Aluminum-doped zinc oxide transparent conductors deposited by the sol–gel process

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Abstract

Thin films of transparent conducting aluminum-doped ZnO have been deposited using a sol–gel process. The dependence of electrical characteristics upon aluminum concentration in the films and upon post-deposition heat treatment in vacuum was examined. The effect of changing the aluminum-to-zinc ratio from 0% to 4.5% (atomic) and the heat treatment temperature in vacuum has been thoroughly investigated. Resistivities of $(7–10) \times 10^{-4}$ Ω cm have been achieved for ZnO:Al films with Al/Zn ratios of 0.8 at.% heated to 450 °C in vacuum. Transmittance in the visible region is above 90%. Similar results were obtained using aluminum chloride and aluminum nitrate as the aluminum precursor.

1. Introduction

Zinc oxide holds considerable promise as an optical transparent conducting material due to its wide band gap ($\sim 3.3\text{eV}$), its amenability to defect or impurity doping, and other desirable properties such as low cost and non-toxicity [1]. Thin films of transparent conducting zinc oxide have been prepared by a wide variety of techniques, including reactive evaporation [2, 3], r.f. sputtering, d.c. and ion beam sputtering [4–10], chemical vapour deposition [11–14] and spray pyrolysis [15–20].

As an n-type semiconductor, the material can be effectively doped with an appropriate donor. Both stoichiometry and dopant impurities affect the electrical and optical characteristics to the point that ZnO can either be a near-insulator or a semi-metal. A potential low-cost alternative to tin-doped indium oxide, ZnO films could be used as less expensive transparent electrode material for use as a window layer for solar cell devices and a transparent conducting layer for electroluminescent devices. For practical applications undoped ZnO films are inferior to indium- or tin- based oxide films. However, doped films can be made to have very stable electrical and optical properties. The electrical properties of as-deposited films appear to be highly dependent upon the deposition methods, perhaps due to different stoichiometries and oxygen chemisorption on the surface of films and grain boundaries in polycrystalline ZnO films. Although aluminum-doped ZnO (ZnO:Al) films can be deposited using many methods, the sol–gel process is simpler and less expensive and has the general advantage of producing high purity, homogeneous films at relatively low temperatures.

This paper describes the preparation of aluminum-doped ZnO films by the sol–gel process and the optimization of aluminum-doped ZnO to produce highly transparent conductive films by controlling the dopant concentration and by annealing in vacuum.

2. Experimental procedure

A solution of ZnO precursor was made by dissolving zinc acetate ($Zn(CH_3CO_2)_2 \cdot 2H_2O$) in anhydrous ethanol or methanol. Solutions of the solid were prepared in increasing concentrations to establish maximum solubility. Without acid additions the maximum concentration reached was 6 wt.% in ethanol and 12 wt.% in methanol. To achieve aluminum doping, anhydrous aluminum chloride ($AlCl_3$) or aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) was added to the solution. As various parameters involved in the process are mutually dependent on each other, only the doping concentration was changed. The doping concentration, *i.e.* aluminum/zinc atomic ratio as a percentage (Al/Zn at.%), was varied from 0 to 4.5 at.% in the solution.

The solutions were hydrolysed with 2 mol H_2O per mol metal acetate by adding water dissolved in ethanol at 10 wt.% concentration dropwise together with roughly 5 wt.% lactic acid. Turbidity and precipitation occurred which was readily eliminated by introducing additional concentrated lactic acid until the turbidity permanently disappeared. Using this proce-

dure the stable solutions were prepared as required to carry out the experiments described.

Previous work has shown that dipping was capable of producing controlled thickness sol–gel coatings. The drain coating method was used in our work. In this case the substrate remains stationary, and the solution is drained from vessel. Some of the parameters in the fluid mechanics expression are changed, but the results are generally similar to the dip-coating method. The thickness of the coating layer depends upon the speed at which the solution level falls, the concentration of the solution, the viscosity of the solution, the surface tension of the solution, and the vapour pressure, temperature and relative humidity above the coating bath. The average baked thickness was determined to be 30–50 nm per coating cycle. Thicker films need multiple coatings. After coating, the substrates were loaded carefully into an electrically heated furnace, where they were heated in circulating air to the desired temperature at a rate greater than 10 °C min^{-1}. Repeating the above process of coating and heating substrates increased the thickness of ZnO:Al films on the substrates. Figure 1 presents the flow diagram for ZnO:Al films from preparation of the solution to production of the coated substrates.

The electrical resistivity and Hall coefficient of the films at room temperature were measured by Van der Pauw methods. A constant current source and electrometer (Keithley 614) having an impedance greater than 5×10^{13} Ω were used to measure the electrical and galvanomagnetic properties. The visible transmittance was measured using UV-240 and Hewlett-Packard 8452A UV–visible recording spectrophotometers, which gave identical results. X-ray diffraction measurements were carried out on a Philips diffractometer using Cu Kα ($\lambda = 1.542$Å) as the source line. The films were treated in air or in a vacuum system at different temperatures.

3. Results and discussion

3.1. Structural properties

X-ray diffraction of ZnO and ZnO:Al films deposited by the sol–gel process showed the annealed films to be polycrystalline. After annealing in air at 400 °C, the films showed evidence of conversion from an amorphous to polycrystalline structure with a degree of preferential orientation when a substrate of (100) silicon was used. In this case there was a tendency for the c axis to be perpendicular to the substrate. Further annealing in vacuum led to no further increase in crystallinity or degree of orientation. Figure 2 shows the X-ray diffractograms of ZnO and ZnO:Al films.

3.2. Optical properties

All films with different doping concentrations were highly transparent in the visible region. The free electrons in the doped films modified some of the film's optical properties. In the visible, however, the films are highly transparent and their spectra are comparable with those of dielectric coatings. As is shown in Figs. 3 and 4 the films have an average transmission of about 90% in the wavelength range 0.40–0.9μm.

The transmission spectrum for ZnO:Al films with Al/Zn 0.8 at.% both before and after annealing at 400 °C in vacuum are shown in Fig. 3. Oxygen is chemi-
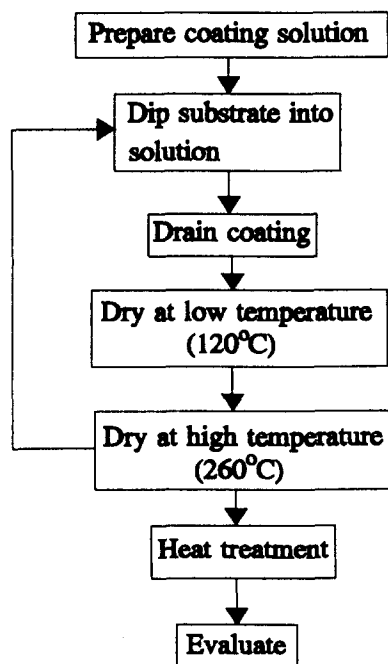

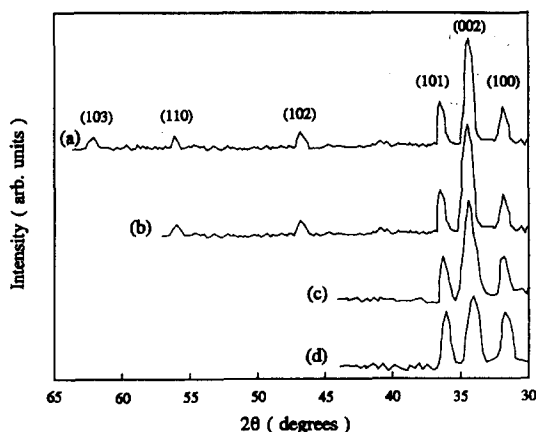Fig. 1. Flow diagram of the sol–gel process for depositing ZnO:Al films.

Fig. 2. X-ray diffractograms for undoped air-annealed ZnO films (a) before and (b) after annealing in vacuum and ZnO:Al films with Al/Zn 0.8 at.% (c) before and (d) after annealing in vacuum.
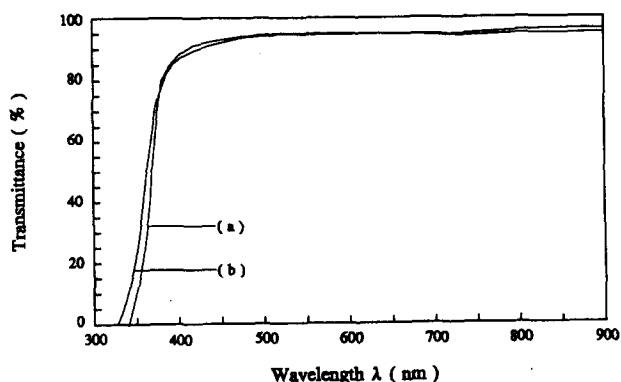
Fig. 3. Comparison of optical transmission spectra for ZnO:Al films with Al/Zn 0.8 at.% (a) before annealing and (b) after annealing in vacuum.
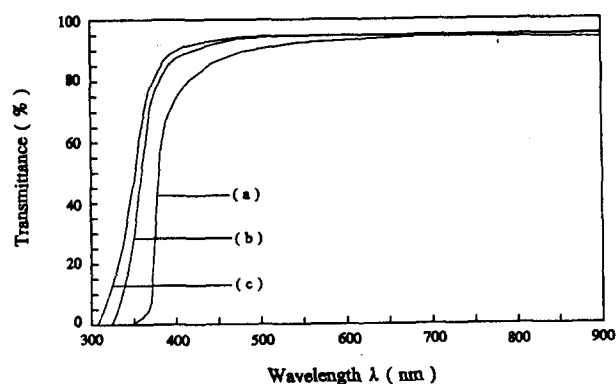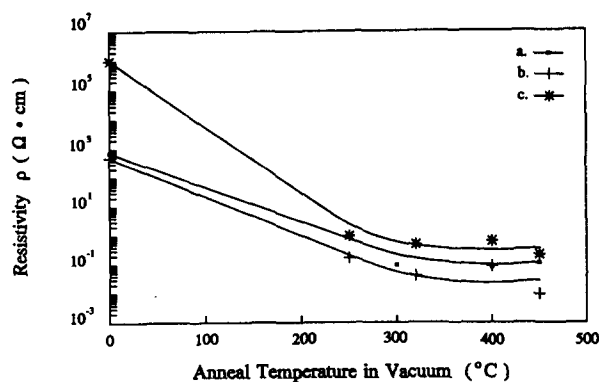

Fig. 5. Resistivity dependence on anneal temperature in vacuum for ZnO:Al films with Al/Zn 1.5 at.%. The films were initially annealed at: (a) 300 °C, (b) 400 °C and (c) 500 °C in air.

Fig. 4. Comparison of transmission spectra for (a) undoped ZnO film and ZnO:Al films with (b) Al/Zn 0.8 at.% and (c) 1.3 at.%.
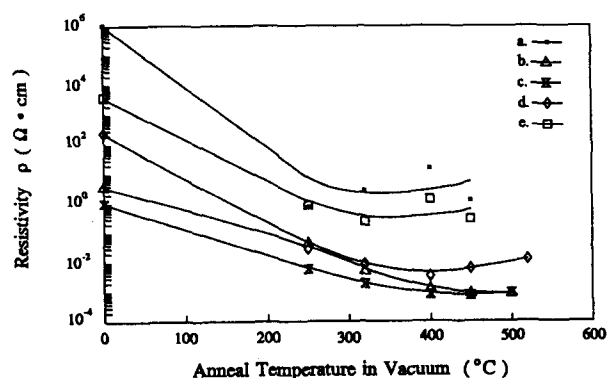

Fig. 6. Resistivity dependence on anneal temperature in vacuum for the films with Al/Zn: (a) 0.0 at.%, (b) 0.4 at.%, (c) 0.8 at.%, (d) 1.3 at.% and (e) 4.5 at.%.

sorbed on the ZnO surface and in pores in the films as O_2^- by accepting an electron from occupied conduction band states. Heating of the surface leads to the desorption of oxygen with the increase in annealing temperature. From those results, the shift in the absorption edge can be ascribed mainly to the increase in carrier concentration as detailed below in the description of electrical properties.

The spectra of undoped and aluminum doped ZnO films annealed in air at 400 °C, then annealed in vacuum at 400 °C are shown in Fig. 4. Such a shift in absorption edge as a function of carrier concentration has been described by Roth et al. [21] whose findings show that the shift is due to an increase in the effective band-gap with increasing carrier concentration.

3.3. Electrical properties

In the application of ZnO:Al films as a transparent conductor, especially in solid-state display devices, the electrical properties of the films must be the important factor. Therefore, the emphasis in studies of transparent conducting films has concentrated mainly on how to prepare low resistivity films.

To study the effect of annealing temperature and Al concentration on optical and electrical properties, a series of films with different Al/Zn atomic ratios was fabricated and annealed at various temperatures. Figure 5 shows resistivities of the films with Al/Zn 1.5 at.% which were annealed initially at 300 °C, 400 °C and 500 °C in air respectively, and then annealed in vacuum. The results show that the film annealed at 400 °C in air has the lowest resistivity. Figure 6 shows resistivities of the films with different Al concentrations annealed in vacuum. The resistivities generally are a minimum when annealed at about 400 °C. Figure 7 shows resistivities of the films with various Al concentrations annealed at 400 °C in air, and at 250 °C and at 400 °C in vacuum respectively. The film with Al/Zn 0.8 at.% annealed at about 400 °C exhibits the lowest resistivity ($\sim 7 \times 10^{-4}$ Ω cm).

The accuracy of the measurements on the high resistivity films will be somewhat less than the others owing to surface leakage effects, etc.. The degree of uncertainty in the measurements is difficult to quantify, but
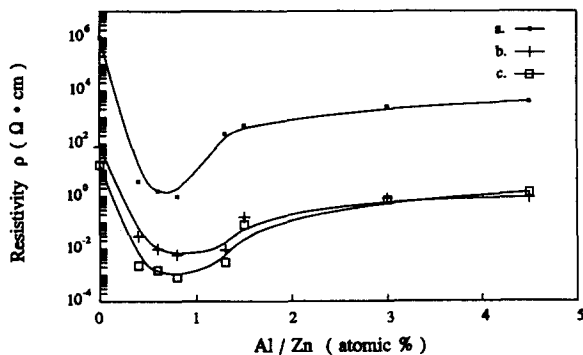
Fig. 7. Relation between resistivity and Al concentration. The films were annealed at: (a) 400 °C in air; (b) 250 °C in vacuum; (c) 400 °C in vacuum.

Fig. 9. (a) Resistivity, (b) carrier concentration and (c) Hall mobility as a function of Al/Zn at.% ratios for ZnO:Al films annealed at 400 °C in vacuum.
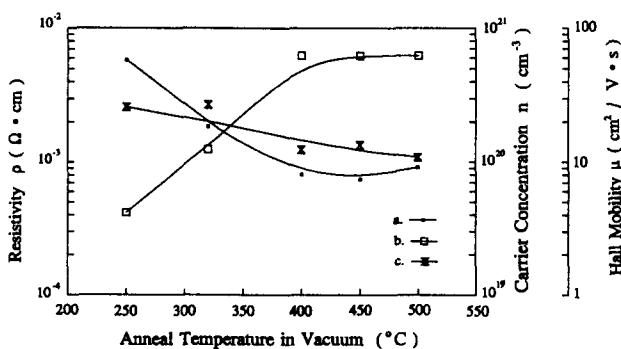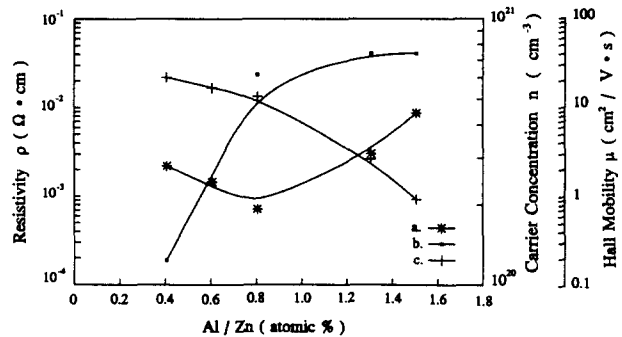

Fig. 8. (a) Resistivity, (b) carrier concentration and (c) Hall mobility as a function of anneal temperature in vacuum for ZnO:Al film with Al/Zn 0.8 at.%.

the errors will be mostly systematic and the relative behaviour of different films will be accurate.

Figure 8 shows that resistivity ρ, carrier concentration n and Hall mobility μ of the film with Al/Zn 0.8 at.% depend upon the anneal temperature in vacuum. The resistivity decreases with anneal temperature up to 450 °C and increases slightly at 450–500 °C. The carrier concentration increases largely owing to saturation while Hall mobility decreases slightly with temperature. The chemisorption of oxygen and the location of Al atoms which are not on zinc sites result in a low carrier concentration before heat treatment in vacuum. The chemisorption of acceptor oxygen on the ZnO:Al surface, in the pores of the film and between grain boundaries forms an electronic depletion layer which acts as a surface potential barrier and causes low mobility. Therfore, we consider that the decrease of resistivity during annealing in vacuum results in a change of carrier concentration and mobility from the movement of Al atoms to Zn lattice sites and the desorption of oxygen from the ZnO:Al surface, pores and grain boundaries. The increase in conductivity is not due to any increase in crystallinity since the X-ray diffraction measurements show no effect owing to vacuum annealing.

The relationships between ρ, n, μ and Al concentration are shown in Fig. 9. The carrier concentration of the film was found to increase with doping concentration except at higher doping concentration, where a tendency towards saturation was observed. Such behaviour was expected as a result of substitutional doping of Al^{3+} at the Zn^{2+} site creating one extra free carrier in the process. As the doping level is increased, more dopant atoms occupy lattice sites of zinc atoms, resulting in more charge carriers. However, after a certain level of doping, no more zinc sites can be occupied by dopant atoms because of the limited solubility of Al in the ZnO crystallites. The ionic radius of aluminum is smaller than that of zinc and therefore excess aluminum may occupy interstitial positions as suggested by Cossement and Streydio [22] leading to distortion of the crystal structure. High doping concentrations will therefore lead to ionized impurity scattering from the substitutional donors and also scattering from the interstitials. The aluminum atoms may also segregate to the grain boundaries in the form of Al_2O_3 which will increase the grain boundary barrier. Thus, the doping concentration reaches a maximum when the substitutional doping of the zinc oxide by aluminum is at a maximum whereas the mobility will continue to fall as more scattering and grain boundary barrier effects occur. The destruction of the films under treatment at high temperatures also causes the decrease in mobility and the increase in resistivity.

From the work of Kawamoto *et al.* [23] it was suggested that the decrease of resistivity below 400 °C was due to the formation of oxygen vacancies, whereas the increase at 400 °C was mainly due to Al donors. They reported that the X-ray photoelectron spectroscopy (XPS) feature occurring between those of Al_2O_3 (74.70 eV) and Al (72.65 eV) shifted and new peaks appeared which were attributed to Al_2O and AlO after heat treatment at 400 °C. Therefore, the authors concluded that Al atoms substitute for Zn atoms in
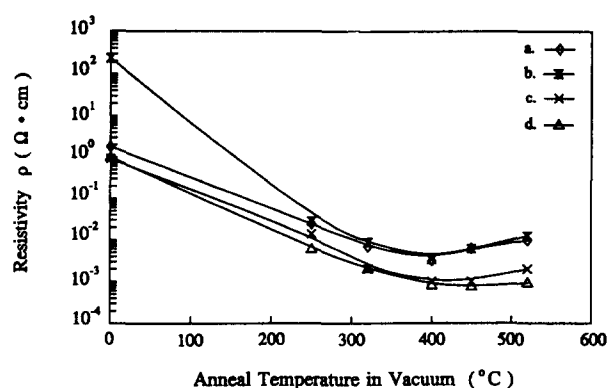
Fig. 10. Comparison of resistivity for ZnO:Al films with Al/Zn (a) and (b) 1.3 at.% and (c) and (d) 0.8 at.% using aluminum nitrate and aluminum chloride as dopants respectively.

ZnO:Al films after heat treatment and they should act as Al donors.

As aluminum chloride ($AlCl_3$) hydrolyses easily, aluminum nitrate ($Al(NO_3)_3 9H_2O$), which is more chemically inert and less expensive, was selected as dopant. Figure 10 shows that the resistivities of the films with Al/Zn 0.8 at.% and 1.3 at.% prepared using aluminum chloride and aluminum nitrate as dopant show very similar behaviour after annealing at 400 °C in vacuum.

4. Conclusion

Highly transparent and conductive ZnO:Al films have been successfully deposited from zinc acetate and aluminum chloride or aluminum nitrate by the sol–gel process. The techniques developed for production of ZnO:Al films are relatively inexpensive and simple to implement and consequently should be amenable to large area production. It was found that the electrical properties such as resistivity, carrier concentration and Hall mobility, and optical properties such as transmittance and optical band-gap, were closely related to both the annealing temperature in air and in vacuum and the aluminum concentration. The important results of the study so far can summarized as follows.

1. ZnO:Al transparent conducting films with transmittances above 90% and resistivities of about (7–10) × 10^{-4} Ω cm can easily be obtained.

2. Transparent conducting ZnO:Al films can be deposited by an inexpensive sol–gel technique from zinc acetate and aluminum nitrate or aluminum chloride solutions.

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