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Deposition of Al-doped and Al, Sc-co-doped zinc oxide films by RF- and DC-sputtering of the ZnO and Al–*x*Sc (*x*=0, 0.4, 0.8 and 1.7 wt.%) targets

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ABSTRACT

Innovative films ZnO: Al–*x*Sc (in which *x*=0, 0.4, 0.8 and 1.7 wt.%) were prepared through RF-sputtering on the ZnO target and DC-sputtering on the Al–*x*Sc alloy targets. X-ray diffraction (XRD) of the films displayed a hexagonal wurtzite textured at (002) and the peak (002) shifted to a little higher angle with increasing the Sc-content in the films. Transmission electron microscopy (TEM) revealed smaller uniform columnar grains (diameter around 65 nm) in the ZnO: Al–*x*Sc films than in the ZnO: Al. The transmittance was higher than 80% for all the films and the adsorption edge indicated a blue-shift for the films ZnO: Al–0.4 wt.%Sc and ZnO: Al–0.8 wt.%Sc but a red-shift for the film ZnO: Al–1.7 wt.%Sc. The electrical conductivity (S/cm) of the films increased from 2.64×10^2 to 7.94×10^2 with increasing of wt.%Sc from 0 to 1.7 in the target, due to the increase in both the electron concentration and electron mobility. X-ray photoelectron spectroscopy (XPS) analysis inferred that higher electrical conductivity of the films is ascribed to the deficient oxygen (*i.e.*, O(III)). The corrosion resistance of the films in 3.5% NaCl increased with increasing the Sc-content.

1. Introduction

Transparent conducting thin film made of aluminum-doped zinc oxide (AZO) becomes more competitive than that of indium doped tin oxide (ITO) used in the optical electronic industries, due to the non-toxicity, inexpensive, and rich reserve in the earth crust of both the components. AZO is preferred to ITO due to its better electronic matching, lower price [1], and non-toxicity of ZnO in comparison with other host oxides like CdO, In_2O_3 and SnO_2. As a result, there has been a considerable impetus to develop transparent conducting oxide films based on ZnO. Elements such as B, Al, Ga, In (Group IIIA) [2], Si, Ge (Group IV A) and Ti, Zr, Hf (Group IV B) [3] were used to dope ZnO for enhancing their transparent conductive characterization. The involvement of dopant introduced ternary transparent conductive oxides (TCO) such as $Zn_2In_2O_5$ [4], ZnO–In_2O_3, In_2O_3–SnO_2 [5]. Minami et al. [3] sputtered ZnO films doped with rare earth elements (*e.g.*, Sc and Y) using a target made of a mixture of ZnO, Sc_2O_3, and ZnO, Y_2O_3 powders. They concluded that the electrical and optical properties, as well as the thermal stability of resistivity were better for the ZnO: Sc films than for the ZnO: Al film. Suzuki et al. [6] co-doped some impurities such as Co, Cr and V in AZO [7] to form a quaternary film to improve its electronic property. They found, by accident, that the film AZO co-doped with V is more corrosion-resistant than the usual AZO in both acidic and alkaline solutions. In our previous work [8], we prepared a new quaternary film (*i.e.*, Sc-co-doped AZO) through sputtering ZnO by RF and sputtering Al–1.7 wt.%Sc alloy by DC. This film revealed higher electrical conductivity than the usual AZO and its conductivity could be annealed. In addition, this film was more resistant to corrosion in 3.5 wt.% NaCl solution than the AZO. However, a systematic study in Sc-doped AZO is still lacking.

In this work, we have investigated the influence of Sc-content in the alloy targets (*i.e.*, Al–*x*Sc alloy in which *x*=0, 0.4, 0.8 and 1.7 wt.%) on the crystalline structure and characterization of the sputtered Sc-co-doped AZO films. Dependence of the corrosion behavior of those films (in 3.5 wt.% NaCl solution) upon the Sc-content in the Al–Sc alloy targets was also investigated.

2. Experimental

The Sc-doped AZO films were prepared with a sputtering system where RF and DC were served as the power sources. A target of zinc oxide (ZnO, 4 N) was sputtered with RF at 200 W. Pure aluminum (Al, 5 N) or Al–*x*Sc alloy (*x* at 0.4, 0.8, and 1.7 wt.%) was the second target to be sputtered with DC at 20 W. The chamber was first evacuated to a vacuum of 3.73×10^{-4} Pa and purged with argon to 0.93 Pa to proceed to sputtering. Pieces of super twisted nematic (STN, Central glass Taiwan Trading) glass in 5 cm×5 cm were cleaned in supersonic de-ionized water, in 1% KOH solution, de-ionized water, and dried ready for sputtering. The glass was pre-heated to 200 °C and set out to sputter to facilitate the adhesion of the film. The Sc-doped AZO films should be set at a constant thickness of 230 nm for their rational comparison in the electrical conductivity and optical

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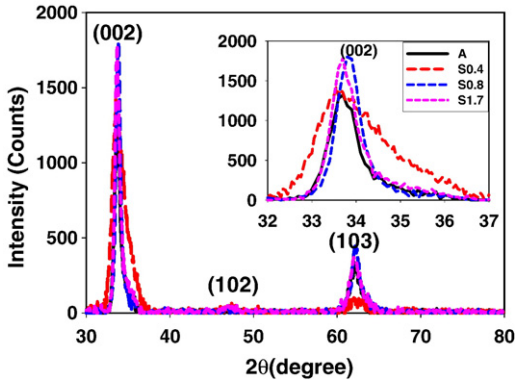

Fig. 1. XRD diffraction patterns for the sputtered films ZnO: Al–*x*Sc where *x* at 0, 0.4, 0.8 and 1.7 wt.%.

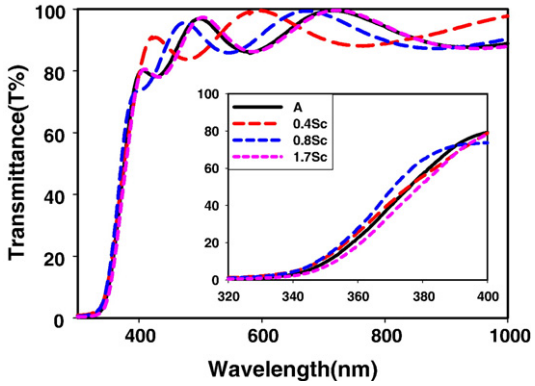

Fig. 3. Optical transmission spectra for the sputtered films ZnO: Al–*x*Sc where *x* at 0, 0.4, 0.8 and 1.7 wt.%.

transmittance. Accomplished sputtering, the specimen was removed from the chamber and ready for measurements.

The films were examined by X-ray diffractometer (XRD, Philips PW 1830) to determine their crystal structures, and explored using transmission electron microscopy (TEM, JEM-100cx II) to observe the image and confirm their crystal forms. The transmittance of the UV–visible light passing through the films was measured by a UV–visible spectrophotometer (Heliox Gamma). The electrical conductivity was determined by a four-point probe (Napson RT-70). The chemical state on the surface films was analyzed with an X-ray photoelectron spectroscopy (XPS, or ESCA, PHI 1600). The corrosion behavior of the specimens in an artificial seawater (3.5% NaCl) was investigated through electrochemical polarization via a potentiostat (Auto-Lab).

3. Results and discussion

3.1. X-ray diffraction (XRD) of the films

Fig. 1 depicts the XRD diffraction patterns for various sputtered ZnO: Al–*x*Sc films. There are three characteristic peaks of a hexagonal ZnO wurtzite and their intensity decreasing in the order $I_{(002)}>I_{(103)}>I_{(102)}$. The strongest (002) peaks were magnified in the inset of Fig. 1. According to JCPDS 36–1451, the (002) peak should be positioned centrally at 34.42° for pure ZnO and it shifted to a lower angle (*i.e.* 33.89°) for the Al-doped ZnO. In the inset of Fig. 1, the shift of (002) peak to lower angle was mitigated in the co-dope of Al, Sc in ZnO. This mitigation is more prominent with increasing Sc in the Sc-doped AZO. In the viewpoint of ionic radius, it reveals a distinct difference between Al^{3+} (0.535 Å) and Zn^{2+} (0.740 Å) but a negligible difference between Sc^{3+} (0.745 Å Zn^{2+}) and Zn^{2+} (0.740 Å). A dope of Al(III) in the Zn(II)O film may arise a lattice strain. The higher concentration of the dopant, the greater is the strain in the lattice. Higher lattice strain gives rise to greater lattice constant (*i.e. d*) in a specific direction. According to Bragg's law ($n\lambda=2d\sin\theta$), a rise in *d* arises a fall in $2\sin\theta$ (and so 2θ) when λ keeps at constant (=1.514 Å). Consequently, the doped of Al in ZnO leads to a shift of the (002) peak shifts to lower angle. On the other hand, co-dope of Sc(III) in AZO will mitigate the lattice strain caused by Al(III) and reduce the shift of (002) to lower angle.

The degree of texture on (002) crystal plane could be defined as TF (002) using the following equation:

$$\mathrm{TF}(002)=\frac{I_{(002)}}{I_{(002)}+I_{(102)}+I_{(103)}} \tag{3.1}$$

where $I_{(002)}$ is the XRD intensity on (002) crystal plane and $I_{(103)}$ the intensity on (103). Calculated from the data coming from both AZO and Sc-doped AZO films, the value of TF(002) decreases in the order: AZO (0.9)>Al–0.4 wt.%Sc (0.88)>Al–1.7 wt.%Sc (0.85) Al–0.8 wt.%Sc (0.83). This means that the degree of texture on (002) decreases with increasing the concentration of dopant Sc. This is an indirect evidence for Sc-co-doped to relax the lattice strain caused by Al-doped.

3.2. Microstructure examined through TEM

Fig. 2 depicts the bright field image of transmission electron microscopy (TEM) for the cross-section of the film ZnO: Al–1.7 wt.%Sc. The selective area diffraction (SAD) is illustrated in the inset. This film consists of uniform columnar grains with finer diameter (roughly at 65 nm) than those found in the simple AZO film. The participation of

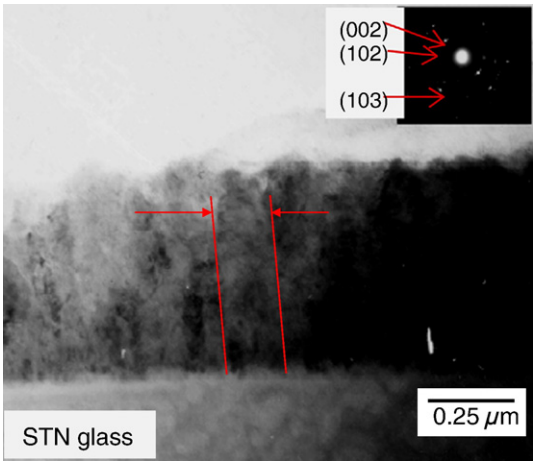

Fig. 2. TEM bright field image for the cross-section of the film ZnO: Al–1.7 wt.%Sc with its selective area diffraction (SAD) in the inset.

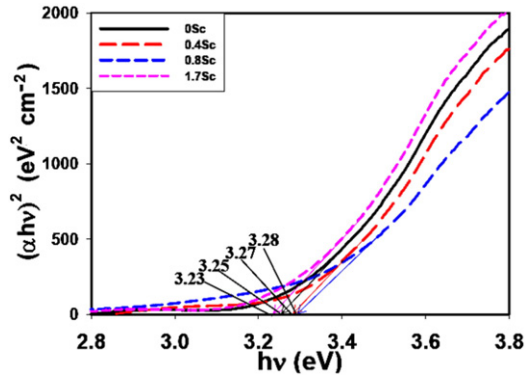

Fig. 4. Plots of $(\alpha h\nu)^2$ against $h\nu$ for sputtered films ZnO: Al–*x*Sc where *x* at 0, 0.4, 0.8 and 1.7 wt.%, and the energy gap was obtained by extrapolating the linear absorption edge part.