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The Microstructure of Aging ZnO, AZO, and GZO Films

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***Abstract*—**RF magnetron sputtering is used on the ceramic targets, each of which contains zinc oxide (ZnO), zinc oxide doped with aluminum (AZO) and zinc oxide doped with gallium (GZO). The electric conduction mechanism of the AZO and GZO films came mainly from the Al and Ga, the oxygen vacancies, Zn interstitial atoms, and Al and/or Ga interstitial atoms. AZO and GZO films achieved higher conduction than did ZnO film, it being ion vacant and nonstoichiometric. The XRD analysis showed a preferred orientation along the (002) plane for ZnO, AZO, and GZO films.

***Keywords*—**ZnO, AZO, GZO, Doped, Sputtering .

I. Introduction

IT is common to use transparent conducting oxides (TCOs), such as indium tin oxide (ITO), in optoelectronic devices such as solar cells and flat panel displays due to its low electrical resistivity (about ~10-4 Ωcm) and relatively high work function [1]. However, the cost of preparing ITO films is very high because indium is a rare and expensive element [2]. Transparent conducting zinc-oxide (ZnO), a II-VI n-type semiconductor with a wide band gap of approximately 3.3 eV at room temperature, has been widely used as a TCO material because it is low in cost, readily available, and non-toxic and has good chemical stability and high optical transmission [3]. Although ZnO is a potential candidate to replace ITO, its conductivity is lower than those of other metals. To eliminate that drawback, the introduction of metal dopants and/or metal-nanoparticles has been investigated [4].

Impurity-doped ZnO thin films such as Ga-doped zinc oxide (GZO) and Al-doped zinc oxide (AZO), having high transmittance and low resistivity, have attracted much attention as alternatives to ITO film. AZO and GZO films are advantageous because their primary components are inexpensive zinc oxide series films. These AZO and GZO films are known to demonstrate increased conductivity due to the oxygen defects of ZnO, which is their primary component, and the increased use of AZO and GZO films can be realized if the conductivity and optical transparency can be raised to levels close to those of ITO film. Although both AZO and GZO are promising TCO candidate materials, GZO still has three main advantages over AZO for several reasons. First, Ga has a higher resistance to oxidation during deposition than Al. Second, the diffusivity of Ga is relatively low compared to that of Al, so fewer diffusion-related problems (e.g., contamination) occur in the final products. Finally, less lattice distortion and fewer lattice defects are generated in GZO than in AZO, even at high concentrations of Ga, because the Ga-O bond length (0.192nm) is close to that of Zn-O (0.197nm) [5], [6].

Currently, TCO films can be prepared by RF magnetron sputtering, metal organic chemical vapor deposition (MOCVD), pulsed laser deposition (PLD), molecular beam epitaxy (MBE), and Sol-Gel methods. Among them, RF magnetron sputtering can be performed at lower temperatures with better quality, and it is widely used in industry and academia [7]-[12]. Some researchers think that the electrical properties of AZO and GZO thin films can be improved with the use of different annealing conditions [13]-[16], but almost no reports have examined the influence of chemical etching on the electrical properties of these films. Therefore, in the present study, ZnO, GZO, and AZO thin films were deposited by RF magnetron sputtering and then annealed and chemically etched by NaOH solution. The surface morphologies, crystal structures, and electrical and optical properties of the thin films were also investigated.

II. Experimental Procedure

ZnO, AZO, and GZO thin films with thicknesses of 200nm and 400nm were deposited on glass by RF magnetron sputtering using 4-inch-diameter targets of ZnO, AZO (ZnO: Al_2O_3 =98:2 wt. %, and GZO (ZnO:Ga_2O_3 = 95:5 wt. %). The base pressure of the deposition chamber was kept at 2.5×10^{-6} torr and the working pressure at 2.5×10^{-3} torr by a rotation-type mechanical pump and a turbo pump, and the sputtering power during deposition was 150 W. Further post-treatments of annealing (air furnace, 230°C for 30min) and wet etching (1 wt.% NaOH aqueous solution at 40°C for 5min) on the ZnO, AZO, and GZO films/glass were tested.

III. Results and Discussion

Fig. 1 shows SEM images of ZnO, AZO and GZO films with a thickness of 200nm after post treatment of 230°C annealing for 30min and etching in 1 wt.% NaOH aqueous solution for 5 min. The films display well-crystallized angular grains and smooth grains; Figs. 1 (a), (c), and (e) are side-view images showing the ZnO, AZO and GZO to have thicknesses of 200 nm and columnar structures. Figs. 1 (b), (d), and (f) are top-view images showing the ZnO, AZO and GZO films to have sub-micron and nano-sized grains.

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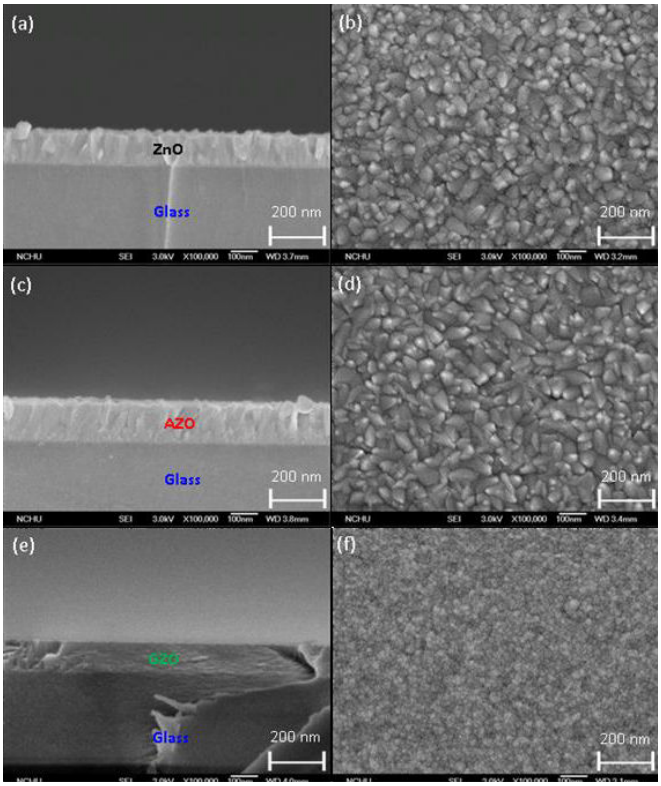

Fig. 1 SEM images of ZnO, AZO and GZO films after annealing at 230°C for 30min and etching in 1 wt.% NaOH for 5min; (a), (c), and (e) side-view images show ZnO, AZO and GZO films with thicknesses of 200nm, (b), (d), and (f) top-view images show ZnO, AZO and GZO films with sub-micron and nano grain sizes.

Fig. 2 shows SEM images of ZnO, AZO and GZO films with thicknesses of 400nm after post treatment. Figs. 2 (a), (c), and (e) are side-view images showing the ZnO, AZO and GZO films to have thicknesses of 400nm; Figs. 2 (b), (d), and (f) are top view images showing that the ZnO, AZO and GZO films, like those in Fig. 1, have sub-micron and nano-sized grains. The 400nm GZO film had void defects on the surface, in contrast to the smooth surface of the 200nm GZO film. However, both the 200nm and 400nm films of ZnO and AZO had continuous, smooth surfaces. Furthermore, AFM of a zone of 2μm x 2μm revealed that the GZO film had the smallest surface roughness values of 1.06nm (Ra) and 1.45nm (Rms), the AZO film had surface roughness values of 2.32nm (Ra) and 3.02nm (Rms), and the ZnO film had roughness values of 4.43nm (Ra) and 5.56nm (Rms).

IV. Conclusions

ZnO, AZO and GZO films were synthesized by RF magnetron sputtering. The above analytical results support crystal columnar structures were observed in all the films. The AZO film was better crystallized, displaying angular grains. The voids in the GZO film made the continuity poor.

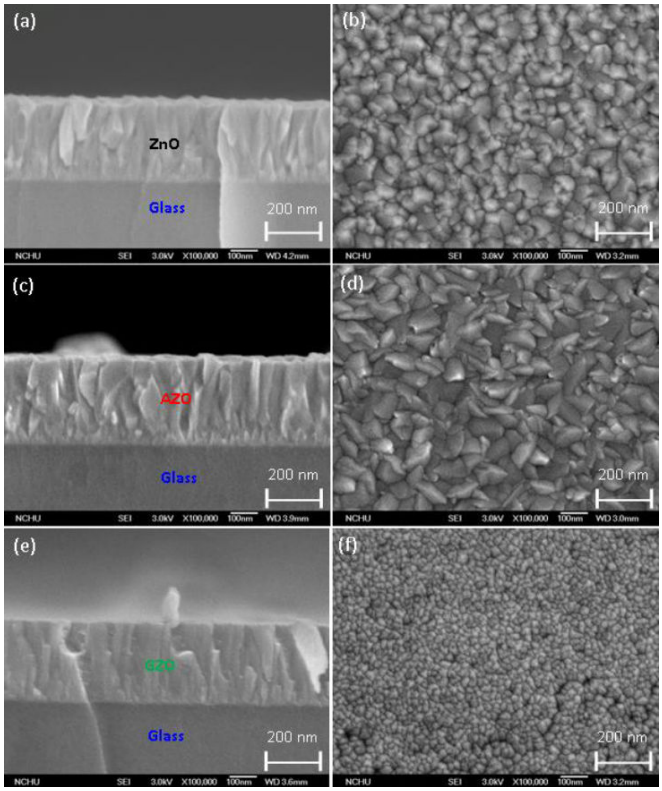

Fig. 2 SEM images of ZnO, AZO and GZO films after annealing at 230°C for 30min and etching in 1 wt.% NaOH for 5min; (a), (c), and (e) side-view images show ZnO, AZO and GZO films with thicknesses of 400nm, (b), (d), and (f) top-view images show ZnO, AZO and GZO films with sub-micron and nano grain sizes.

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