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Effects of post-deposition heat treatment on the microstructure and properties of Al-doped ZnO thin films prepared by aqueous phase deposition

Pin-Chuan Yao [a,*], Shih-Tse Hang [b], Menq-Jiun Wu [b], Wen-Tse Hsiao [c]

[a] *Department of Materials Science and Engineering, Da-Yeh University, Dacun, Changhua 51591, Taiwan*
[b] *Department of Mechatronics Engineering, National Changhua University of Education, Changhua 50007, Taiwan*
[c] *Instrument Technology Research Center, National Applied Research Laboratories, Hsinchu 30076, Taiwan*

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ABSTRACT

In this study, transparent conducting aluminum-doped ZnO thin films (AZO) were deposited on glass substrates by a water-based liquid phase deposition method. The results show that by employing a two-step post-deposition heat treatment, the preferential orientation of ZnO (002) appeared as soon as the polycrystalline films were formed. Under a reducing atmosphere, the crystallinity of the films was effectively improved. Furthermore, the reducing atmosphere was also beneficial for the removal of the residual stress of the prepared films and the c-axis lattice constant was less stretched as compared to those under an inert atmosphere at identical T_p. Both the atomic force micrograph and scanning electron micrograph clearly exhibited that the heat treatment induced considerable grain growth. The X-ray photoelectron spectrum revealed that the heat treatment atmosphere had little impact on the bonding state of zinc and that the reducing atmosphere was favorable for the non-stoichiometric alumina, which in turn, resulted in more oxygen vacancies and led to improvement in electrical conductivity. The ratio of chemisorbed oxygen declined substantially when applying the reducing atmosphere. Accordingly, hydrogen was helpful for the reduction of chemisorbed oxygen onto AZO films. Generally, the electrical resistivity declined linearly with T_p. A minimum resistivity of $9.90 \times 10^{-3}\ \Omega \cdot \text{cm}$ was obtained with a doping concentration of Al/Zn = 2.25 at.% at $T_p = 700\ ^\circ\text{C}$. The largest mean free path of the carriers was 1.2 Å, which was much smaller than the observed grain sizes of the AZO films. Accordingly, the grain boundary scattering was not the detrimental scattering mechanism. In contrast, the scattering within the grains was responsible for the low mobility. An increase in optical transparency with the heat treatment temperature was observed due to the compact and smooth topography with larger grains, among which, less porous structures were formed at elevated temperature.

1. Introduction

Al-doped zinc oxide (AZO) is one of the most promising transparent conducting electrode materials owing to its low electrical resistivity and high transparency in the visible (VIS) range and the near infrared (NIR) region. In comparison to the commonly used fluorine-doped tin oxide and tin-doped indium oxide, doped zinc oxide is more resistant against hydrogen plasma reduction during film processing [1]. A variety of thin film deposition techniques have been developed to prepare AZO thin films, including DC and RF magnetron sputtering [2,3], electron beam evaporation [4], pulsed laser deposition [5], spray pyrolysis [6,7], chemical vapor deposition [8] and sol–gel processing [9–18]. Among them, the sol–gel method is simpler and more cost effective when employing zinc acetates and aluminum nitrates/chlorides as precursor and dopant, respectively, in an alcoholic solution including methanol [9,10], ethanol [11,12], propanol [13,14], methoxyethanol [14–17], ethyl glycol and glycerol [18]. Usually, monoethanolamine, diethanolamine or tetramethyl ammonium hydroxide are introduced as stabilizer [15,18].

The use of heat treatment is particularly challenging and has become one of the crucial steps for ZnO-related thin film growth. Gupta and Mansingh [19] showed that the RF sputtered ZnO films on quartz substrates become almost stress free after applying a post-deposition annealing treatment at 673 K for 1 h in air. Lee et al. revealed that the drying conditions as well as the first- and second-heat treatments have prominent effects on the structural, electrical and optical properties of sol–gel ZnO thin films deposited on silica glass substrates [16]. With second-heat treatment at 500 °C, the conductivity of the film was subsequently improved. This could be partly attributed to the increase in the grain-packing density of the film. Oh et al. studied the annealing of AZO films deposited on glass substrates by RF magnetron co-sputtering [20]. They concluded that the improved electrical properties are ascribed to desorption of the negatively charged oxygen species from the grain boundary surfaces by the hydrogen annealing treatment. For Al-doped ZnO films prepared by the sol–gel method, as concluded by Musat et al. [17], the resistivity of the films (Al content: 2 wt.%)

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[*] Corresponding author. Tel.: +886 4 8511247; fax: +886 4 8511280.
E-mail address: pcyao@mail.dyu.edu.tw (P.-C. Yao).

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could be reduced to $1.3\times10^{-3}\ \Omega\cdot$cm after being heated under a reducing atmosphere of forming gas.

The reducing atmosphere plays an important role during the post-deposition heat treatment process. For precursor films annealed under reducing atmosphere, the crystallinity of the films was effectively improved [15]. The reducing atmosphere results in the elongation of unit cell along the c-axis of ZnO. As reported by Sagar et al. [10], they confirmed that the presence of hydrogen atoms incorporated at the interstitial site making an O – H bond that acts as a shallow donor. In addition, when the second-heat treatment is performed in a reducing atmosphere, the carrier's concentration may increase by desorption of oxygen in the grain boundaries which act as traps for the carriers [16].

Water-based wet chemical synthesis is more economical and environmental friendly as compared to the traditional sol–gel process. This method has been employed for the synthesis of several ferroelectric ceramics [21]. For thin film preparation, Mondelaers et al. [22] deposited ZnO films on a SiO_2/Si (111) substrate after overcoming the poor affinity between the film-substrate interfaces by means of a chemical cleaning treatment [23]. Recently, transparent conducting AZO thin films were grown on Corning 1737F glass substrates by this method in our laboratory [24]. By adding aluminum chloride as dopant, c-axis oriented polycrystalline ZnO thin films with thicknesses of 100–150 nm could be derived. The conductivity of the films was further improved by varying the dopant concentration as well as by applying additional heat treatment. By varying the doping concentrations, the optical and electrical properties could be further adjusted [24]. However, detailed information about the influence of post-deposition treatment on aqueous phase deposited AZO thin films is still unavailable. In this study, we reported the effects of heat treatment temperature and atmosphere on the properties of AZO films on glass substrates prepared by aqueous phase deposition. Emphasis was put on the structural, optical and electrical characteristics of the AZO films under a reducing atmosphere at various temperatures. We anticipated that more information on how to manipulate the heat treatment processes could be acquired for aqueous phase deposited AZO films with desirable optoelectrical properties.

2. Experimental details

In this study, AZO thin films were prepared by aqueous phase deposition. Zinc acetate dihydrate ($Zn(OOCCH_3)_2\cdot 2H_2O$; Riedel-de Haën, 98+%) was used as a starting material. Aluminum chloride ($AlCl_3\cdot 6H_2O$, Riedel-de Haën, 98+%) was added as a dopant with a doping concentration of Al/Zn = 2.25 at.%. Citric acid ($C(OH)(COOH)(CH_2COOH)_2$; Aldrich, 99%) acted as a complexing agent to prevent early precipitation during gel synthesis. The citric acid was dissolved in an aqueous solution of zinc acetate (0.3 M) in a molar ratio of $[Zn^{2+}]$:[citric acid] = 3:1. The pH of the solution was adjusted by a concentrated ammonia solution (NH_3; Katayama, ca 28% in H_2O) to assure a complete deprotonation of citric acid ($pK_{a3}=6.4$) for maximum coordination of Zn^{2+} [25]. Under magnetic stirring at 25 °C for 24 h, an opaque and homogeneous hydrosol appeared. A 2 cm × 2 cm Corning 1737F glass substrate was cleaned ultrasonically for 5 min in acetone, isopropanol and de-ionized water baths, respectively. In order to deposit thin films from aqueous solutions, the affinity of the water–substrate interface was improved by means of a chemical cleaning treatment modified by the recipe published elsewhere [23]. The detailed procedure consisted of a thorough cleaning with a H_2SO_4 (10 M, 30 ml)/H_2O_2 (30 wt.%, 30 ml) mixture which oxidized the organic residues, followed by etching in a 0.5% HF solution for 15 s. The etched substrate was rinsed with de-ionized water and blown dry with nitrogen until ready for use. The hydrophilicity of the substrate was evaluated by measuring the contact angle of water by a photographic method using the geometry for Toshev's model [26]. After the chemical cleaning treatment, the contact angle of a 5 μl sessile drop of water had declined from 29.6° (without chemical cleaning treatment) to 15.2°. The precursor films were spin-coated on glass substrates at 1000 rpm for 10 s followed by drying in an environmental chamber kept at 25 °C and with relative humidity of 60% for 8 h [27]. This process was repeated several times until the desired thickness of the sintered films was reached. An average of five layers was necessary to deposit films with thicknesses from 100 to 150 nm. The as-deposited films then underwent a post-deposition heat treatment procedure. Five modes of heat treatment procedure were applied in this study. The procedures of these modes are described briefly in Table 1.

The thicknesses of the AZO thin films were measured by a stylus profilometer (Kosaka laboratory ET3000). X-ray diffraction (XRD, Shimadzu XRD-6000, CuKα, λ = 1.5405 Å) was employed to characterize the crystallinity of the AZO films. The current and voltage of the X-ray tube was maintained at 30.0 mA and 30.0 kV, respectively during the measurement. 2θ-scans from 20 to 70° by Bragg-Brentano geometry were performed. The crystal size of the AZO film was estimated by Scherrer's formula [2]:

$$D=\frac{0.9l}{\beta\,\mathrm{cos}q} \tag{1}$$

where D is the average dimension of the crystallites normal to the reflecting planes, β is the crystallite-size breath defined by $\beta^2=B^2-b^2$ in which B is the full width at the half maximum (FWHM) of the observed peak and b is the instrumental factor (b = 0.13 in our derivation). Surface morphology was observed by a field emission scanning electron microscope (FE-SEM, JEOL, JSM-7401F, the operating voltage was 4.0 kV) and an atomic force microscope (AFM, Veeco CP-II, operating in tapping mode and using standard Si_3N_4 cantilevers). The chemical states of the films were investigated by X-ray photoelectron spectroscopy (XPS, ULVAC-PHI 5000) with the Al Kα X-ray source (1486.6 eV) typically set at 3 kV, 24 W and an angle of 45° was used in this experiment. Each sample was ion-etched by Ar^+ sputtering (1 kV acceleration voltage with a beam current of 10 mA) for 1 min before XPS analysis. The position of the C_{1s} peak was taken as a reference with a typical binding energy of 284.6 eV. The electrical properties, including resistivity (ρ), mobility (μ) and carrier concentration (N), were evaluated at room temperature by the Hall-effect measurement system (ECOPIA HMS-2000) in Van der Pauw four-point probe configuration. The optical transmission spectra were recorded with a UV/VIS/NIR spectrophotometer (Shimadzu UV-1700E) ranging from 190 to 1100 nm in wavelength. Photoluminescence (PL) spectra were carried out by excitation of a He–Cd laser (λ = 325 nm) at room temperature.

3. Results and discussion

To prevent redundant description, detailed information about the structural evolution of the precursor films has been described elsewhere [24]. Previous studies have shown that for the sol–gel deposited AZO films, if the heat treatment temperature (T_p) is too high, the conductivity of the films is degraded considerably [15]. However, the poor c-axis growth of ZnO frequently arises when employing a low boiling point solvent such as water or isopropyl alcohol. This needs to be overcome to achieve better optical and electrical properties [28]. Accordingly, a high

Table 1
Post-heat treatment procedures.

Mode	Single stage (1 h)	
PT1	Heat-treated at the set temperature, T_p (O_2/Ar = 10/190 sccm)	
PT2	Heat-treated at T_p (H_2/Ar = 10/190 sccm)	
PT3	Heat-treated at T_p (Ar = 200 sccm)	
Mode	Two stages (1 h)	
	First stage(0.5 h)	Second stage(0.5 h)
PT4	Heat-treated at T_p (vacuum)	Heat-treated at T_p (H_2/Ar = 10/190 sccm)
PT5	Heat-treated at T_p (vacuum)	Heat-treated at Tp (Ar = 200 sccm)