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Effect of Pyrolysis Temperatures on the Electrostatic Spray-Deposited SnO_2 Layers

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Abstract:

Tin oxide (SnO_2) thin films were prepared on soda-lime-silica slide glass substrates by a cost-effective electrostatic spraying deposition process at a different pyrolysis temperatures. As-deposited films were pyrolyzed at 150°C, 250°C and 400°C for 30 min in air flow, followed by final heat treatment at 550°C for 30 min in argon. Crystal structure, surface microstructure, transmittance at visible spectral range and resistivity were analyzed by X-ray diffractometer, field emission-scanning electron microscopy, scanning probe microscope, UV-vis-spectrophotometer and Hall measurements, respectively. Highly-transparent films exhibited nanocrystalline SnO_2, which was in tetragonal system with a rutile-type structure. Microstructure and electrical properties of the films were found to strongly depend on pyrolysis temperature.

Keywords **—SnO2 film, Electrostatic spraying, Nanocrystalline, Pyrolysis**

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I. INTRODUCTION

Tin (IV) oxide is an oxygen-defect type of semiconductor with a wide band gap (3.7 eV) and a high mobility. The compound is transparent in the visible spectra range and reflective in the infrared region [1, 2]. It crystallizes in the tetragonal rutile type of structure, $P4_2/mnm$ with twin Sn and 4 oxygens per unit cell. The lattice parameters are $a = b = 0.4737$ nm, $c = 0.3186$ nm and $c/a = 0.6726$ nm. An important property of SnO_2 is that is the most chemically stable in atmospheric ambient amongst the other metal oxides [3]. The unique physical properties of SnO_2 thin films have allowed its promising in applications for various devices, such as gas sensors, liquid crystal displays, transparent conducting oxide (TCO) electrodes, and solar cells [4, 5].

Various processing routes, both physical and chemical deposition methods, have been utilized to prepare SnO_2 thin films, including pulsed laser deposition, radio frequency sputtering, a sol-gel process, spray pyrolysis, electron beam evaporation and plasma enhanced chemical vapour deposition [4-6]. Among several techniques used to obtain high-quality SnO_2 films, spray pyrolysis represents the less expensive alternative, since it can be produce larger area, high-quality and low cost thin films [2].

The authors suspected that the films might be excessively locally heated to high temperatures because organic compounds that decompose during the prefiring are rapidly burned out. This may cause random nucleation and heterogeneous crystal growth. Thus, comparison between the prefiring-temperature was considered to be important in order to achieve homogeneous nucleation resulting in high-quality films.

In order to develop high-quality SnO_2 thin films for devices with good performance, it is necessary

to clarify the effect of heating conditions on growth. In this work, prefiring temperatures were varied in order to clarify the effect of organics on the properties of films.

II. EXPERIMENTAL PROCEDURE

Stannous chloride ($SnCl_2 \cdot 5H_2O$) (10g) was dissolved in 6 mL of concentrated hydrochloric (HCl) acid by heating at 90°C for 10 min. The transparent sol was then diluted with methanol and 2-methoxy ethanol to form the starting solution.

Deposition of films was performed using an electrostatic spraying method with a vertical configuration. The details of the setup used have been reported before [7]. A stainless steel needle (0.1 mm and 0.23 mm inner and outer diameter, respectively) was connected to a syringe pump (KD 200, KD Scientific Inc., U. S. A.) using a silicon rubber tube. The flow rate of a starting sol was kept at 0.05 mL/60min. In order to obtain a stable cone-jet mode of electrostatic atomization, a high voltage (20 kV) was applied between the needle tip and ground electrode using a DC power supply. Soda-lime-silica glasses cleaned in a H_2O_2 solution, and rinsed in methanol were used as substrates. Substrates on the ground electrode were heated at 150°C for 30 min in air. A precursor sol was pumped through the nozzle which was placed 20 cm above the substrates.

As-deposited films were prefired at 150°C, 250°C and 400°C for 30 min in air. Pyrolyzed films were finally annealed at 550°C for 30 min in argon, followed by fast cooling to room temperature.

Annealed films were characterized by high resolution X-ray diffractometer (HRXRD, X'pert PRO, Philips, Netherlands). Surface morphology of the films was investigated by field emission scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan) and scanning probe microscope (SPM, XE-200, PSIA, Korea). Optical properties were measured using UV-Vis-spectrophotometer (CARY500 Scan, Varian, Australia). The electrical studies were carried out Hall measurements (HL5500PC, Accent Optical, U.S.A.).

III. RESULTS AND DISCUSSION

Fig. 1 shows TGA curve of the precursor used in this work. A larger weight loss corresponding to evaporation of organics in the sol began around 150°C and was completed about 400°C. TGA curve of the precursor sol (heating rate: 2°C/min) showed large weight loss due to the vaporization and pyrolysis of organics were recognized in the stage of pyrolysis at 150 ~ 300°C. As seen in Fig. 1, the temperatures 150°C and 250°C correspond to the initial stage and the intermediate stage of the pyrolysis. The weight decrease at 150°C was found and weight loss about 0.7 mg was obtained. This value is very smaller than that 2.75 mg by gradual heating to 400°C. So a larger amount of organics is supposed to still remain in the precursor film after pyrolysis at 150°C.

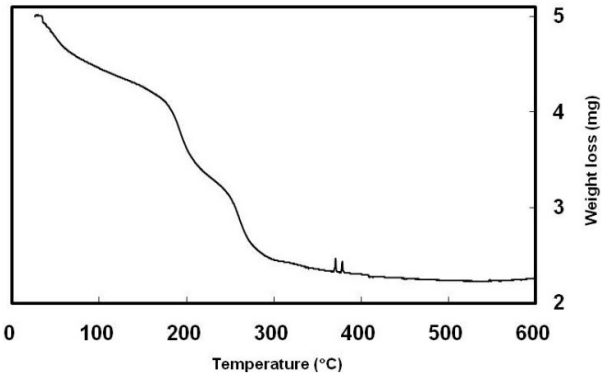

Fig. 1 TGA curve of the precursor sol.

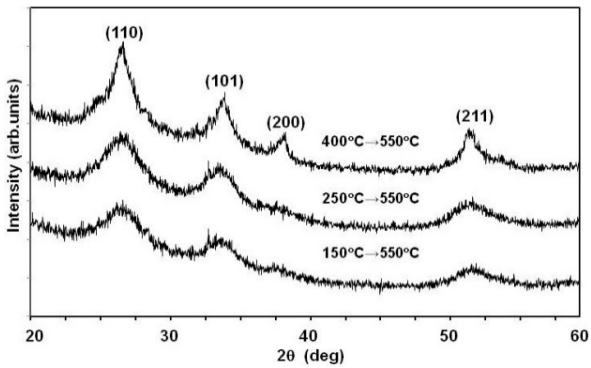

Fig. 2. XRD patterns of annealed SnO_2 films as a function of pyrolysis temperatures.

The precursor films, pyrolyzed through the three annealing paths, were found amorphous by XRD and smooth surfaces without cracks or voids by FE-SEM observation and significant difference was not recognized between these films. There were differences, however, about the content of residual volatile organics in the precursor films, as shown in Fig. 1.

Fig. 2 shows XRD spectra of the films pyrolyzed at 150°C, 250°C and 400°C, followed by final annealing at 550°C. Based on these XRD analyses, the films are polycrystalline in nature and consisted of a single phase of SnO_2(cassiterite) with the rutile structure. The films pyrolyzed at 150°C and 250°C have little crystallinity with a broad (110) and (101) reflections, whereas thatpyrolyzed at 400°C exhibits a better crystallinity. It should be noted that the peak intensity of films was significantly affected by pyrolysis temperature although the final annealing temperature was the same. The lower peak intensity of resultant film pyrolyzed at 150°C and 250°C may be attributed to the presence of residual organic components. The above result of TGA indicated that the film pyrolysis at low temperature is assumed to contain some residual organics. In this case, crystallization of film and decomposition of organic components concurrently proceeded during final heat treatment [8]. Crystal growth may be suppressed by residual organic components during the final heat treatment, resulting in lower peak intensity of film pyrolyzed at low temperature.

FE-SEM photographs of the free surfaces of the films are shown in Figs. 3 (a) and (b). Distinct grain structure of the film pyrolyzed at 400°C, while the surface of the film pyrolyzed at 150°C was smooth and no observed texture.

In order to elucidate surface roughness and morphology of the films according to pyrolysis temperature, SPM analysis was performed. SPM images for the films pyrolyzed at 150°C and 400°C are shown in Figs. 3 (c) and (d), respectively. The surface of film pyrolyzed at 400°C was wholly covered with many grains, while that of the film pyrolyzed at 150°C had a relatively low surface roughness. At 400°C, the surface roughness of the film had increased greatly due to a larger amount of grain growth, resulting in a higher root mean square (RMS) roughness. This may be attributed to the effect of the residual organics in the film pyrolyzed at 150°C, e.g., which suppresses excessive grain growth and creates a reducing atmosphere in the final heat treatment. Crystal growth may be suppressed by theresidual organics during the final annealing for the film pyrolyzed at 150°C [8].

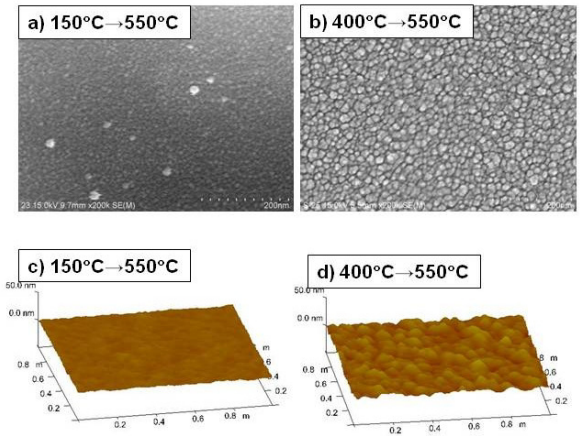

Fig. 3. FE-SEM and SPM images of the films pyrolyzed at 150°C [(a) and (c)] and 400°C [(b) and (d)].

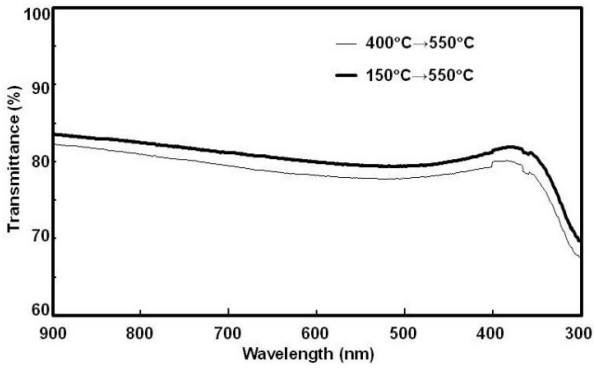

Fig. 4. Transmittance at visible spectral range of the SnO_2 films on soda-lime-silica slide glass substrates pyrolyzed at 150°C and 400°C, followed by final annealing at 550°C.

UV transmission measurements were carried out for optical characterization of the films. Fig. 4 shows the visible spectra in the wavelength range from 300 nm to 900 nm of films annealed at 550°C on glass substrates. A relatively high transmittance on the visible spectral range was obtained. The high

transmittances of the films are attributed to the small particle size which eliminates light scattering [9]. The transmittance in the UV spectral region decreased abruptly near 380 ~ 300 nm, resulting from band-to-band transition. In this transition, UV absorption occurs due to the excitation of electrons from the filled valence band to the conduction band.

As shown in Fig. 4, a comparison of transmittance spectra between the films treated at different pyrolysis temperatures shows a red shift in the pyrolyzed film at high temperature. Generally, band gap widening with the increasing defects and carrier concentrations could be explained by Burnstein-Moss effect due to a shift in the Fermi level caused by a high intrinsic electron density [10]. Nonstoichiometry may increase the defect concentration or alter the crystalline structure. We assume that this widening of the banding gap with decrease of the pyrolysis temperature may be originated by residual organics in the pyrolyzed films, resulting in nonstoichiometry of the finally annealed films, although further research will be needed to identify precise defect concentration.

TABLE I
RESISTIVITY, CARRIER CONCENTRATION AND MOBILITY OF THE FINALLY ANNEALED FILMS AS A FUNCTION OF PYROLYSIS TEMPERATURES

Pyrolysis temp. (°C)	Resistivity (Ω·cm)	Concentration (cm^{-3})	Mobility ($cm^2/V·s$)
150	3.53×10^{-2}	-3.8×10^{-19}	12.78
250	0.89×10^{-2}	-2.7×10^{-19}	12.93
400	4.84×10^{-3}	-4.7×10^{-18}	14.82

The effects of the pyrolysis temperature on the carrier concentration, the mobility and the resistivity are summarized in Table 1. Table 1 suggests that the films pyrolyzed at 150 ~ 400°C are typical n-type conducting, with carrier concentration as high as from -3.8×10^{-19} to -4.7×10^{-18} cm^{-3}. The carrier concentration increases as the pyrolysis temperature increases. The pyrolysis temperature dependence of electrical property can be explained by considering the existence of donors (intrinsic defects such as oxygen vacancies and tin interstitials) in the films [11]. Based on the results of transmittance and electrical measurements, the resistivity decreased with an increase of pyrolysis temperature from 150°C to 400°C. Further, the increases of mobility with the increases of pyrolysis temperature can be explained as due to the grain boundary scattering effect reported by Shanthi et al [12]. As shown in Fig. 3, the increase of grain size as the pyrolysis temperature increases the grain boundary scattering of the electrons.

IV. CONCLUSIONS

Transparent and conductive tin oxide thin films were prepared using electrostatic-spraying method. With increasing the pyrolysis temperature from 150°C to 400°C, XRD results showed the films were the rutile structure and the crystallinity of the film increased with increasing pyrolysis temperature. The surface of film pyrolyzed at 400°C was wholly covered with many grains, while that of the film pyrolyzed at 150°C had a relatively low surface roughness. Experimental results showed that the pyrolysis temperature allowed tocontrol the grain size and electrical resistivity of the SnO_2 thin film.

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