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Influence of Al concentration and annealing temperature on structural, optical, and electrical properties of Al co-doped ZnO thin films

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ABSTRACT

The pure ZnO and Al-doped ZnO (AZO) thin films (thickness: 200 nm) were prepared on both side polished silica (SiO_2) substrates via RF magnetron sputtering at room temperature by using 2.5 inches high-purity ZnO (99.9%) and Al (99.9%) targets. The samples were annealed at 300 °C, 400 °C and 500 °C for 45 min in N_2 ambient in quartz annealing furnace system, respectively. We investigated the effects of various Al concentrations and annealing treatment on the structural, electrical, and optical properties of films. The preferred crystallization was observed along c axis (single (0 0 2) diffraction peak) from substrate surface assigning the single crystalline Würtzite lattice for pure ZnO and AZO thin films. Although increasing Al concentration decreases the order of crystallization of as-grown films, annealing process increases the long range crystal order. The crystallite sizes vary between minimum 12.98 nm and maximum 20.79 nm for as-grown and annealed samples. The crystallite sizes decrease with increasing Al concentration but increase with increasing annealing temperature as general trend. The grain size and porosity of films change with annealing treatment. The smaller grains coalesce together to form larger grains for many films. However, a reverse behavior is seen for $Al_{2.23}ZnO$ and $Al_{12.30}ZnO$ samples. That is, Al concentration plays critical role as well as temperature on grain size. Low percent optical transmittance ($T\%$) is observed due to higher Al concentration and worse crystal quality for as-grown AZO films. $T\%$ decreases until 34.5% for as-grown $Al_{15.62}ZnO$ film. $T\%$ increases by increasing annealing temperature. AZO samples annealed at 500 °C have around 80% transparencies in the visible range of spectrum. Optical energy band gap values range between 3.17 eV and 3.60 eV for as-grown and annealed samples. Band gap increments are attributed to increasing free electron concentration depending on doped Al ratio known as Burstein–Moss effect. Annealing process increases the band gap values, too. The electrical conductivity and carrier concentration of the films increased with increasing Al content. The mobility decreases due to increase in Al concentration that deteriorates the crystal nature. Annealing process especially at 400 °C enables the AZO samples to exhibit best electric conductivity due to long range crystal structured nature and increasing free electron concentration in the films. The maximum electrical conductivity value of $1.06 \times 10^4\ (\Omega\text{cm})^{-1}$ was measured from $Al_{12.30}ZnO$ sample annealed at 400 °C.

1. Introduction

Transparent conducting oxide films (TCOs) have received great attention due to their distinguished performance in electronics, optics, photonics, and recently for energy-saving devices. Most of these oxides are based on group II, group III, and group IV metals. Especially, ZnO became a key material because of its applications as sensors, transducers and catalysts [1]. Moreover, ZnO is a wide band gap (3.2 eV at room temperature) semiconductor that is suitable for short wavelength optoelectronic applications [2]. The band structure and optical properties of ZnO are very similar to GaN, which is well known material for the fabrication of optical devices such as light emitting diodes or laser diodes [3].

Zinc oxide has wide conductivity range changing with respect to different oxidation conditions. Doping with group II, group III and group VII elements such as indium (In), aluminum (Al), gallium

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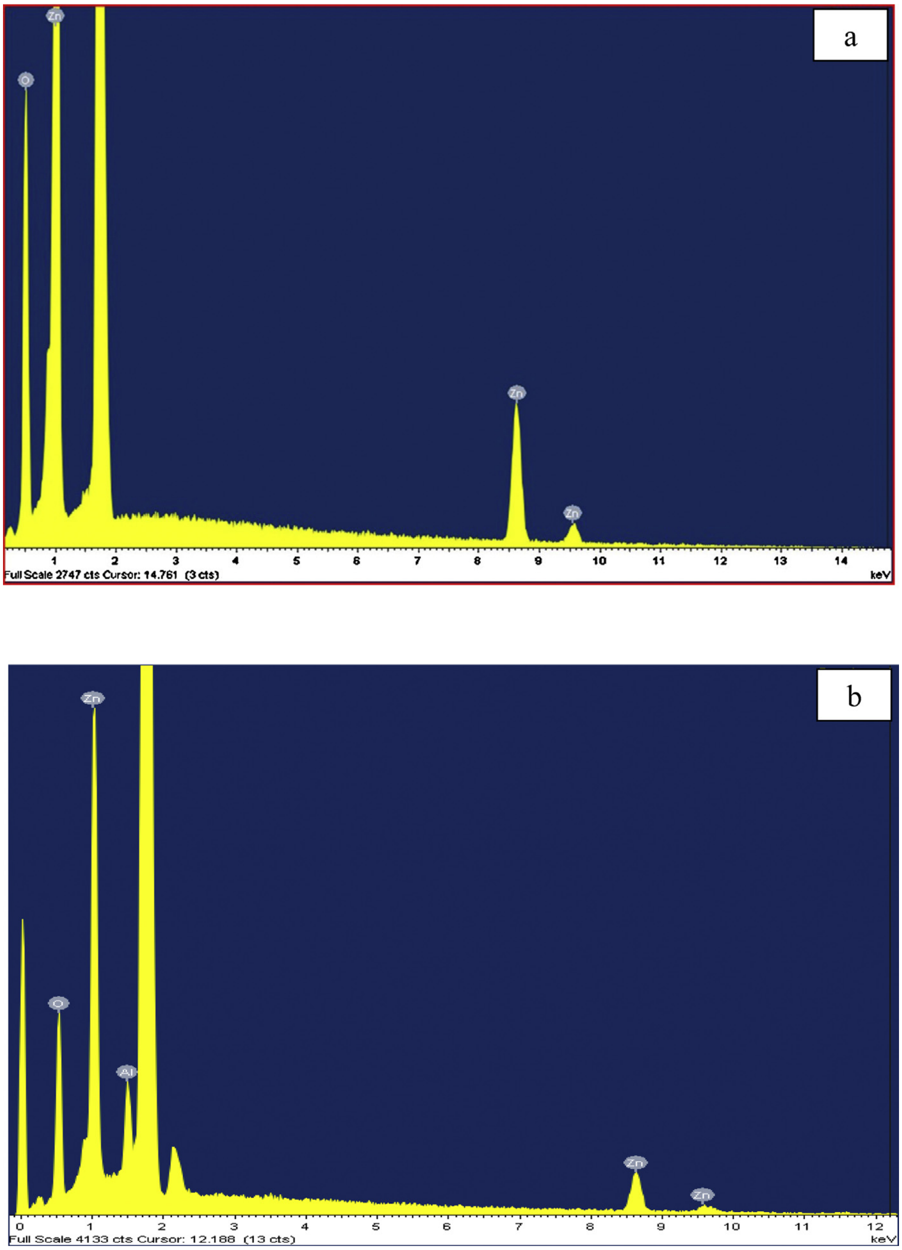

Fig. 1. The EDS spectra recorded from (a) pure ZnO and (b) AZO film that includes 12.30 at.% of Al.

(Ga), copper (Cu), cadmium (Cd), fluorine (F), etc. increases the stability, conductivity and transparency of ZnO films [4,5]. Aluminum doping is particularly suitable for those purposes. Aluminum doped ZnO (AZO) thin films have high transmittance in the visible region, low resistivity and the optical band gap can be controlled by using different concentration [6]. The electrical conductivity is primarily due to the contribution from Zn, Al interstitial atoms and oxygen vacancies in the crystal structure. Kim et al. indicated that the conductivity is strongly depended on the crystallinity of the thin films [7]. AZO also has additional applications such as antistatic coatings, solid-state display devices, heaters, defrosters, etc. [3,6].

The physical properties and crystal structure of the films depend on the deposition method, the growth conditions, post deposition treatment and substrate orientation for epitaxial layers. ZnO films have been prepared by several techniques such as reactive e-beam evaporation [8,9], sputtering [10], pulsed laser ablation [11], chemical vapor deposition [12], sol–gel process [13]. To our knowledge, RF magnetron sputtering technique provides economical and efficient usage of Al and ZnO evaporants, too. In the literature, it is mentioned that AZO films grown on Si(1 1 1), Si(1 0 0) and silica (SiO_2) substrates in hexagonal Wurtzite crystal structure prominently oriented in (0 0 2) direction [8–13].

2. Experimental

The pure ZnO and AZO thin films were deposited on fused silica (SiO_2) substrates with dimension of 10 mm × 10 mm by RF and DC magnetron sputtering techniques. The deposition chamber was pumped down to 1×10^{-5} Torr by using a rotary pump and a turbo molecular pump. The deposition pressure was 3.2×10^{-2} Torr. Al and ZnO targets were used to deposit AZO thin films in this work. The AZO targets were specially designed by high-purity zinc oxide (ZnO, 99.9%) and aluminum (Al, 99.9%).