Original Paper

Low-Cost Deposition of Aluminum-Doped Zinc Oxide Transparent Conducting Films on Alkali Glass Substrate with Undercoat by Dip Coating Process

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Production cost of transparent conducting films can be drastically reduced if they are fabricated on a cheap alkali glass (soda-lime glass) substrate instead of a non-alkali glass substrate. Aluminum-doped zinc oxide films, which are cheaper and more environmentally-benign than indium oxide films, were fabricated successfully on an alkali glass substrate with an SiO_2 undercoat via a dip coating process, which is cheaper than physical vapor deposition such as a sputtering process. The lowest resistivity after post-deposition annealing in reducing atmosphere (N_2-0.1 % H_2) at 600 °C for 1 h was 6.4×10^{-3} $\Omega \cdot cm$ (0.8 at.% Al; thickness, 236 nm). This value agrees excellently with that (6.6×10^{-3} $\Omega \cdot cm$) fabricated on non-alkali glass in our previous work (0.8 at.% Al; film thickness, 246 nm). The resistivity of the films without the undercoat after annealing was more than one order higher that of the films with undercoat.

1. Introduction

Transparent conducting films are used for displays, solar cells and infrared-shielding windows etc. The prices of transparent conducting films are determined mainly by the glass substrate. Non-alkali glasses such as Corning 7059, EAGLE 2000 etc. are often used but they are very expensive; the price is approximately 10 US dollars for a 5 cm × 6 cm × 0.7 mm substrate. Alkali glass (soda-lime glass) of the same size is much cheaper (approximately 0.2 US dollars). Gordon[1] stated that the sodium in alkali glass can diffuse to damage the deposited transparent conducting films. He also introduced the use of an SiO_2 layer (undercoat) as a diffusion barrier which he did not cite in an academic report but in two patents. The effect of an SiO_2 undercoat fabricated by cheap a dip coating process was investigated in the present study to lower the cost of transparent conducting films. However, an investigation of sodium ions in the undercoat and transparent conduction films was not attempted in the present paper as the authors expect to address this issue in a future work.

A typical transparent conducting material is ITO (Indium-Tin-Oxide, or tin-doped In_2O_3), which consists of the rare element, indium. Fine ITO powder and undoped In_2O_3 were found to damage human lungs[2,3]. A more environmentally-benign material, aluminum-doped zinc oxide (AZO), was fabricated in the present study by dip coating and heating. The dip coating process is advantageous because of negligible material loss and low-cost deposition instruments although the film resistivity was higher[4-6] than those fabricated by physical vapor deposition such as sputtering process[7]. Analysis of sodium ions in the films was not attempted in the present study.

2. Experiment

2.1 Glass substrate

Alkali glass (Matsunami micro slide glass, S9213, 76 × 52 × 1.2 mm) was used as a substrate. The composition (wt.%) determined by X-ray fluorescence analysis was 75.9 % (SiO_2), 11.0 % (Na_2O), 7.4 % (CaO), 3.3 % (MgO), 1.5 % (Al_2O_3), 0.7 % (K_2O) and 0.1 % (Fe_2O_3). The substrates were washed ultrasonically with an organic alkali solution (Furuuch Chemical Corporation, Semicoclean 56) for 10 min, rinsed with reverse osmosis water several times and pulled up from the boiled acetone.

2.2 Coating solutions

The coating solution for the SiO_2 undercoat was prepared from tetraethoxysilane $(C_2H_5O)_4Si$ (Wako Pure Chemical Industries, Ltd., purity 95 %, 6.51 g) and ethanol (purity 95 %, 55 ml) added by nitric acid (27.6 %, 1.85 g) before stirring for more than 48 h. Coating solutions for aluminum-doped zinc oxide films were prepared as reported elsewhere[6] from zinc acetate $(CH_3COO)_2Zn$ (purity 95 %, Kanto Chemical Co., Inc.) and aluminum chloride hexahydrate $AlCl_3 \cdot 6H_2O$ (Wako Pure Chemical Industries, Ltd., purity 98 %) dissolved in ethanol with 3 vol.% of diethanolamine $(CH_2CH_2OH)_2NH$ (Wako Pure Chemical Industries, Ltd., purity 98 %) before stirring for more than 12 h. The total metal ion concentration in the solution was 0.3 mol·l⁻¹.

2.3 Film deposition and post-deposition annealing

The process of dip coating (withdrawal rate: 2.0 cm·s⁻¹) and heating at 500 °C in air for 30 min in a muffle furnace was repeated three times to deposit the SiO_2 undercoat (total thickness:

approximately 300 nm) and eight times for AZO films (total thickness: approximately 200 nm). The AZO films with and without the SiO_2 undercoat were annealed in a reducing atmosphere (N_2-0.1 %H_2) at 600 °C for 1 h in order to lower the resistivity.

2.4 Film thickness determination

The thickness of a zinc oxide film (0.8 at.% Al; repeating number of coating and heating, 8 times) was determined using a stylus profilometer (Veeco Instruments, dectack[3]ST; stylus pressure 10 mg). The film was chemically etched using ITO-02, Kanto Chemical Co., Inc. for 1 min after photolithography (spin-coating, 2000 rpm, 10 s; halogen lamp radiation, 1 min). Thicknesses of all zinc oxide films were determined via X-ray fluorescence analysis (JEOL , JSX-3200, energy dispersive type, Rh 30 kV, fundamental parameter method) assuming that the density of the films was equal to 5.60 g·cm^{-3} (bulk zinc oxide crystal). Determination of the aluminum concentration in the films via X-ray fluorescence analysis was abandoned because of strong background from the glass substrate. Therefore the aluminum concentration of the coating solution is indicated in the figures of the present paper. The thickness of the SiO_2 undercoat was determined as follows. Dip coating and heating were initially executed only once to fabricate a single SiO_2 layer. The thickness as measured using the stylus profilometer was approximately 100 nm. Since the dip coating and the heating were repeated three times for the present study, the thickness of the SiO_2 undercoat was estimated to be approximately 300 nm. Thickness measurement using an ellipsometer was unsuccessful in the present SiO_2 films even though they are deposited on an Si substrate.

2.5 Other measurements

The crystal phase of films was evaluated by X-ray diffraction analysis (Rigaku Co., Ltd., Model RINT-2200Ultima+) with X-ray source of Cu $K\alpha$ (acceleration voltage, 40 kV; the target current, 40 mA; graphite monochromator) at a scan speed of 2.0 $^{\circ}$·min^{-1}. The optical transmittance and reflectance was measured using a conventional spectrometer. Aluminum was used as a standard for 100 % reflectance. The resistivities of the films were measured using a four-point-probe method (probe current, 1 mA) with a digital multimeter (Hewlett-Packard Co., Ltd., Model 34401A). Measurement of carrier electron concentration and mobility was attempted by the van der Pauw method using a Hall coefficient measuring instrument (Sanwa Radio Measurement Works Co., Ltd., Model MI675, probe current 1 mA). However the measurement was impossible because of the high resistivity of the present films.

3. Results and Discussion

3.1 Film thickness

Thickness of aluminum-doped zinc oxide film without an SiO_2 undercoat (0.8 at.%; repeating number of dip-coating and heating, 8 times; as-deposited) was 251 nm (a stylus profilometer) and 218 nm (X-ray fluorescence analysis). The relative density (86.9 %) was high. Thickness of aluminum-doped zinc oxide films (0.8 at.% Al) are shown in Fig.1 as a function of repeating number of coating and heating. The thickness was proportional to the repeating number; 33 nm / one coating.

3.2 Crystal state

X-ray diffraction spectra for aluminum-doped and undoped zinc oxide films deposited on glass substrate with an SiO_2 undercoat are shown in Fig.2. In this figure, the spectrum (a halo) for uncoated alkali glass is indicated for reference. All diffraction peaks were weak and assigned to zinc oxide (ZnO). Aluminum oxide (Al_2O_3) and aluminum-zinc oxide ($ZnAl_2O_4$) was undetected. This figure shows the results before the post-deposition annealing. The XRD of the film deposited on the glass substrate without an SiO_2 undercoat was not indicated but no apparent difference was detected. The peak shift after the post-deposition annealing was negligible. In this
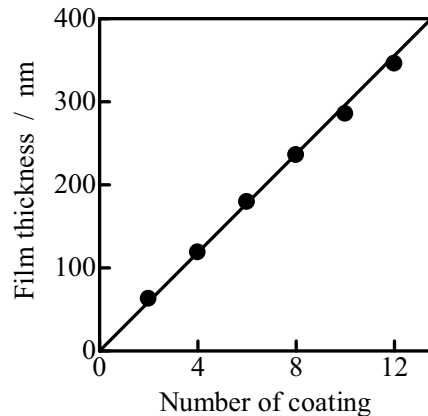

Fig.1 Thickness of 0.8 at.% aluminum-doped zinc oxide films as a function of repeated coating and heating. In this figure the film thickness was determined using X-ray fluorescence analysis.
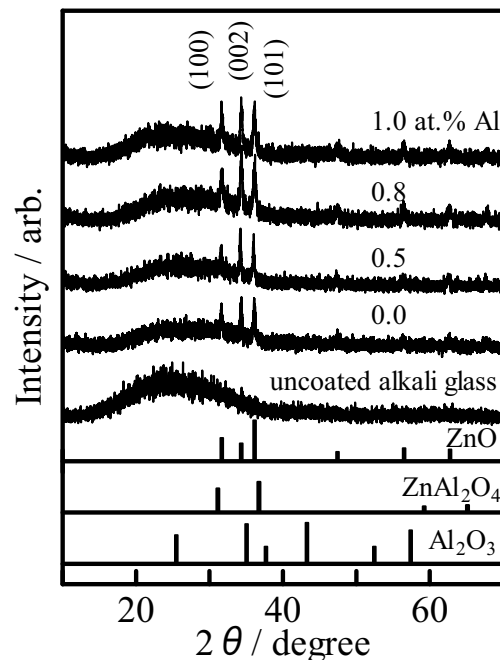

Fig.2 X-ray diffraction spectra for aluminum-doped and undoped zinc oxide films deposited on an alkali glass substrate with an SiO_2 undercoat. (Zinc oxide film thickness: approximately 200 nm)

figure peak positions of $ZnAl_2O_4$ are also indicated. Diffraction peaks of $ZnAl_2O_4$ were not duplicated with those of ZnO. Detection of $ZnAl_2O_4$ peaks seems impossible in the present films because of minute absolute amount of the specimen and low concentration of aluminum ($\leq$ 1 at.%). Dependence of diffraction peak angles of zinc oxide films on the aluminum concentration is shown in Fig.3. The peaks appeared at slightly lower angle than those of the bulk crystal reported in the literature. This means the lattice constants in case of the present films were slightly larger. The peak angles were the lowest at 0.5 at.% Al and increased slightly at the higher doping concentration. Figure 4 shows the X-ray diffraction spectra for zinc oxide (0.8 at.% Al) films prepared via different conditions. The results of alkali glass with an SiO_2 undercoat without a zinc oxide film and uncoated alkali glass substrate were also indicated for reference. Angles of diffraction peaks were approximately the same. The lattice constants of zinc oxide were not influenced by an SiO_2 undercoat and the post-deposition annealing.

3.3 Optical spectra

Figure 5 shows the optical spectra of aluminum-doped and undoped zinc oxide films deposited on an alkali glass substrate with an SiO_2 undercoat. The spectra of an uncoated glass substrate are indicated for reference. The average transmittance in the visible range exceeded 81 % for all films. The reflectance was mainly due to optical interference. All transmittance curves are duplicated in the ultraviolet range. This suggested low carrier electron concentration.
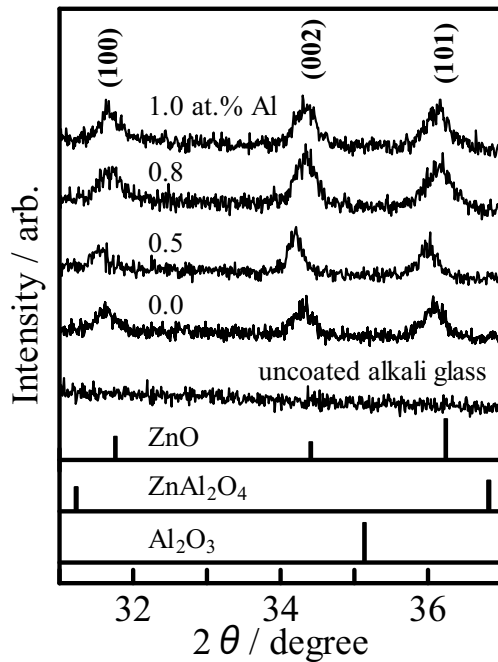
3.4 Resistivity

Dependence of resistivity on the doping concentration is shown in Fig.6. Resistivity was high in case of as-deposited films. The resistivity of the films with an SiO_2 undercoat was slightly lower than those without the undercoat. This suggested that diffusion of sodium into aluminum-doped or undoped zinc oxide films was negligible for the as-deposited high-resistivity films. The resistivity decreased drastically after post-deposition annealing in the reducing atmosphere. The lowest resistivity (6.4×10^{-3} $\Omega \cdot cm$) was achieved at 0.8 at.% Al (film thickness, 236 nm) with an SiO_2 undercoat. This value agrees excellently with that (6.6×10^{-3} $\Omega \cdot cm$) deposited on non-alkali glass (film thickness, 246 nm) in our previous study[6]. The lowest resistivity without the undercoat after annealing was more than one order higher than that of the film with the undercoat. Thus the SiO_2 undercoat fully prevented the

Fig.3 Dependence of diffraction peak angles of zinc oxide films on the aluminum concentration. This figure is an enlargement of Fig.2.
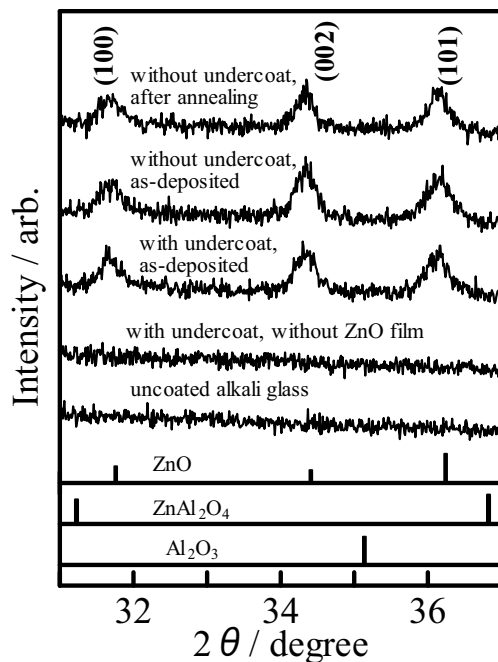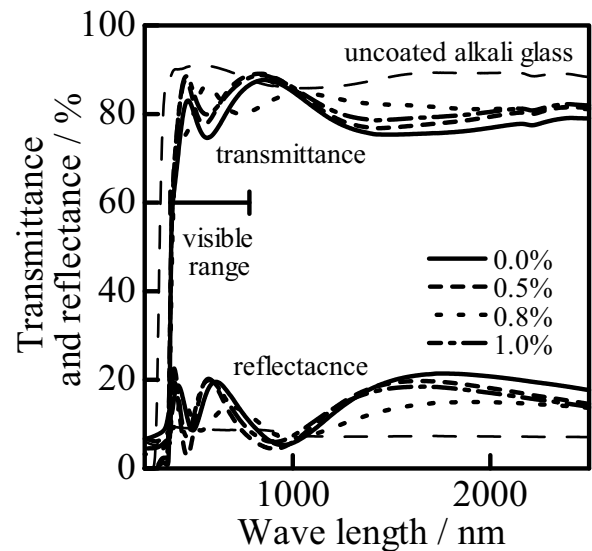

Fig.5 Optical spectra for aluminum-doped and undoped zinc oxide films deposited on alkali glass substrate with an SiO_2 undercoat.

Fig.4 X-ray diffraction spectra for zinc oxide films (0.8 at.% Al) prepared via different conditions.
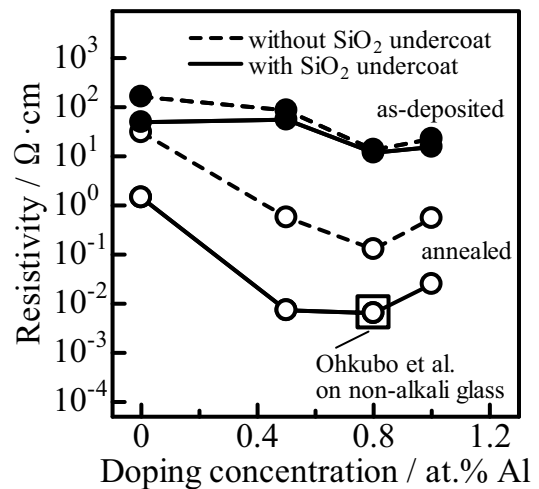

Fig.6 Dependence of resistivity on doping concentration for aluminum-doped and undoped zinc oxide films deposited on alkali glass with and without an SiO_2 undercoat as-deposited and after post-deposition annealing at 500 °C in N_2-0.1 % H_2 for 30 min. (Zinc oxide film thickness: approximately 240 nm)
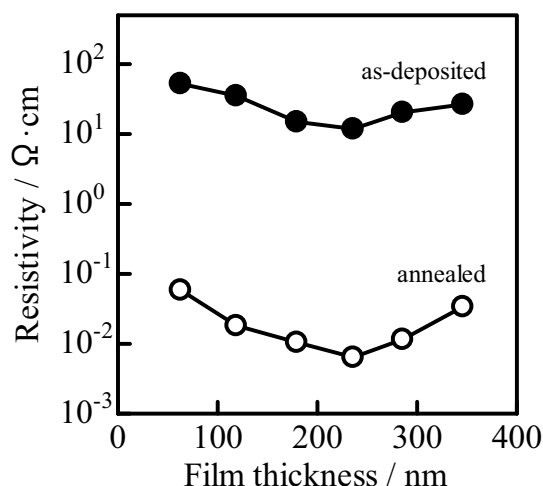
Fig.7 Resistivity as a function of thickness for 0.8 at.% aluminum-doped zinc oxide films with an SiO_2 undercoat.

increase in resistivity. Figure 7 shows resistivity as a function of thickness for aluminum-doped zinc oxide film with an SiO_2 undercoat. Post-deposition annealing in a reducing atmosphere drastically lowered the resistivity. The resistivity was lowest at the thickness of 236 nm. The lowest resistivity after annealing was 6.4×10^{-3} $\Omega \cdot$cm. Although a more detailed investigation will be necessary, higher resistivity for the thinner or thicker films was, tentatively attributed to insufficient contact between grains and SiO_2 undercoat damage respectively, the latter resulting from a longer total heating period. Thus the SiO_2 undercoat fully prevented an increase in resistivity.

4. Conclusion

Aluminum-doped zinc oxide transparent conducting films were fabricated successfully by a dip coating process on much cheaper alkali glass (soda-lime glass) substrate with an SiO_2 layer (undercoat). The lowest resistivity after post-deposition annealing in reducing atmosphere (N_2-0.1 % H_2) at 600 °C for 1 h was 6.4×10^{-3} $\Omega \cdot$cm (0.8 at.% Al; thickness, 236 nm). This value agrees excellently with that (6.6×10^{-3} $\Omega \cdot$cm) deposited on non-alkali glass (0.8 at.% Al; film thickness, 246 nm) in our previous work. The resistivity of the films without the undercoat after annealing was more than one order higher.

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