3$-compound target under argon and oxygen atmosphere with a 1-hour deposition time. Thermal annealing was treated to the samples at different temperatures of 400°C, 600°C and 800°C by a furnace. The purpose of this study is to investigate the structure morphology, electrical and optical behaviour based on different thermal treatment temperature films..

II. Methodology

A. Thin Film fabrication

In preparation of the sample, indium thin oxide (In_2O_3:Sn) or ITO coated glass in 2 × 2 cm2 was used as a substrate. The sequential cleaning of substrate was done using acetone, methanol and de-ionized water to ITO/glass in an ultrasonic bath for 15 minutes each. The moisture of the substrate were dehumidified using a furnace in 70°C ambience. In deposition process, the RF magnetron sputtering was set up with 100W of RF power sources, frequency of 1365 Hz, chamber base pressure of 7.7×10^{-6} Torr and working pressure 5 mTorr. Pure argon and oxygen reactive gas are composed of 75% and 25%, respectively. The distance between target and substrate was set to 120 mm non perpendicular height. The target was SSO depleted compound (99.9% purity, 3 inch in diameter and 0.125 inch in thickness) by Plasmaterials. One cathode connected to RF power source was assigned and its angle of target to the base is 45° degrees. Programmable furnace Carbolite ELF-1100°C 14 L was applied for temperature treatment to the thin films. Fig. 1 depicts the process of samples annealing after RF magnetron sputtering.

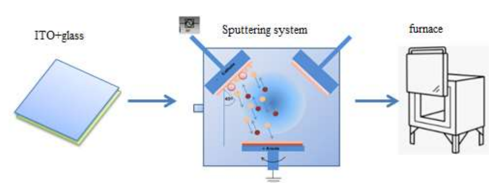


Fig. 1 ITO+glass sputtered samples annealing process

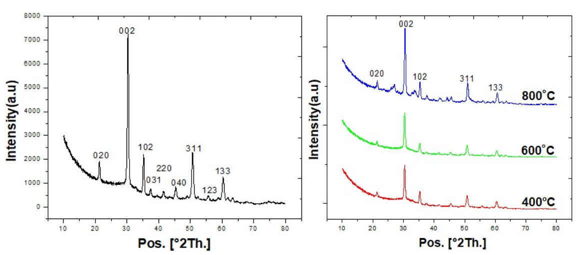
B. Measurement and Characterization

There are four samples of SSO thin films, which indicated sample 1 as-deposited, annealed sample 2 as-annealed at 400ºC, sample 3 as-annealed at 600ºC and sample 4 as-annealed at 800ºC. Each annealed samples were placed in a furnace for 1 hour. The structure of as-deposited and annealed SSO films were characterized X-Ray diffraction (XRD) employing Cu-Kα (PANalatycal X'Pert Pro XRD System, α = 0.152 nm) radiation and data analysis using X'Pert HighScore. Hitachi 5100N atomic force microscope (AFM) was used for surface morphology observation. UV-VIS Shimadzu was employed to measure transmittance at wavelength range 200-1000 nm using ITO glass as a base and four point probe Pro 4 was used for electrical properties.

III. RESULT AND DISCUSSION

A. Morphology

The XRD spectra of the prepared films are shown in Fig. 2(a) and 1(b). The polycrystalline $SrSnO_3$ films can be observed and the peaks namely (020), (002), (102), (031), (220), (311), (123) and (133) using the ICSD database. After the annealing process, as shown in Fig. 2**Error! Reference source not found.** (b) at 400ºC affects the decrease of peak (031), (220), (040) and (123). After 600ºC annealing, the enhancement of crystallinity begin to fashion, the intensity of amplitude peak (020), (102), (311) and (133) follow to decrease which means peak (002) at 2θ (=30.47) has been dominant. From an atomic perspective, the arrangement of atoms $SrSnO_3$ leads to high crystalline film. However, upper temperature at 800ºC has attracted other peaks to enhance, such as (020), (102) and (311) as compared to thermal study analysis by Mary C.F Alves et. al. which synthesized by calcination of powder. The sputtering technique shows preferable consistency of peaks appearance since as deposited. It has been reported that annealing at 700ºC, the peak (002) starts formed after amorphous phase at lower degrees by calcination technique [8]. Difficulties in forming high intensity of peaks have been reported by annealed sol-gel thin film [7].



(a) (b)

Fig. 2 (a) XRD pattern of as-deposited RF magnetron sputtered SrSnO3 on ITO substrate (b) After annealing at different temperatures

The lattice behaviour of an atom could be determined by crystallinity value parameter which can be affected by intrinsic or extrinsic factors. The crystal size usually obtained by full width at half maximum (FWHM) and Scherrer's equation [9]. Table I**Error! Reference source not found.** summarizes position 2θ, FWHM, d-spacing or interplanar spacing and crystallite size of the peak (002) for every samples only assumed without microstrain. It shows a decrase in FWHM value from as-deposited 0.472 to post-annealing 0.354. Crystallite size increases as-deposited 198.25 Å to annealed ±266.30 Å which indicated improvement of crystallinity has undergone. Improvement of crystallinity could be determined by decreasing FWHM value and increasing grain size [10].

TABLE I. CRYSTAL COMPARISON AMONG DIFFERENT ANNEALING TEMPERATURE AT (002) ORIENTATION

Sample	2θ ±0.001	FWHM ±0.001	d-spacing (Å)	Crystallite Size(Å)
As deposited	30.35	0.472	2.9444	18.21
400 ºC	30.51	0.354	2.9298	24.29
600 ºC	30.47	0.354	2.9332	24.29
800 ºC	30.46	0.354	2.9344	24.29

The AFM examined the surface morphology of the films by observation area of 1 × 1 μm^2. Fig. 3(a) depicts a 3D surface on as-deposited $SrSnO_3$ on an ITO substrate. As deposited sample has roughness (R_a) of 1.714 nm with a grain size 110 nm, and the post-annealed samples are 0.9174 nm, 1.761 nm and 4.833 nm. After annealed at 400ºC, 600ºC and 800ºC, it shows grain size 56.89 nm, 80.13 nm and 30.14 nm, respectively. The higher temperature on annealing process usually affects the increase of grain size, there was exception at 800ºC annealed sample which decreased grain size since over-limit temperature could be semi melting on the material.

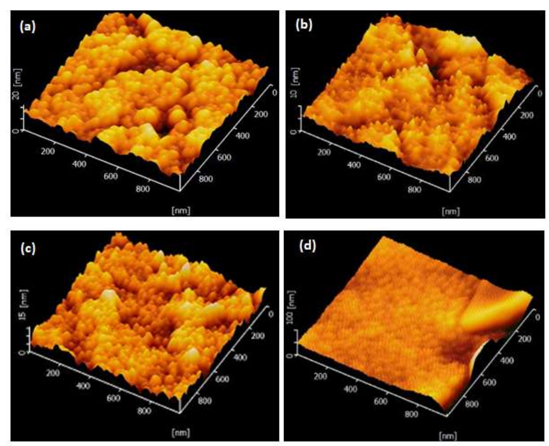


Fig. 3 3D surface topographies of SrSnO3 on different annealed film (a) as-deposited (b) 400oC. (c) 600oC (d) 800oC

Fig. 3 (b)-(d) shows post-annealed samples at different temperatures in 1 hour each using a Carbolite furnace. As depicted in Fig. , the surface of samples has undergone microstructure change. It has probably been high forced microstructure arrangement by too high temperature. Remarkably, at 800ºC, the film became smooth surface slightly different the surface change from as deposited, at 400ºC and 600ºC.

B. Electrical and Optical Properties

Fig. depicts annealing effect to resistivity of three samples with different temperatures. Generally, the resistivity of the as-deposited film decreases with annealing temperature. Thus, electrical conductivity is robustly affected by tunneling the charge carriers through the barrier of grain boundary and re-crystallization during annealing, as reported by Ahmed et. al. on (ITO) post-annealing resistivity analysis [11].

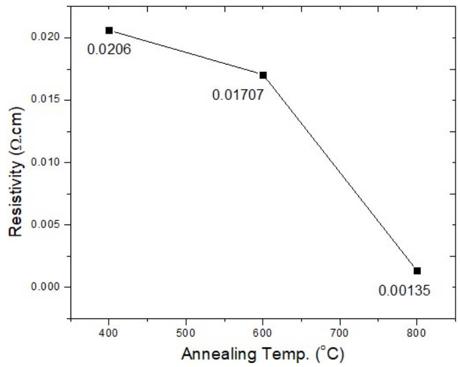


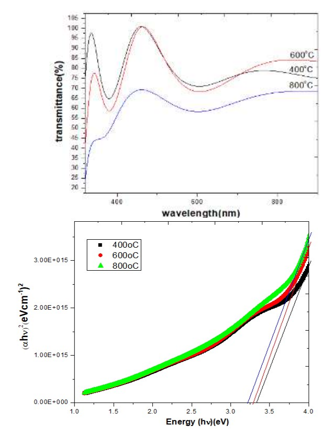
Fig. 4 Sheet resistivity of different annealing temperature

Tabel 2 summarizes the electrical and optical parameters of post-annealed samples. From Fig. 4 and Table II, the value of sheet resistivity decreases due to increasing annealing temperature.

TABLE II. SHEET RESISTANCE AND ABSORBED WAVELENGTH BASED ON TRANSMITTANCE

Post-annealed Sample	Sheet resistvity (Ω.cm)	1st Absorbed Wavelength (nm)	2nd Absorbed Wavelength (nm)
400ºC	0.0206	378	601
600ºC	0.01707	380	606
800ºC	0.00135	365	598

The intensity of light transmitted through heat-treated film was measured using UV-vis. As annealing effect, transmittance percentage of higher temperature applied was decreased and a absorbed the first wavelength shifting from 378 nm to 365 nm and second wavelength shifting from 601 nm to 598 nm as shown in Fig. 5 and Table II.



(a) (b)

Fig. 5 (a)Transmittance of SrSnO3 films by temperature treatment and (b)Energy band gap

Fig. 5(b) depicts plots of *(αhν)*^{2} vs. *hν* for SSO thin film thickness 203 nm after being heated at different temperatures for 1 hour each. The plot *(αhν)*^{2} *= f(hν)* in the observed area was linear function. By Tauc plot, the energy gap point of film annealing at 400ºC, 600ºC, 800ºC obtain 3.33 eV, 3.28 eV and 3.20 eV, respectively. Thermal treatment has shifted the width of the material energy bandgap since increasing temperature accelerate oxygen to evaporate during the process, more realigning and robust interaction between film and substrate [11], [12]. This wide bandgap (>3 eV) exhibits optical transparency with electrical conductivity [7].

IV. Conclusion

This experiment has successfully demonstrated thermal annealing treatment by three different annealed temperatures of 400ºC, 600ºC and 800ºC. By analyzing microstructure evolution using XRD data, FWHM decreased value of (002) peak has been shown by annealing process from 0.472 to 0.354 and its crystallite size has improved by 30% without microstrain assumption. The trend of their sheet resistivity showed decreasing value due to increasing temperature. The wavelength absorbed by post-annealed sample exhibits at 380 nm and 600 nm. The increasing temperature treated on the sample has implied to oxygen evaporation that affected the energy gap between conduction band and valence band approaching. The energy bandgap of annealed thin film of SrSnO3 at 400ºC, 600ºC and 800ºC were 3.33 eV, 3.28 eV and 3.20 eV, respectively. Based on their morphology and optical properties, the optimum preference was 600ºC annealed sample.

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