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Ceramics International 34 (2008) 1051–1054
CERAMICS INTERNATIONAL
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Tin oxide thin films deposited by ultrasonic spray pyrolysis

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Available online 7 October 2007

Abstract

This study investigated microstructure of SnO_2 thin films deposited by ultrasonic spray pyrolysis technique using 0.2 M of $SnCl_4{\cdot}5H_2O$ in absolute ethanol as a precursor. The deposition temperature (350–450 °C) and time (20–90 min) were varied. The influence of film-deposition conditions on grain size and orientation were discussed. The deposited SnO_2 films were textured polycrystalline films. The preferred orientation of SnO_2 films were quantitatively evaluated by texture coefficient (TC). The mean grain size and film thickness determined by SEM could be controlled over a range of 50–325 nm and 80–2690 nm, respectively.
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Keywords: A. Films; A. Grain growth; B. Grain size

1. Introduction

For metal oxides deposition (e.g., SnO_2, ZnO, In_2O_3, WO_3, etc.), the pyrosol process is a method of films deposition on a heated surface based on aerosol produced by ultrasonic atomization. The main advantages of this method over other methods (e.g., vacuum sputtering, spin coating, etc. [1–3]) are its ease of operation, low cost and the quality of coating obtained. Under certain conditions, pyrosol process could be assimilated to a chemical vapour deposition (CVD) method, but it removes restrictions of the CVD such as high vapour pressure and thermal stability of precursor.

Tin oxide is a wide band gap n-type semiconductor (E_g = 3.6 eV at 300 K) where inherent oxygen vacancies act as an n-type dopant [4]. Tin oxide films are attractive for several optoelectronic devices, hybrid microelectronics, solar energy [5] and gas sensor applications [6].

For polycrystalline thin film, structural parameter that influenced the sensing properties can be both size and orientation of the crystallites [7]. However, from the reports till now, structure–sensitivity relationship is not reviewed.

The main objective of this preliminary work is to characterize both crystalline size and texture of SnO_2 films deposited by an ultrasonic spray pyrolysis technique. In addition, the dependence of film deposition condition on its structure is investigated. This information would be an important parameter for understanding the effect of film structure on gas sensitivity.

2. Experimental procedure

The films were deposited on glass substrates (Soda lime glass, 5 cm × 5 cm × 2 mm) by ultrasonic spraying from solution of 0.2 M $SnCl_4{\cdot}5H_2O$ (*Puriss grade*, RDH), in absolute ethanol. Before the deposition, the substrates were cleaned subsequently with toluene, acetone, hot diluted HCl and de-ionized water. The pyrosol equipment essentially consists of a pyrosol generator and a pyrolysis chamber. Within the pyrosol generator, the starting solution was separated from a piezoelectric transducer (900 kHz) by a thin non-permeable film. The transducer produces an aerosol from the solution which transported by air (110 mL/min) onto a heated substrate (350–450 °C) where pyrolysis and film deposition occur. The deposition time was varied between 20 and 90 min for each deposition temperature. Schematic diagram of the set up was shown in Fig. 1.

The structure, surface morphology, and film thickness of deposited SnO_2 films have been investigated. The crystalline structure was characterized by means of X-ray diffraction (XRD, model D8 Advance, Bruker AG) technique. The preferred

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0272-8842/$34.00. Published by Elsevier Ltd and Techna Group S.r.l.
doi:10.1016/j.ceramint.2007.09.096

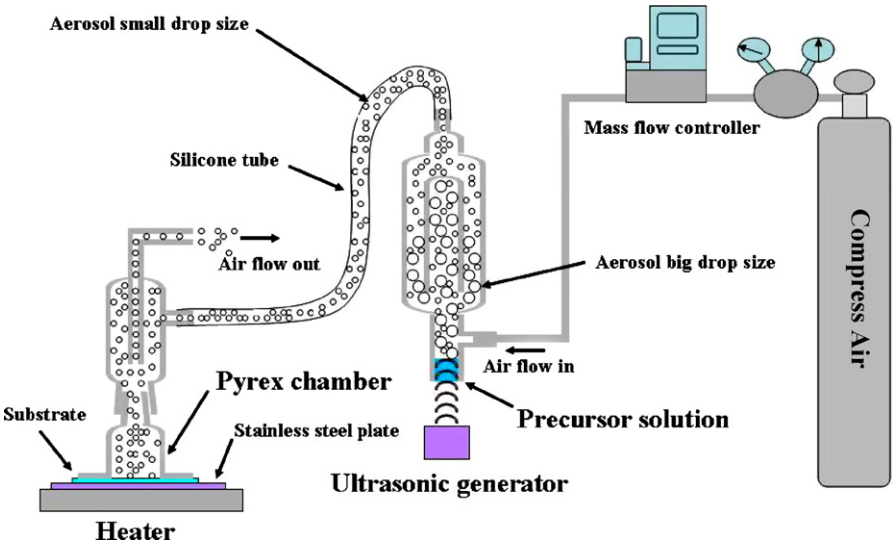

Fig. 1. Schematic diagram of ultrasonic spray pyrolysis set up.

orientation of SnO_2 films was qualitatively evaluated by calculating the texture coefficient (TC) as described below [8].

$$TC_{(hkl)} = \frac{I_{(hkl)}/I_0}{1/N\left[\sum_{i=1}^{N} I_{(hkl)}/I_0\right]} \quad (1)$$

where TC is the texture coefficient of the (*hkl*) plane, $I_{(hkl)}$ is the relative intensity measured, $I_{0(hkl)}$ is the relative intensity of the standard tin oxide powder (cassiterite, ASTM card: 41-1445), and N is the reflection number of significant peaks. The grain size, surface morphology and film thickness were analyzed by scanning electron microscope (SEM, JSM-6301F, JEOL).

3. Results and discussion

3.1. Structural characterization

XRD spectra of SnO_2 films are shown in Figs. 2–4. The experimental results indicate that at mild pyrolysis deposition temperature (T_{dep} ~350 °C), the SnO_2 films are amorphous or may well be composed of highly dispersed small crystallites. As the deposition temperature increases (T_{dep} ~400–450 °C), peaks for polycrystalline SnO_2 appear in XRD spectra. The peaks are characteristic of the cassiterite phase.

The XRD spectra of SnO_2 films show predominant reflections from the crystallographic (2 0 0), (1 1 0), parallel to substrate, or (3 0 1), as observed in previous work [9]. The intensities of the reflections from other main planes of cassiterite (1 0 1), or (2 1 1) are small. This indicates that the films have texture (or preferred orientation). The degree of texturing depends on both of deposition temperature and film thickness. For (2 0 0) plane, it is larger for the films deposited at 400 °C, as compared to that of 450 °C. With this result, the SnO_2 film with (2 0 0) preferred orientation could be prepared by ultrasonic spray pyrolysis. The preferred orientation of SnO_2 films are also qualitatively evaluated by texture coefficient and reported in Table 1. The TC value larger than unity indicated preferred orientation of such particular plane.

Table 1
The influence of SnO_2 film thickness on $TC_{(hkl)}$

Reflection (*hkl*)	$TC_{(hkl)}$											
	350 °C				400 °C				450 °C			
	80 nm	125 nm	140 nm	170 nm	220 nm	390 nm	595 nm	1450 nm	330 nm	680 nm	920 nm	2690 nm
110	–	–	–	–	–	–	0.19	–	1.20	0.66	0.31	0.46
101	–	–	–	–	–	–	–	0.61	0.80	0.44	0.54	0.53
200	–	–	–	–	–	–	1.81	2.02	–	2.00	1.33	2.13
211	–	–	–	–	–	–	–	0.37	–	0.90	0.93	0.68
310	–	–	–	–	–	–	–	–	–	–	–	–
301	–	–	–	–	–	–	–	–	–	–	1.89	1.21
400	–	–	–	–	–	–	–	–	–	–	–	–

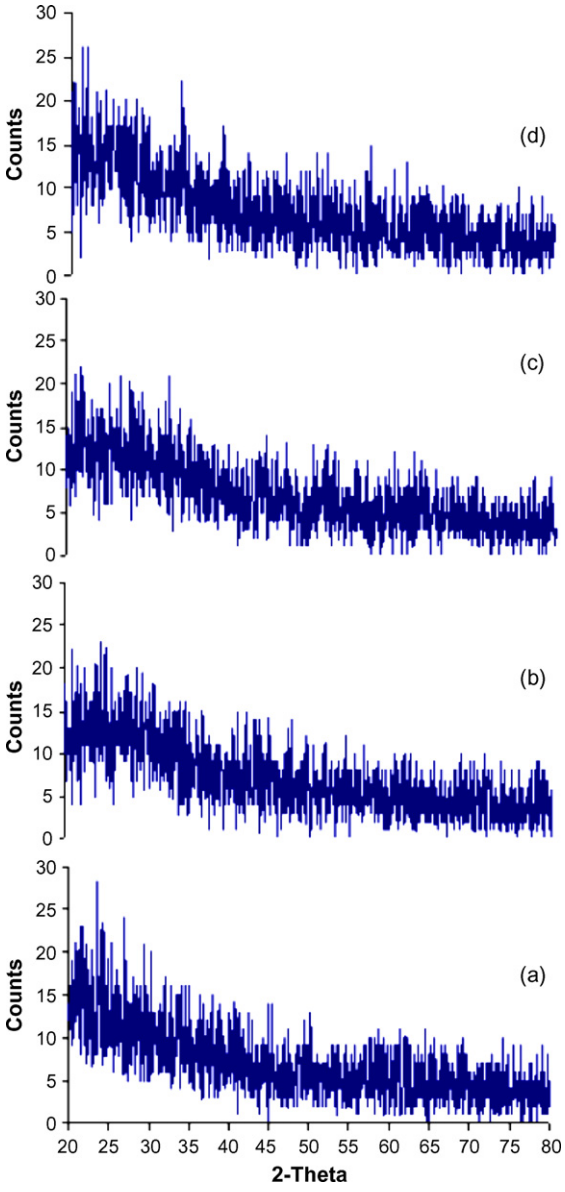

Fig. 2. Influence of SnO_2 film thickness deposited at 350 °C on the XRD spectra: deposited time (a) 20 min (∼80 nm); (b) 30 min (∼125 nm); (c) 60 min (∼140 nm); (d) 90 min (∼170 nm).

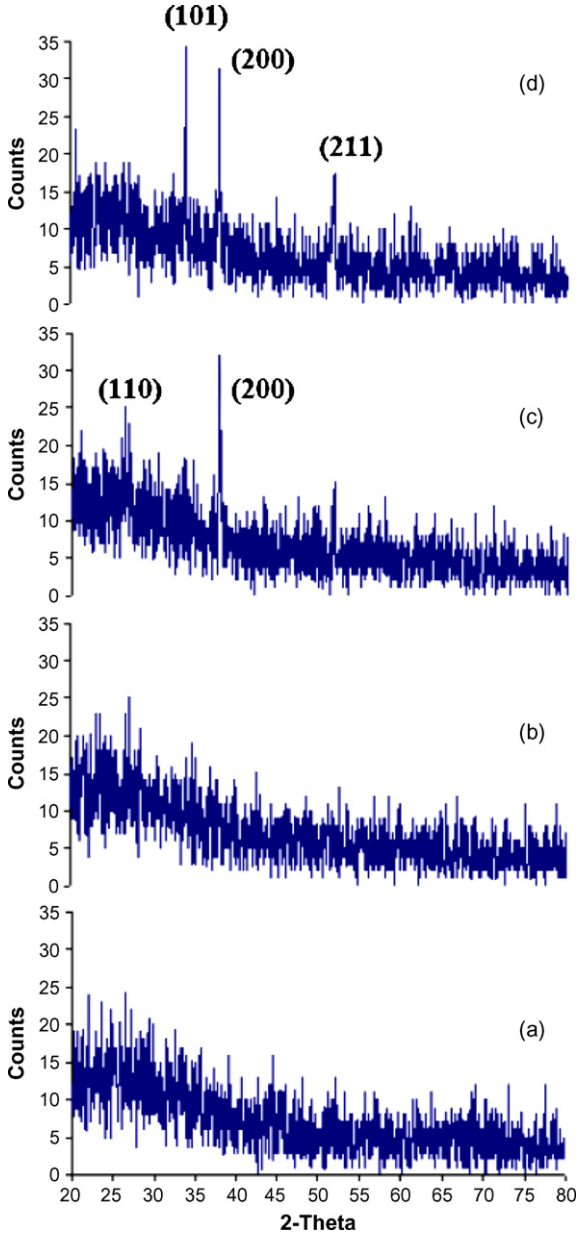

Fig. 3. Influence of SnO_2 film thickness deposited at 400 °C on the XRD spectra: deposited time (a) 20 min (∼220 nm); (b) 30 min (∼390 nm); (c) 60 min (∼595 nm); (d) 90 min (∼1450 nm).

3.2. Morphology characterization

From SEM results, thicknesses of all films are in the range of 80–2690 nm and the mean grain size could be controlled over a range of 50–325 nm. The influence of SnO_2 deposition time on films thicknesses and mean grain size are shown in Fig. 5(a) and (b). It is found that deposition rate and grain growth of SnO_2 films deposited at 350 °C are lower than that at higher deposition temperatures (400 and 450 °C). From Fig. 5, it is found that the rate of grain growth is lower than the rate of film deposition. In other words, the film growth mechanism on the substrate surface seems to be derived from a rapid nucleation of new crystallite on the existing one, rather than grain growth of the primary nuclei. The result suggests that the thickness of the film with small grain size can be increased by a multiple deposition using short-time pyrolysis. For thin film gas sensor application, a smaller grain size provides a higher sensitivity.

4. Conclusions

The SnO_2 films were deposited by ultrasonic spray pyrolysis technique using 0.2 M of $SnCl_4{\cdot}5H_2O$ in absolute ethanol as a precursor. The deposited SnO_2 films show textured cassiterite polycrystalline films characteristic. The films with (2 0 0), (1 1 0), or (3 0 1) planes are three dominant reflections. The mean grain size and films thicknesses determined by SEM

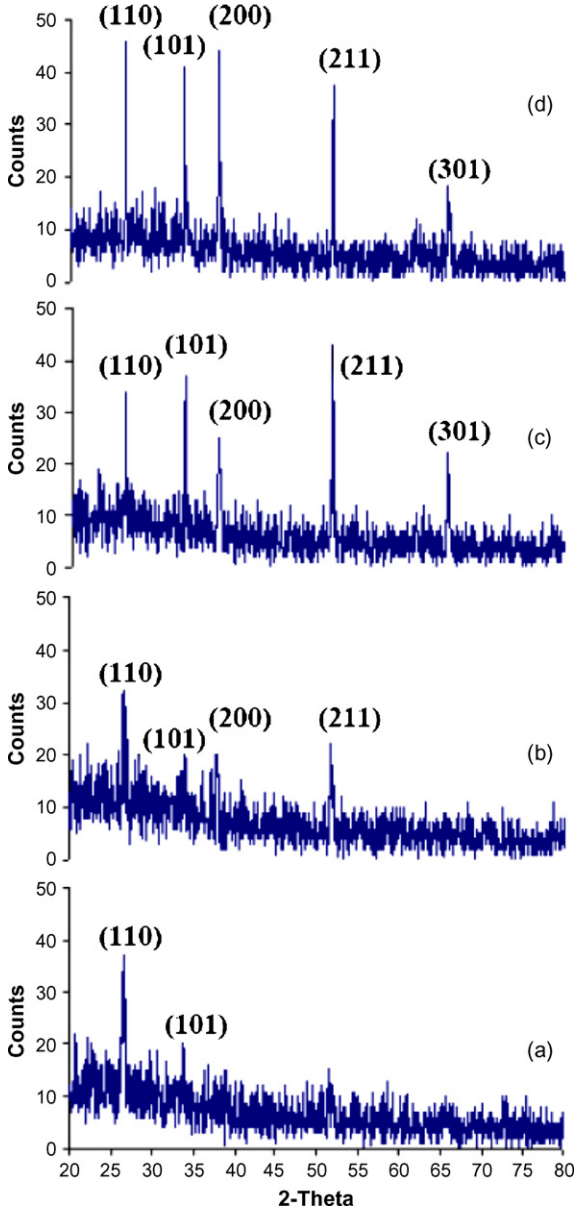

Fig. 4. Influence of SnO_2 film thickness deposited at 450 °C on the XRD spectra: deposited time (a) 20 min (∼330 nm); (b) 30 min (∼680 nm); (c) 60 min (∼920 nm); (d) 90 min (∼2690 nm).

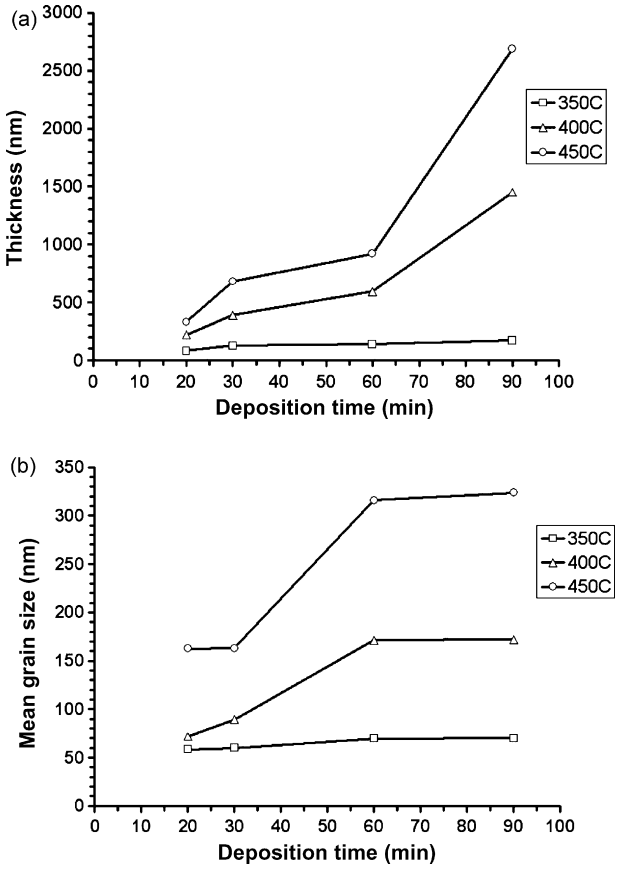

Fig. 5. Influence of SnO_2 deposition time on (a) thickness and (b) grain size (data got from SEM technique).

could be controlled over a range of 50–325 nm and 80–2690 nm, respectively.

Acknowledgements

This study has a financial supported from National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA) (budget year 2006). The author also gratefully acknowledged Thailand Graduate Institute of Science and Technology (TGIST), and National Science and Technology Development Agency (NSTDA) for Ph.D. scholarship.

References

[1] K.H. Yoon, D.J. Nam, Photoelectrical behavior of SnO_2 thin film electrodes prepared by ultrasonic spray pyrolysis, J. Mater. Sci. 30 (1995) 3415–3420.
[2] D. Liu, Q. Wang, H.L.M. Chang, H. Chen, Variant structure in metal-organic-chemical-vapor-deposition-derived SnO_2 thin films on sapphire (0001), J. Mater. Res. 10 (1995) 1516–1522.
[3] J.L. Huang, D.W. Kuo, B.Y. Shew, The effects of heat treatment on the gas sensitivity of reactively sputtered SnO_2 films, Surf. Coat. Technol. 79 (1996) 263–267.
[4] R. Summitt, J.A. Marley, N.F. Borrelli, The ultraviolet absorption edge of stannic oxide (SnO_2), J. Phys. Chem. Solids 25 (12) (1964) 1465–1469.
[5] E. Shanthi, V. Dutta, A. Banerjee, K.L. Chopra, Electrical and optical properties of undoped and antimony-doped tin oxide films, J. Appl. Phys. 51 (12) (1980) 6243–6251.
[6] P. Serrini, V. Briois, M.C. Horrilo, A. Traverse, L. Manes, Chemical composition and crystalline structure of SnO_2 thin films used as gas sensors, Thin Solid Films 304 (1997) 113–122.
[7] G. Korotcenkov, M. DiBattista, J. Schwank, V. Brinzari, Structural characterization of SnO_2 gas sensing films deposited by spray pyrolysis, Mater. Sci. Eng. B77 (2000) 33–39.
[8] D. Briand, M. Labeau, J.F. Currie, G. Delabouglise, Pd-doped SnO_2 thin films deposited by assisted ultrasonic spraying CVD for gas sensing: selectivity and effect of annealing, Sensor. Actuat. B 48 (1998) 395–402.
[9] D. Jadsadapattarakul, C. Euvananont, C. Thanachayanont, T. Sooknoi, (2 0 0) preferred orientation SnO_2 film prepared by ultrasonic spray pyrolysis, in: Proceedings of the 4th Thailand Materials Science and Technology Conference, 2006, pp. 326–328.