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Optical and Electronic Properties of SnO_2 Thin Films Fabricated Using the SILAR Method

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Abstract

Tin oxide thin films were fabricated on glass substrates by the successive ionic layer adsorption and reaction (SILAR) method at room temperature and ambient pressure. Before measuring their properties, all samples were annealed at 500°C for 2 h in air. Film thickness increased with the number of cycles; X-ray diffraction patterns for the annealed SnO_2 thin films indicated a SnO_2 single phase. Thickness of the SnO_2 films increased from 12 to 50 nm as the number of cycles increased from 20 to 60. Although the optical transmittance decreased with thickness, 50 nm SnO_2 thin films exhibited a high value of more than 85%. Regarding electronic properties, sheet resistance of the films decreased as thickness increased; however, the measured resistivity of the thin film was nearly constant with thickness (3×10^{-4} ohm/cm). From Hall measurements, the 50 nm thickness SnO_2 thin film had the highest mobility of the samples (8.6 $cm^2/(V\cdot s)$). In conclusion, optical and electronic properties of SnO_2 thin films could be controlled by adjusting the number of SILAR cycles.

Keywords: SnO_2, Oxide semiconductors, SILAR method

1. INTRODUCTION

In recent years, transparent oxide semiconductors (TOS) have received significant attention for application in a wide range of electronic devices requiring transparency, such as light emitting diodes, solar cells, optical sensors, CMOSs and displays [1]. One such transparent oxide semiconductor material is tin oxide (SnO_2), which has high optical transmittance in the visible range and low electrical resistance [2-4]. SnO_2 is an n-type semiconductor that forms as a result of an excess of electrons produced by ionization of oxygen vacancies, and interstitial tin atoms that are generated during the crystal growth process. In addition, SnO_2 thin films are mechanically strong and thermally stable in oxidizing environments at high temperatures, and chemically stable in both acidic and basic solutions. However, compared to other TOS materials, SnO_2 films exhibit poor performance in some areas, such as having low values for mobility and for on-off ratio. The optical and electronic properties of SnO_2 films can be improved by doping. The upper limit on the electron density, which determines mobility, is set by the solubility of the dopants. However, if the concentration of dopants introduced exceeds the maximum solubility, the excess can form clusters in the lattice, accompanied by a loss of crystallinity. An increased sheet resistance then occurs as a result of atomic disorder and impurity scattering, which reduces mobility of the electrical carriers [5]. However, the presence of impurities at grain boundaries can reduce the barriers between crystallites and may consequently increase the mobility and decrease the sheet resistance [6]. Properties of SnO_2 films impurity-doped with group III, V, VI, and VII elements [6] such as In, F [7], Te, Sb, Cl [8], Al, and Br [8] have been studied. SnO_2 can be either an n-type or p-type semiconductor, determined easily by dopant selection. Before considering such modification of SnO_2 films, uniform SnO_2 thin films should be investigated as preceding researches. Many researches groups have studied fabrication of SnO_2 thin films using various ways such as vacuum evaporation, sputtering [9], CVD, MOCVD, and spray pyrolysis [8]. A chemical method for the deposition of a thin film is the successive ionic layer adsorption and reaction (SILAR) method, which has a number of advantages, including a simple procedure. The SILAR method is known as modified version of chemical bath deposition method by which thin films of compound semiconductors can be

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deposited in accordance with dipping the substrate in the aqueous solution which contain ions for each component. It offers an easy means for depositing thin films, in which the thickness is simply controlled by deposition rate and number of deposition cycles. Moreover, there are no restrictions on a substrate's material dimensions or its surface profile. It is also relatively convenient for large area deposition, inexpensive, and simple [10]. Recently, various thin films such as CuO [11], Cu_2O [12], NiO [13] was fabricated by SILAR method and measured optical and electronic properties. For example, the NiO thin films by using SILAR method showed the thickness grew from 125 nm to 312 nm as increased in the number of cycles from 40 to 100 cycles. In addition, the resistivity of the films obtained between 4.2 and 802.1 Ωcm.

In the present investigation, we report on synthesis of SnO_2 thin films by the SILAR method, and their structural, surface morphological, and electrical properties.

2. EXPERIMENTAL

2.1. SnO_2 Thin Film Fabrication.

In this study, SnO_2 thin films were deposited on glass substrates using the SILAR method at room temperature and ambient pressure. To deposit a SnO_2 thin film, 0.025 M tin (II) chloride ($SnCl_2 \cdot 2H_2O \geq 98\%$, Aldrich, USA) was chosen for the cation precursor as a source of Sn^{4+}. The anionic precursor was 1% H_2O_2. Both the cationic and anionic precursors were kept at room temperature (~300 K). One SILAR cycle consists of four steps: (i) adsorption of Sn^{4+} ions on the substrate surface for 10 s, (ii) washing to remove excess salt, (iii) reaction with H_2O_2 solution for 20 s to form a stable SnO_2 thin film on the substrate, and (iv) washing to remove residue. The number of cycles ranged from 20 to 60. After deposition, all samples were annealed at 500°C for 2 hours in air.

2.2 Characterization of SnO_2 Thin Films

Surface and electronic properties of the SnO_2 thin films were measured at three or four different positions on each sample to verify reproducibility. Structural properties of SnO_2 thin films were characterized by X-ray diffraction (XRD, Rigaku). Optical properties of the thin films were measured using UV-visible spectroscopy (Lambda 18, Perkin Elmer) in the range 200–900 nm. Thicknesses of the thin films were measured by field emission environmental scanning electron microscopy (FE-ESEM, XL-30). Electronic properties of the thin films were investigated by Hall measurements and with a four point probe (MS-TECH).

3. RESULTS AND DISCUSSIONS

3.1 Film Formation Mechanism

The formation mechanism of SnO_2 film is presented in Fig. 1. The $SnCl_2$ solution contains Sn^{4+} ions that hydrolyze to form $Sn(OH)_4$, which precipitates on the immersed substrate surface. The substrate is then rinsed in dilute H_2O_2 solution, where formation of SnO_2 takes place through the second reaction shown in Fig. 1. This completes one cycle in the formation of a SnO_2 monolayer; the cycles are repeated to achieve a desired film thickness. By repeating this process, it is established that the thickness can be controlled, and the variation of film properties with thickness is studied.

3.2 Structural Analysis

The structural analysis of SnO_2 thin films deposited on the glass substrate and annealed at 500°C was carried out using XRD. The X-ray diffraction patterns of the thin films, obtained by varying the diffraction angle 2θ from 20 to 90°, indicate the existence of a SnO_2 single phase as shown in Fig. 2. The peaks at 2θ = 26.5, 33.8, 37.8, and 51.6° correspond to the (110), (101), (200), and (211) planes of SnO_2, respectively (JCPDS card no. 77-0450).

SEM images were used to analyze the microstructure and thickness of the films. Fig. 3 (a) and (b) shows the cross-sectional images of SnO_2 thin film on glass substrate after 30 and 60

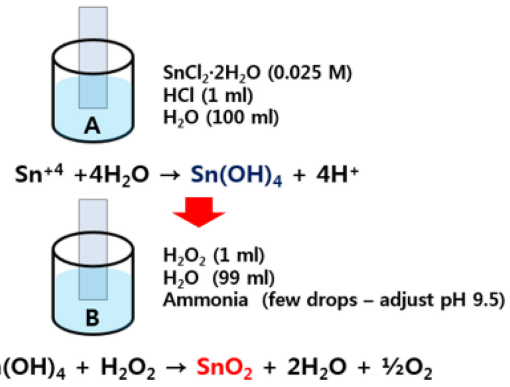

Fig. 1. SnO_2 thin films formation mechanism.

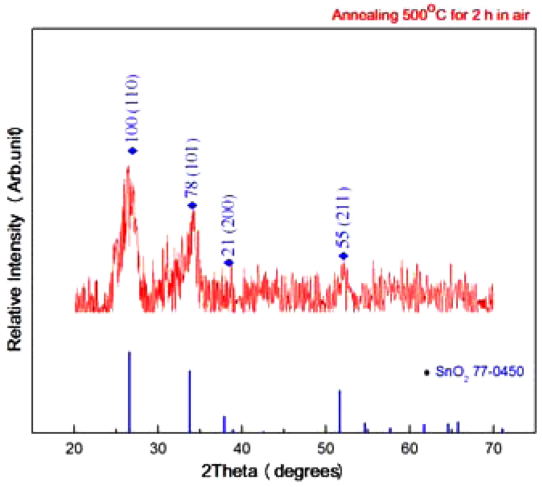

Fig. 2. XRD pattern of SnO_2 thin film on a glass substrate.

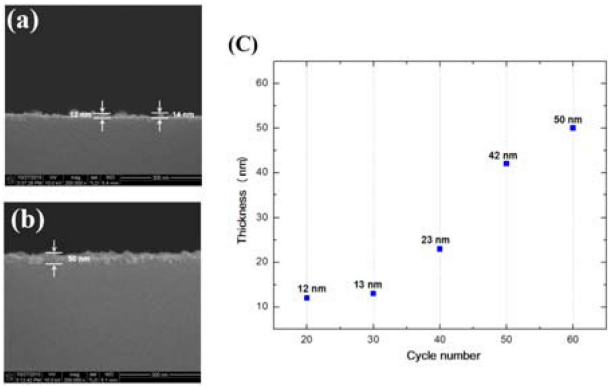

Fig. 3. SEM images for the cross-section of the (a) 30 cycles and (b) 60 cycles SnO_2 thin films. (c) Thickness profile for cycles.

SILAR cycles. The thickness of the films at 30 and 60 cycles are 13 and 50 nm, respectively. The variation of film thickness with number of cycles is shown in Fig. 3 (c). The thickness of the film increases with number of deposition cycles from 20 to 60 cycles.

3.3 Optical Analysis

Optical transmittance in the wavelength range 200 to 900 nm for the SnO_2 films deposited on glass substrates is shown in Fig. 4. Typically, optical transmittance for a display device is measured at a standard wavelength of 550 nm, corresponding to the peak sensitivity of the human eye. The SnO_2 thin film at 20 cycles (12 nm) shows the highest transmittance (92%), while the film at 60 cycles (50 nm) shows the lowest transmittance (85%) using the 550 nm wavelength standard. As the number of layers increases, the thickness of the films increases, lowering the transmittance of the sample; however, at 60 cycles the transmittance [14] of SnO_2 thin films deposited on glass substrate is still more than 85%.

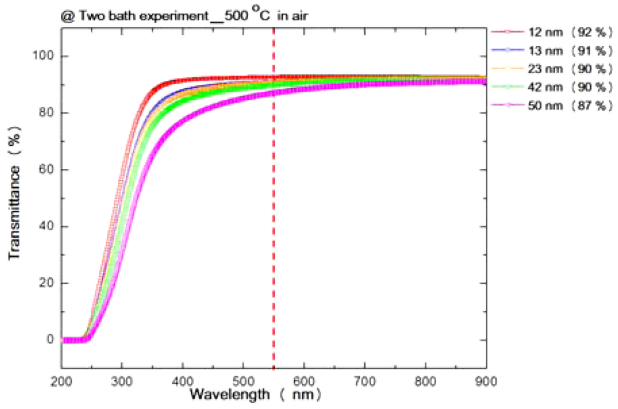

Fig. 4. Transmittance of annealed SnO_2 thin films for thickness.

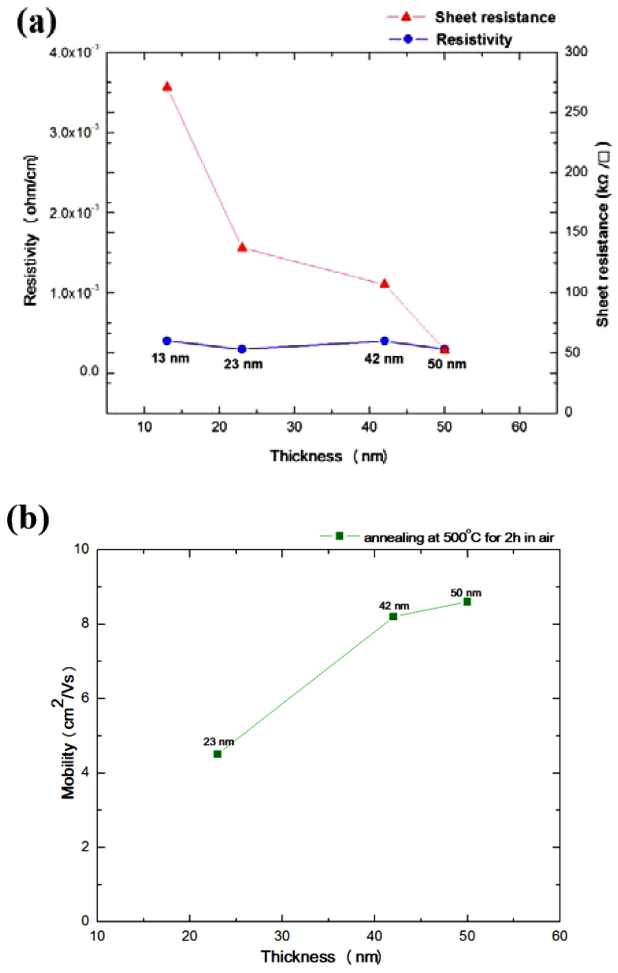

Fig. 5. (a) Resistivity and sheet resistance, (b) Mobility of annealed SnO_2 thin films for different thickness.

3.4 Electronic analysis

The resistivity and sheet resistance of SnO_2 thin films measured by using four point probe is shown in Fig. 5 (a). The sheet resistance of annealed SnO_2 films on glass substrates was

measured by using four point probe method. The sheet resistance of the films is decreased as number of layers increases because the sheet resistance is depended on thickness. [15] Whereas, the measured resistivity of thin film was confirmed as almost constant value (3×10^{-4} ohmcm) as thickness of the films increases. The resistivity value of the films is lower than the result from the recent study for SnO_2 thin film which was measured between 10^5 and 10^7 ohm·cm made by SILAR method [16].

Fig. 5 (b) is shown the mobility of SnO_2 thin films measured by using Hall measurement. The 50 nm SnO_2 thin film at 60 cycles out of the films was shown the highest mobility (8.6 cm^2/Vs) because the mobility of thin films is increased with thickness increase [17].

4. CONCLUSIONS

SnO_2 thin films can be successfully deposited on glass substrates by the SILAR method. The film thickness increases with the increase in number of cycles whereas the transmittance of the films decreases. In addition, sheet resistance of the films decreases with increased thickness, while resistivity of the films is almost independent of thickness. Moreover, the mobility of thin films increases with thickness. As the number of layers increases, crystallite size increases and grain boundaries decrease, and as a result the mobility of the sample increases. The SnO_2 thin films of 50 nm thickness (60 cycles) show good optical and electronic properties. Therefore, we can tailor the number of cycles to obtain specified properties. Furthermore, we are able to fabricate large-area thin film applied electronic devices by the SILAR method, in a simple and inexpensive manner.

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