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Effect of annealing temperature on properties of p-type conducting Al/SnO_2/Al multilayer thin films deposited by sputtering

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Transparent p-type conducting a sandwich structure Al/SnO_2/Al multilayer thin films deposited on quartz substrate have been prepared by RF sputtering method using SnO_2 (99.99%) and Al (99.99%) targets. In order to study the effect of thermal diffusing temperature and time on the structural, electrical and optical performances of Al/SnO_2/Al films, the deposited films were annealed at different temperatures for different durations, respectively. X-ray diffraction results show that all p-type conducting films possessed polycrystalline SnO_2 with tetragonal rutile structure. The microstructure, Hall effect and optical property were checked by FE-SEM, Hall effect measurement and UV–Visible absorption spectra. As the annealing temperature increases, the transparence (%) and energy band (Eg) increase. Especially, Hall effect results indicate that 450 °C for 4 hrs were the optimum annealing temperature for the resistivity (Ω·cm) with a relatively high hole concentration of 2.09×10^{19} cm^{-3} and a low resistivity of 5.38×10^{-1} Ω · cm.

Key words: TCOs, SnO_2, RF Sputtering, Annealing, Multi-layer.

Introduction

Transparent conducting oxide (TCO) films have important applications in the optoelectronics field [1], such as flat panel displays, light emitting diodes (LED), touch screens, organic light emitting diodes (OLED), thin film solar cells, and electronic devices. [2-6]. The most popular TCO used for some applications is Sn-doped In_2O_3 (ITO), because of it is low resistivity and high transmittance in the visible rays region of the electromagnetic spectrum (380-770 nm). The defect of ITO is the expensive cost of indium, this it is necessary to develop new TCO based on inexpensive elements. Tin oxide (SnO_2) is one of the most important TCO materials, and has numerous applications in modern technologies [7-10], due to its attractive properties of a wide band gap ($E_g = \sim 3.6$ eV), high electrical conductivity, high transmittance in the ultraviolet-visible (UV-Vis) region and high infrared (IR) reflectance, abundance in nature and absence of venenosity [7, 11]. It is well known that widely-used TCO thin films such as ZnO, SnO_2, SnO_2 : In are n-type because of the existence of intrinsic defects (oxygen vacancies and/or metal interstitials) [12], but research on p-type TCOs has only begun in recent years. Singh et al. [13] found that the incorporation of group-IIIA atoms (In, Ga, and Al) in the Sn site produces low acceptors that exhibit better solubility and a low degree of self-compensation. Different dopants such as Al [14, 15], Sb [16], In [17], Ga [18] and Li [19], and techniques such as sputtering [16, 18], sol-gel [14, 17] and spray thermal decomposition [15, 19], have been used to obtain p-type doping SnO_2. Recently, p-type doping of SnO_2 thin films was studied using elements with a lower valence cation as the acceptor impurity, which increases the hole concentration [14, 15]. However, there is no report available on the systematic study of p-type SnO_2 : Al thin films obtained by Radio Frequency (RF) sputtering. The sputtering and evaporation techniques are the often used methods for industrial applications. The RF sputtering technique has been effectively suitable for production because of its high throughput and controllable thickness, besides has high uniformity and flexibility. In this studied, the p-type SnO_2 : Al thin films were prepared from the thermal diffusion of a sandwich structure of Al/SnO_2/Al multilayer thin films deposited on quartz substrates which were got using a RF sputtering process [20]. To know the crystal structure, electrical, optical properties of the films, we used the X-ray diffraction (XRD), Raman spectrometry, field emission scanning electron microscopy (FE-SEM), energy dispersive X-ray spectroscopy (EDX), Hall-effect measurements, and UV-Vis spectrometry. The effects of annealed temperature

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and time on the structural, electrical and optical properties of the Al/SnO_2/Al thin films were investigated and discussed.

Experimental

The sandwich structure of Al/SnO_2/Al multilayer thin films was deposited layer by layer on quartz substrates with a conventional RF magnetron sputtering system. An Al (99.99% pure) and SnO_2 (99.99% pure) disk was used as the RF magnetron sputtering target. The quartz substrates were ultrasonically cleaned in acetone, ethanol and deionized water for 10 min in each solution, then dried in a nitrogen atmosphere. When the chamber pressure was evacuated to below 2.0×10^{-3} Pa, pre-sputtered 40 sccm argon gas (purity 99.999%) was delivered for 10 min in order to clean the target surface. The deposition conditions of Al and SnO_2 thin fims are listed in Table 1. The target-substrate distance equal to 20cm was fixed in all experiments. By controlling the deposition time, the Al/SnO_2/Al multilayer films were deposited with the thickness of about 50/800/50 nm. For obtaining the p-type transparent conducting SnO_2 : Al thin films, the Al/SnO_2/Al multilayer thin films were annealed at 350-500 °C for different durations.

The structural characteristics were examined with XRD (X'pert MPD 3040) with monochromatic Cu Kα radiation ($\lambda = 1.5405$ Å) and a Ni filter. The operating voltage and current were 40 kV and 30 mA, respectively. The scanning range was between $2\theta = 20^o$ and 80^o. The lattice spacing (d) between two different crystallographic planes can be determined from Bragg's law ($n\lambda = 2d\sin\lambda$) [21], and the relationship between lattice spacing and lattice parameters (a and c) of the tetragonal structure of SnO_2 is expressed as:

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \tag{1}$$

Where h, k and l are the Miller indices of the reflection plane. The Raman spectra were measured at room temperature by using a Raman spectrometer (NRS-3100/low wave number (~ 10 cm^{-1})). Laser irradiation at the wavelength of 532 nm was used for the excitation. The laser power was set at an approximate level of 100 mV to avoid damaging the samples. The surface and cross-sectional morphology were observed with FE-SEM (MIRA II LMH/H.S Code: 9012.10.1000). The Hall effect was measured at room temperature using an HMS5000/AMP55T. To realize the reliability and repeatability of the conduction of the films, these measurements were carried out five times and concordant results were observed. The transmittance of the films measured in the wavelength range 300-800 nm was measured using an UV-Vis spectrophotometer (Agilent 8453).

Table 1. Deposition conditions of Al and SnO_2 thin films.

	Al	SnO_2
Argon gas pressure (SCCM)	40	4
Power (W)	RF 100	RF 100
Deposition time (min)	12.5	76.5
Chamber pressure (Pa)	2.0×10^{-3}	2.0×10^{-3}
Target-substrate distance	20 cm	20 cm

Results and Discussion

Crystal structure and morphology of thin films

Fig. 1 illustrates the XRD patterns of the as-deposited Al/SnO_2/Al multilayer thin films annealed at various temperatures and times in air. It reveals that all the patterns of the thin films annealed between 400 and 500 °C were SnO_2 with a tetragonal rutile structure (JCPDS card No. 41-1445), without other phases being detected. Moreover, Fig. 1 also indicates that the intensity of the reflection peaks was markedly affected by the annealing temperatures and times. The XRD pattern of the as-deposited Al/SnO_2/Al film shows the strong (110) reflection and relatively weaker (100), (200), (211) and peaks. The intensity of the (110) reflection only changed slightly when the annealing temperature was between 400 and 500 °C, while it rapidly decreased when the temperature increased from 450 to 500 °C. In addition, the (211) reflection became the most intense when annealed at 450 °C for 4 hrs. However, the reflection intensity of (211) also decreased as the temperature and time increased. Furthermore, the intensity of the (211) reflection substituting (110) became the major reflection when the Al/SnO_2/Al thin films were annealed between 350 °C and 500 °C. It shown in Fig. 2 that tetragonal SnO_2 with a rutile structure has the lattice parameters of a = 4.737 Å and c = 3.186 Å (JCPDS card No. 41-1445). The lattice parameters of a = 5.208 Å and c = 2.697 Å of SnO_2 : Al thin films annealed at 450 °C for 4 h were calculated from Eq. (1). It reveals that the a-axes are larger than the tetragonal SnO_2, while a con- traction of the c-axes occurred. This is because the smaller ionic radius of Al^{3+} (0.51 Å) replaced Sn^{4+} (0.71 Å) [20]. The SEM surface

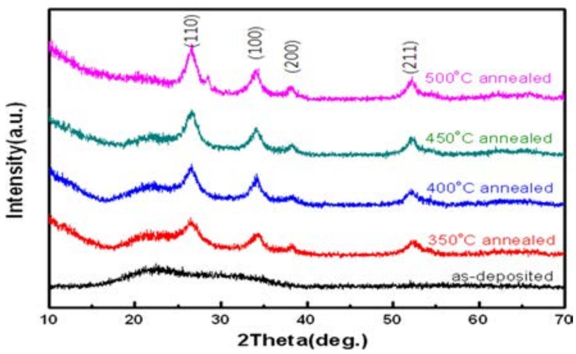

Fig. 1. XRD patterns of Al(50 nm)/SnO_2(800 nm)/Al(50 nm) films annealed at different temperature.

morphologies of the as-deposited and Al/SnO$_2$/Al thin film annealed at 450 ºC for 4 h are shown in Fig. 3(a) and (b), respectively. From Fig. 2(a), it can be found that the Al layer with a grain size of about 50 nm was distributed in the film. Fig. 4(b) reveals that the annealed film shows a particulated structure with higher roughness [20]. Fig. 4(a) and (b) shows the SEM morphology of the cross-section of the thin film (a) as deposited and (b) annealed at 450 ºC for 4 hrs, indicating an average thickness of about 906 ~ 938 nm.

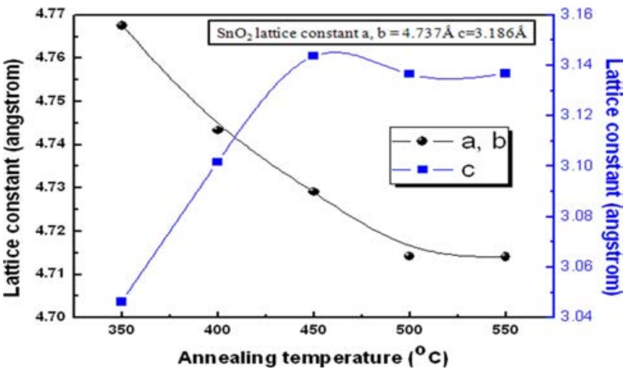

Fig. 2. Lattice constant of the tetragonal SnO$_2$ with a rutile structure has a = 4.737 Å and c = 3.186 Å.

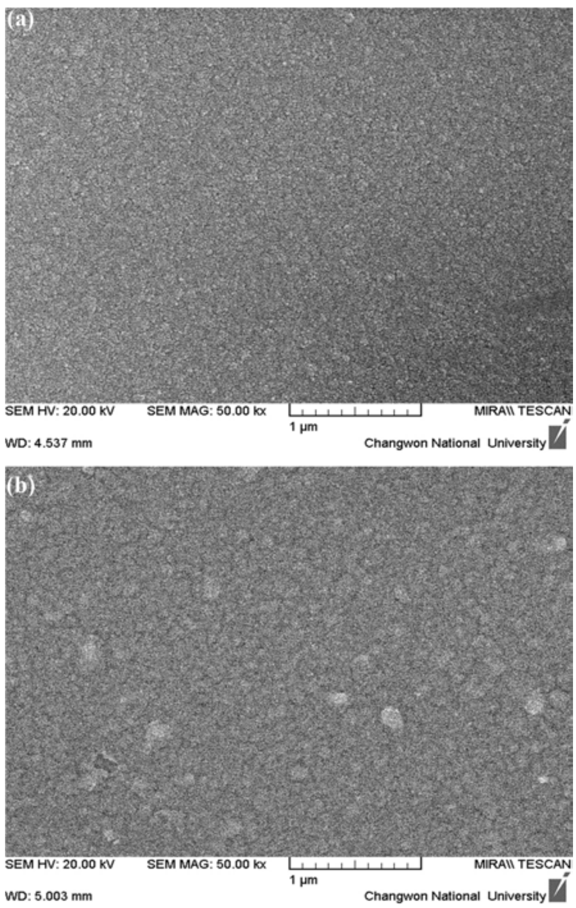

Fig. 3. FE-SEM surface morphologies of (a) as-deposited Al/SnO$_2$/Al thin films and (b) Al/SnO$_2$/Al thin films obtained by thermal diffusion at 450 ºC for 4 hrs.

No obvious interfaces of the Al and SnO$_2$ layers were found in the film, indicating that the Al ions were well diffused into the SnO$_2$ film [20].

Electrical properties

The effects of annealing temperature and time on the electrical properties of the thin films are listed in Table 2. The as-deposited Al/SnO$_2$/Al thin films have n-type conductive properties, and when annealed at 350 ºC for 4h they still maintain this, but the resistivity decreased and carrier concentration increased, indicating that thermal diffusion occurred [20]. The conductive type changed to p-type and n-type as the dominant and secondary conductions, respectively, when annealed at 400 ºC for 4 hrs. As the thin film annealed at 500 ºC for 4 hrs, the film shows only p-type conductivity [20]. Annealing at 500 ºC for 4 hrs causes the conductivity of thin films to convert from p-type alone to p-type and n-type as the major and secondary conductions, respectively. Moreover, with increasing annealing temperature and time from 350 ºC for 4 h to 500 ºC for 4 hrs, the resistivity of the films increases from 2.05 × 10^{-3} to

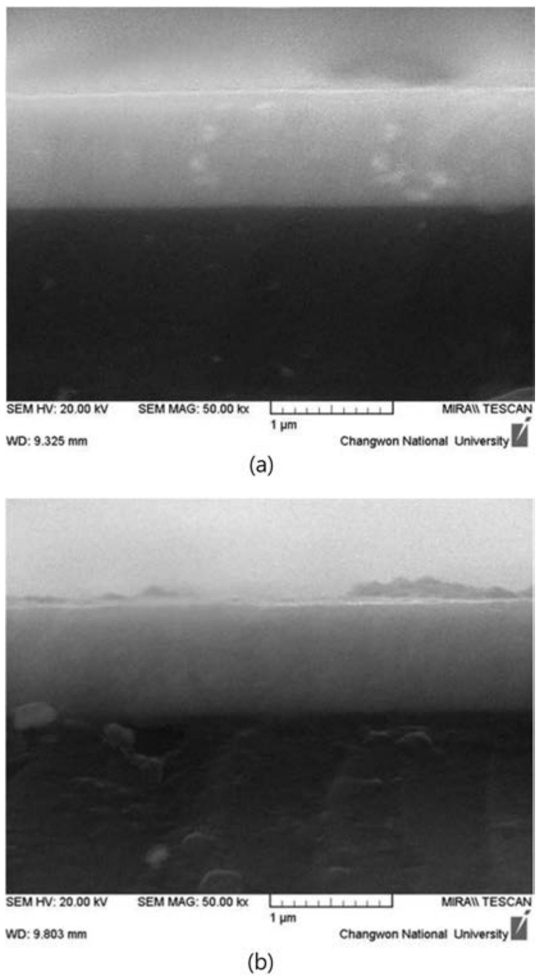

Fig. 4. FESEM images of the cross-section of the as-deposited Al/SnO$_2$/Al thin film (a) and the Al/SnO$_2$/Al thin film obtained by thermal diffusion at 450 ºC for 4 h (b).

Table 2. Results of the Hall measurements of Al(50 nm)/SnO_2(800 nm)/Al(50 nm) films annealed at different temperature.

Temperature (°C)	Concentration (cm^{-3})	Mobility ($cm^2V^{-1}s^{-1}$)	Resistivity (Ω·cm)	Type
as-deposited	-5.586×10^{20}	5.43	2.05×10^{-3}	n
350 °C/4 h	-1.710×10^{19}	1.94	5.36×10^{-2}	n
400 °C/4 h	$+1.010 \times 10^{19}$	42.6	1.45×10^{1}	p
450 °C/4 h	$+2.095 \times 10^{19}$	5.53	5.38×10^{-1}	p
500 °C/4 h	$+1.0183 \times 10^{15}$	2.6	2.35×10^{3}	p

2.35×10^3 (Ω · cm). When the annealing temperature is above 450 °C, the acceptor effect of aluminum substituting tin is activated, which results in the p-type of films. A high temperature commonly leads to good crystallization, thereby decreasing intrinsic defects. However, higher annealing temperatures do not result in p-type conductivity, because both the doping effect and point defects were produced [16]. Gu et al. [22] found that the aluminum atoms are inactive at the amorphous state (lower grain size). Therefore when the annealing temperature is 400 °C aluminum atoms cannot liberate the electrons to replace the Sn^{4+} with Al^{3+} in the SnO_2 lattice. As the grain size increases, aluminum ions become more active and they liberate electrons, which are the source for replacing the Sn^{4+} and thus the film changes to p-type conduction. The optimum annealing temperature for a stable p-type conducting thin film is approximately 450 °C, while the hole concentration and resistivity reaches the maximum of 2.095×10^{19} cm^{-3} and minimum of 5.38×10^{-1} Ω · cm respectively. The Hall mobility is low (5.53 $cm^2V^{-1}s^{-1}$), and the decline in this is due to the increase in ionized acceptors. In p-type SnO_2 films, it is difficult to obtain an optimal value of hole concentration and carrier mobility simultaneously. This phenomenon is consistent with the results of p-type antimony doped tin oxide films reported by Ni et al. [16] and p-type ZnO films reported by Chen et al. [23].

Optical properties

Fig. 5 presents spectral transmittances of the Al/SnO_2/Al thin films as a thinkness of Al. Fig. 5(a) shown in the transmittance of Al(25 nm)/SnO_2(800 nm)/Al(25 nm), and average transmission of the Al/SnO_2/Al thin film is annealed at 450 °C for 4hrs in the visible region (300-800 nm) is about 82%. But, Al(25 nm)/SnO_2(800 nm)/Al(25 nm) with high resistivity. The Results of the optical transmittance of Al(50 nm)/SnO_2(800 nm)/Al(50 nm) multilayer thin films annealed at different temperature and times are shown in Fig. 5(b). The average transmission of the as-deposited Al/SnO_2/Al thin film in the visible region (300 - 800 nm) is about 2%. After annealing between 450 °C and 500 °C, the films are

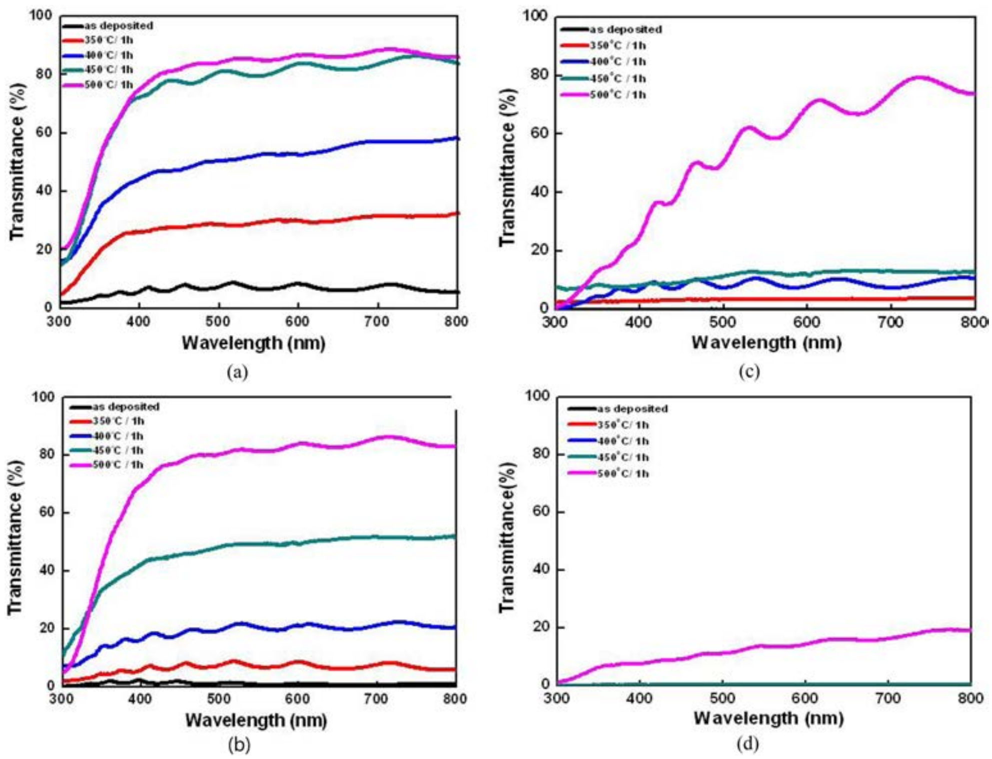

Fig. 5. Results of the transmittance of Al/SnO_2/Al thin films annealed at different temperature: (a) Al(25 nm)/SnO_2(800 nm)/Al(25 nm), (b) Al(50 nm)/SnO_2(800 nm)/Al(50 nm), (c) Al(75 nm)/SnO_2(800 nm)/Al(75 nm), (d) Al(100 nm)/SnO_2(800 nm)/Al(100 nm).

highly transparent in the visible region and the average transmission of the films increases to over 80%. This indicates that the annealing process greatly improves the visible light transmittance. Transmittance of Al(75 nm)/SnO_2(800 nm)/Al(75 nm) and Al(100 nm)/SnO_2(800 nm)/Al(100 nm) thin films are shown in Fig. 5(c) and (d). These samples show very low transmittance. The highest average transmission is about 81% when the film is annealed at 500 °C for 4 hrs, and is about 80% in the range of 450-500 °C.

Conclusions

The p-type transparent conductive Al/SnO_2/Al thin films were prepared from the thermal diffusion of a structure Al/SnO_2/Al multilayer thin films which were deposited on quartz substrates by RF sputtering using Al (99.99% in purity) and SnO_2 (99.99% in purity) targets. Hall measurements come out that the Al/SnO_2/Al multilayer films showed p-type conductivity within a certain annealing temperature range of 400-500 °C, while the films annealed below 400 °C and above 500 °C (continue longer than 4 hrs) showed n-type behavior. It was found that 450 °C was the optimum annealing temperature with a heating duration of 4 hrs to get p-type Al/SnO_2/Al multilayer thin films with relatively high hole concentration (2.095×10^{19} cm^{-3}) and resistivity (5.38×10^{-1} $\Omega \cdot$ cm). XRD results showed that all the p-type conducting films possessed polycrystalline SnO_2 with a tetragonal rutile structure. The optical transmission within a certain annealing temperature range of 400-500 °C of the p-type Al/SnO_2/Al multilayer thin films obtained by thermal diffusion was higher than 80%.

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