**TECHNICAL REPORT**

**Morphological and optical properties of tin oxide nanomaterial thin film deposited using vacuum evaporation**

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A 250 nm thick pure tin film was deposited on quartz substrates by vacuum evaporation of 99.9% pure tin metal. The films were heated in a two-step annealing sequence for 3 h at 200 and 3 h at 400 °C with an electric furnace to decrease their surface roughness. This process transformed the films into tin(II) oxide. Subsequently, the films were annealed at five temperatures for 3 h each: 600, 700, 800, 900 and 1000 °C. The crystal structure of the film on the quartz substrate was completely transformed into SnO2 at 600 °C. With the increase of annealing temperature to 1000 °C, the size of the lattices appeared to decrease on the thin film. In addition, the annealing process led to the formation of pores on the surface, but the number of pores and the lattices volume decreased with increased annealing temperature. The optical properties of the thin film were characterized by the use of visible spectrophotometry which showed a high refractive index at around 2.08–2.27. Interestingly, the SnO2 thin film with the highest refractive index at 2.27, which was obtained at 1000 °C, exhibited the lowest Urbach energy. Therefore, the SnO2 thin film has a high potential for optical applications, especially in dielectric waveguides and solar cells.

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1. Introduction

SnO2 is an n-type semiconductor material that has a high refractive index (2.006–2.486), a high transparency (43.8–75% on visible light), a high conductivity (~10^{-3} Ω cm^{-1}), and a wide bandgap (≥3.6 eV).1)–4) Because of its high performance, researchers have applied SnO2 to research areas such as gas sensor enhancement5) and the anode material of lithium-ion batteries.6)

SnO2 nanoparticles also have great potential benefit in optoelectronics applications.7)–9) They have properties that are significant to waveguide performance improvement. The surface of a SnO2 thin film composed of nanoparticles can act as a dipole layer and increase polarity and nonlinear effects.10) Moreover, SnO2 thin films have high absorbance in the visible region11) which can be utilized in solar cells. However, the film must have a very smooth surface to produce high performance in optical devices.

Researchers have tried using many techniques to fabricate thin films; these include the sol–gel method,12) chemical spray pyrolysis,13) chemical bath deposition,14) thermal evaporation, chemical vapor deposition, spin coating,15) spray ultrasonic, radiofrequency sputtering,16) RF magnetron sputtering, and vacuum evaporation. Among these techniques, vacuum evaporation is a simple method to obtain thin films which have a homogeneous and uniform surface, so it is one of the best choices for SnO2 thin film fabrication.

For this paper, SnO2 nanomaterial thin film was prepared using pure metal Sn film deposition by vacuum evaporation on quartz substrates. The SnO2 nanomaterial was obtained by oxidizing the film in the air. Moreover, the transformation from Sn to SnO2 was also analyzed by oxidizing the SnO2 film. Moreover, the transformation from Sn to SnO2 was also analyzed with respect to temperature. The study of this thermal behavior is becoming important to the optimization of material function.

The characteristics of an SnO2 thin film depend on its deposition method, temperature, duration of annealing, and substrate. When using a quartz glass substrate, tin particles do not wet the glass and form nanospheres at high temperatures. Moreover, the roughness of the surface increases when SnO transforms into SnO2 because of the separation of the spheres.17) This differs from the continuous and smoother surface of tin oxide thin film obtained when a film is deposited on the SiO2 film used by the majority of prior researchers. The smoothness for these substrates results from tin diffusion into the SiO2.

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This paper describes a tin oxide thin film on quartz glass obtained with a three-step annealing process to reduce surface roughness.

2. Experimental procedure

2.1 Substrate preparation

Although the quartz substrates were precleaned, the substrates, which have an area of 5 × 5 mm and a thickness of 1 mm, were cleaned further to reduce or even eliminate some scratches due to surface friction with other objects, dust, and other residues. The cleaning procedure was also needed to get optical smoothness of the substrates for the optimal condition of films. The substrates were washed in ethanol using ultrasonication at 28, 45, and 100 kHz for 20 min sequentially. Then, the surfaces were blown at high pressure to remove dust and dried on a hot plate at 90 °C for 10 min.

2.2 Vacuum evaporation setup

Tin thin films were produced using 99.9% ultra-pure tin metal wire (Nilaco) with a diameter of 0.5 mm in a vacuum evaporation process. The wire was cut into pellets and placed in a tungsten boat. The boat was placed about 15 cm below the substrates in a vacuum chamber. The vacuum chamber pressure was reduced to 1.5 × 10⁻⁵ Torr prior to the start of deposition. The Sn pellets were vaporized by gradually increasing the current through the tungsten boat to 90 A and keeping it there for 1.5 min. The Sn metal boiled and reached the surface of the substrates at that time.

2.3 Thermal oxidation technique

SnO₂ films were prepared by the thermal oxidation of pure Sn thin films. The Sn thin films were annealed in three steps in the air using an electric furnace to avoid film surface deformation with rising temperature. In the first step, the temperature was raised at 1 °C/min to 200 °C and held there for 3 h. In this step, the surface of the thin films was slightly melted for smoothness. For the second step, the melted Sn films were oxidized to become Sn(II) oxide from the oxygen in ambient air while the films were heated at 1 °C/min to 400 °C and kept there for 3 h. Finally, the films were oxidized at each of the temperatures 600, 700, 800, 900 and 1000 °C; they reached each temperature at a rate of 1 °C/min and were held there for 3 h. This step transformed the Sn(II) oxide films into Sn(IV) oxide films through all annealing temperatures.

2.4 Film characterization method

The prepared SnO₂ thin films were measured using X-ray diffractometry (XRD- XRD-Ultima IV, RIGAKU) with Cu-Kα as an X-ray source to evaluate their structural features. Their surface morphology was examined by means of optical microscopy (OM-KH8700, HIROX) while detailed surface analysis of particles was performed using a field emission scanning electron microscope (FESEM- JEM-7600F, JEOL) with an acceleration voltage of 5 kV. In order to measure the refractive indices of the thin films, a prism coupler (SPA-4000, SAILOR TECH. inc.) was employed. Moreover, the SnO₂ optical properties were also represented by transmittance spectra and its Urbach energy vs. wavelength as measured by visible spectrophotometry (N2S type). Urbach energy is an important factor in the investigation of the optical properties of a material because of its dependence on the optical band gap. During observation using spectrophotometry, the samples were placed as shown in Fig. 1.

3. Results and discussion

As discussed in Section II, a homogeneous thin film of tin with a thickness of about 250 nm was deposited on quartz substrates. The XRD patterns of the crystal phases formed at each annealing temperature were compared with the International Centre for Diffraction Data (ICDD) patterns of Sn, SnO and SnO₂ (Fig. 2). After annealing at 200 °C, the tin metal hadn’t oxidized. This Sn phase had a tetragonal structure and its diffraction peak detected at a 2θ of 30.54° corresponded to (200) diffraction according to the data file of ICDD 00-071-4638. A weak Sn peak was also observed corresponding to (400) diffraction at a 2θ of 63.69°.

The thermal oxidation process began at 400 °C. It can be seen in the XRD patterns that correspond with the data of ICDD 00-072-2324. The Sn(II) oxide peak detected at a 2θ of 32.34° corresponds to (011) diffraction; the peak at 34.18° corresponds to (200) diffraction according to the data file of ICDD 00-071-4638. A weak Sn peak was also observed corresponding to (400) diffraction at a 2θ of 63.69°.

The crystal structure of the film on the quartz substrate was fully transformed into SnO₂ at 600 °C via reaction (2). The film’s XRD patterns have two peaks which correspond to the ICDD patterns of tetragonal SnO₂; 00-003-1116. In this database, there are two peaks in the (110) plane at a 2θ of 27° and (101) plane at 34.2°. Herein, the peaks were shifted from the reference peak. For example, the former peak was shifted to 26.98° at 600 °C. The difference of 0.02° isn’t significant in this study.

\[
\text{Sn} + \frac{1}{2} \text{O}_2 \rightarrow \text{SnO} \quad (1)
\]
\[
\text{SnO} + \frac{1}{2} \text{O}_2 \rightarrow \text{SnO}_2 \quad (2)
\]

The crystallite sizes (D) of SnO₂ are calculated with Scherrer’s formula given by:

\[
D = \frac{k\lambda}{\beta\cos\theta} \quad (3)
\]

where \( k \) is Scherrer’s constant (0.94 for full width at half maximum (FWHM) of spherical crystallites with cubic symmetry), \( \lambda \) is the applied X-ray wavelength (1.540598 Å for the Cu-Kα used in this study), \( \beta \) is the FWHM of XRD peak at the ICDD pattern.
peaks, and θ is taken from the diffraction peak position 2θ. The SnO₂ crystallite size was smallest at 800 °C and was largest at 700 °C (Fig. 3). This difference seems to depend on the disappearance of (202) diffraction at 800 °C. We will try to evaluate the residual stress on the film from 2θ-sin²φ plots in future work. The increase in crystallite size between 800 to 1000 °C could contribute to stress relaxation.20)

By comparing the inset scanning electron microscope (SEM) images with optical microscope (OM) images (Fig. 4), it can be seen that the size of the aggregated particles on the SnO₂ thin film surface apparently decreased with the increase in annealing temperature up to 1000 °C. During this annealing process, the pore fraction on the surface of the films gradually decreased with increasing annealing temperature through the well-known surface diffusion and grain boundary diffusion mechanisms of sintering (Fig. 5). The diffusion effect appeared and the pores disappeared at 1000 °C. Pore surface behavior during the sintering process was simulated by Lifeu Du et al. (2018). The simulation showed that shrinkage of pores was caused by diffusion during sintering.21)

The temperature dependence of lattice volume is quite similar to the lattice constant of a-axis (Fig. 6). On the other hand, the lattice constant of c-axis was slightly expanded at 1000 °C. However, this expansion could be ignored because it does not appear as the change in the lattice volume.

The particle sizes of the SnO₂ were calculated based on the SEM images of Fig. 4. In general, crystallites are smaller than particles because particles are composed of crystallites. Therefore, the relative sizes of the two are reasonable (Fig. 6).

The optical properties of tin(IV) oxide thin films are represented by the refractive index measured by prism coupler (Fig. 5). The value of the refractive index gradually increased with increasing annealing temperature. Non-uniformity of film thickness affects the measurement of film spectra. This is related to the pores produced during thermal treatments which can scatter laser beams during prism coupler observation. A continuous thin film surface without pores can have increased surface density and obtain a high refractive index which apparently happened to the thin film annealed at 1000 °C. At the 700 °C annealing temperature, the samples have the lowest refractive index, corresponding to the largest crystallite size which can increase film reflectance.15) The refractive index can also be affected by a higher light velocity through the material due to the larger distance between particles.

The optical transmittance of the SnO₂ thin films was measured for each of five annealing temperatures in wavelengths ranging from 350 to 800 nm (Fig. 7). The discontinuities in the transmittance trends at the 360, 450, and 580–600 nm wavelengths are due to prism changes. Overall, the optical transmittance of SnO₂ thin film increases with increasing light wavelength. This agrees
with previous research about these films. The sample transmittance is highest at about 27 and 29% in the near-infrared (IR) region for 600 and 800 °C, respectively.

The sample annealed at 1000 °C has the lowest percentage of transmittance at about 4.5% in the near IR; this is because its continuous surface has a high density, decreasing the transmitted light. In addition, lower transmittance indicates less scattered light in the substrate because refractive index contrast with substrate. This characteristic is required for SnO\textsubscript{2} thin films used as optical dielectric waveguide core materials in optoelectronics applications.

The absorbance of a thin film can be calculated from its transmittance percentage using (4):

$$A = 2 \cdot \log_{10} \frac{1}{T^2}$$

where $A$ is absorbance. Using this calculation, the absorbance edge will be shifted into shorter wavelengths. It is comparable to the previous research by Huda et al. in which it was reported that the peak of the absorbance spectra of SnO\textsubscript{2} thin oxide is in the 250–300 nm ultraviolet (UV) range. Unfortunately, the absorbance in this research was only observed in the visible range. In this study, contrary to the percentage of transmittance, the sample at the annealing temperature of 1000 °C has the highest absorbance peak at about 2 in the UV range (Fig. 8). The transmittance values are higher than those of commercial solar cells in previous research. This property indicates that the sample has a high ability to absorb light and meets the requirements for solar cell material.
Additional investigation into Urbach energy was undertaken using visible spectrophotometry. The Urbach energy of SnO₂ thin films annealed at 600 to 1000 °C was measured at wavelengths ranging from 350 to 1100 nm (Fig. 10). Urbach energy appears due to the disorder in thin films. It depends on the structural defects, dislocations density, and defects in the vacancy and interstitial states of the films. The lattice strain was calculated by using the Williamson-Hall equation with the parameters from the XRD observation. The equation indicated lattice strain inversely proportional with crystallite size. Peak values of Urbach energy variation (where the highest peak in the energy spectrum have been obtained in wavelength of 750 nm) correspond to absolute value of the lattice strain (Fig. 9). The results are in agreement with Kumar et al. that Urbach energy is essentially controlled by the strain field due to the structural disorder of material. In semiconductor and ionic crystals, Urbach energy is obtained as a result of Wannier-Mott exciton smearing. This value corresponds with transmittance and absorbance in the same wavelength. When Urbach energy decreases the transmittance will decrease and the absorbance increases. This tendency related with crystallite effect to transmittance.
It can be demonstrated by the sample at a temperature of 700°C. While at temperatures of 600, 800, and 900°C which have almost same energy Urbach peak showed same transmittance and absorbance at wavelength of 750 nm. The highest Urbach energy coincides with the highest optical transmittance for the 800°C annealing temperature with an energy of about 334.3 meV; the lowest energy was obtained for temperature 1000°C at about 50 meV. This shows that the thin films annealed at 1000°C have minimal disorder.

4. Conclusions

The tin(IV) oxide thin films were fabricated by vacuum evaporation and thermal oxidation of pure tin films on quartz substrates. XRD observations showed that the pure tin transformation to orthorhombic SnO₂ begins at an annealing temperature of 400°C and completes the transformation to tetragonal SnO₂ at 600°C. The crystallite size of SnO₂ increased with increasing temperature. The morphology of the surface from OM observations showed that the higher annealing temperatures decreased the sample surface roughness. The thermal oxidation process generated surface pores on the sample but they decreased at the higher annealing temperatures. The optical properties of the thin film were characterized with visible spectrophotometry which showed a high refractive index at around 2.08–2.27, a low transmittance from 1000°C annealing, and a high optical absorbance of about 2 in the UV range. The absorbance is higher than that found in commercial solar cells in previous research. The SnO₂ thin films fabricated in this work successfully produced a homogeneous cassiterite tetragonal thin film for potential optical applications, especially in dielectric waveguides and solar cells.

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