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Low-temperature growth of highly conductive and transparent aluminum-doped ZnO film by ultrasonic-mist deposition

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Abstract−Aluminum-doped ZnO (AZO) thin films are grown by ultrasonic-mist deposition method for the transparent conducting oxides (TCO) applications at low temperatures. The AZO films can be grown at a temperature as low as 200 °C with zinc acetylacetonate and aluminum acetylacetonate sources. The lowest resistivity of grown AZO films is 1.0×10^{-3} Ω·cm and the lowest sheet resistance of 1 μm thick films is 10 Ω/□, which is close to that of commercial indium tin oxide (ITO) or Asahi U-type SnO_2 : F glass. The highest carrier concentration and mobility are 5.6×10^{20} cm^{-3} and 15 $cm^2/V\cdot sec$, respectively. Optical transmittance of the AZO films is found over 75% for all growth conditions. We believe that the properties of grown AZO films in this study are the best among all reported previously elsewhere by solution processes.

Key words: Zinc Oxide, Aluminum-doped Zinc Oxide (AZO), Transparent Conducting Oxides, Ultrasonic-mist Deposition

INTRODUCTION

Zinc oxide (ZnO) is one of the most widely studied oxide semiconductors, since it is optically transparent, electrically conductive with impurity doping, safe and versatile material for a number of optical and electrical applications. While indium tin oxide (ITO) is the most popular transparent conductive oxide (TCO), ZnO is considered as a prospective candidate for substituting expensive ITO due to the limited reserves of indium (In). Especially, ZnO thin film has attracted much attention in recent years since ZnO is known to be an adequate TCO for solar cells due to its low material cost and the possibility of textured surface.

For the intentional impurities to enhance the electrical conductivity of ZnO thin films, the elements such as aluminum (Al), gallium (Ga) and fluorine (F) have been commonly utilized. To prepare ZnO thin films, various deposition processes have been used such as sputtering [1], laser ablation [2], chemical vapor deposition (CVD) [3], sol-gel [4-6], atomic layer deposition [7], and spray pyrolysis [8-18]. Among these, spray pyrolysis has several advantages over the others due to simplicity, safety and low-cost of the apparatus and raw materials. In this study, we have utilized the pyrolysis method with ultrasonically pulverized mist to deposit Al-doped ZnO (AZO or ZnO : Al) thin films.

In case of the deposition of AZO thin films by spray pyrolysis, most studies have utilized zinc acetate ($Zn(C_2H_3O_2)_2$) and aluminum chloride ($AlCl_3$) as zinc and aluminum sources, respectively. The electrical resistivity and optical transmittance of AZO thin films grown at temperatures over 300 °C were in the range from 10^{-3} to 10^{-2} Ω·cm and from 70 to 90%, respectively [8-18]. The growth temperature, optical and electrical properties are not as good as conventional TCOs for solar cell applications. To utilize the transparent conducting AZO thin films on flexible substrates such as polyimide films for flexible solar cell applications, the deposition temperature should be reduced below 300 °C. Also, for AZO thin films to be utilized as TCO for solar cell applications, the deposition process should be scalable to large-area and the sheet resistance of the films should be in the range of 10-20 Ω/□, which is the typical value of Asahi U-type SnO_2 : F substrate. To accomplish the requirements, we have used different source materials for AZO film growth, which are zinc acetylacetonate ($Zn(C_5H_7O_2)_2$) and aluminum acetylacetonate ($Al(C_5H_7O_2)_3$) as zinc and aluminum sources, respectively. It was found in this study that the deposition of AZO thin films using the sources could give lower electrical resistivity than the case using other sources such as zinc acetate and aluminum chloride. We also report here a low-temperature deposition process of transparent and highly conducting AZO thin films by using ultrasonic mist, which is scalable to large-area deposition.

EXPERIMENTAL

Transparent conducting aluminum-doped ZnO thin films were prepared by an ultrasonic-mist deposition method. An ultrasonic-mist generation apparatus used in this study is equipped with three piezoelectric vibrators. Zinc acetylacetonate, aluminum acetylacetonate and methanol were used as zinc source, aluminum source and solvent, respectively. Zinc acetylacetonate and aluminum acetylacetonate were first dissolved in a fixed amount of methanol solvent for the total concentration of acetylacetonate sources to be 0.1 M. The aluminum doping concentration is defined as Al/(Zn+Al) atomic percent and varied from 0 to 10 at%. To stabilize the precursor solution, an amount of acetic acid (CH_3COOH) was added.

Bare glasses (5 cm×5 cm) were used as substrates. Nitrogen was used as a carrier gas. The flow rate was fixed at 20 liter/min. The

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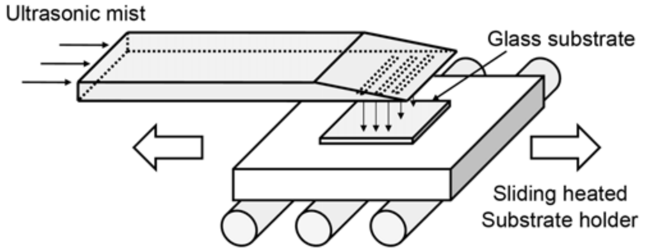

Fig. 1. Schematic diagram of ultrasonic mist deposition apparatus utilized in this study.

AZO films were then deposited in atmospheric environment at substrate temperatures ranging from 200 °C to 350 °C for a fixed deposition time of 40 min. All the measurements were carried out with as-grown films which were not annealed after the deposition. We have shown the ultrasonic-mist deposition apparatus in Fig. 1. As shown, the generated mist from the precursor solution is delivered to multiple linear nozzles by the carrier gas and showered through the nozzles to the heated glass substrate. The distance between the nozzles and substrate is set to 5 mm, which has been chosen for the mist to reach the substrate at the flow rate. To improve film uniformity, a substrate holder is installed on a moving stage. For all experiments the moving speed is set to be 2.5 cm/min.

The thickness of AZO films was measured with a KLA-TENCOR *α*-step profilometer. The sheet resistance and resistivity of the films were measured using a CMT-series four point probe system. Transmittance spectra were recorded by an Agilent 8453 UV-VIS spectrometer. Carrier concentration and mobility of the films were measured with a Hall effect measurement system.

RESULTS AND DISCUSSION

We have grown aluminum-doped ZnO thin films using ultrasonic-mist deposition method at six different deposition temperatures from 200 °C to 350 °C. In the temperature range the growth rate of AZO thin films was found to be in the range from 7.9 to 30.6 nm/min. As shown in Fig. 2, the growth rate increases as growth temperature increases until the temperature reaches 300 °C, and then the growth rate tends to saturate above the temperature because the rate of deposition reaction starts to be limited by the rate of mass transport of precursor mist. From the Arrhenius plot given in Fig. 2, the activation energy of the decomposition reaction of zinc acetylacetonate was found to be about 34 kJ/K·mol from the slope of ln(rate) versus 1/T graph. For comparison, the activation energy of the decomposition reaction of zinc acetate has been reported as 20.6 kJ/K·mol previously by the chemical vapor deposition (CVD) experiment of AZO thin films [19]. Even though we have not shown XRD (X-ray diffraction) data of grown AZO films here, the AZO films have been found to begin being crystallized even at the low growth temperature of 200 °C and the films showed peaks identified as (100), (002), (101), (102), (103) and (112) reflections of wurtzite structure at higher growth temperatures. We have also shown a photograph measuring the electrical resistance of grown AZO films on glass substrate in the figure, which shows the transparency and electrical resistance of the films.

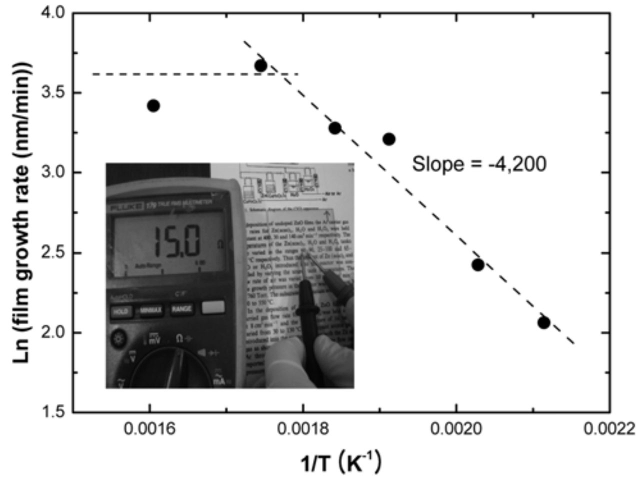

Fig. 2. Arrhenius plots for the decomposition reaction of zinc acetylacetonate to form AZO films.

Fig. 3 shows the variation in electrical resistivity, carrier concentration and carrier mobility as functions of substrate temperature for the AZO films doped with 2.5 at% aluminum. As the substrate temperature increases from 200 °C to 300 °C, the electrical resistivity decreases from 8.6×10^{-2} Ω·cm to 1.3×10^{-3} Ω·cm and then increases again slightly above 300 °C. The decrease in resistivity is due to the increase in both carrier concentration and mobility. Carrier concentration in the AZO films was observed to gradually increase as deposition temperature increased. This increase in carrier concentration may be due to an increase in diffusion of aluminum atoms from interstitial locations and grain boundaries into the Zn cation sites [2,20]. Similar results have been reported previously in the literature [16], even though the reported resistivity is higher and the carrier concentration and mobility are lower than those obtained in this study.

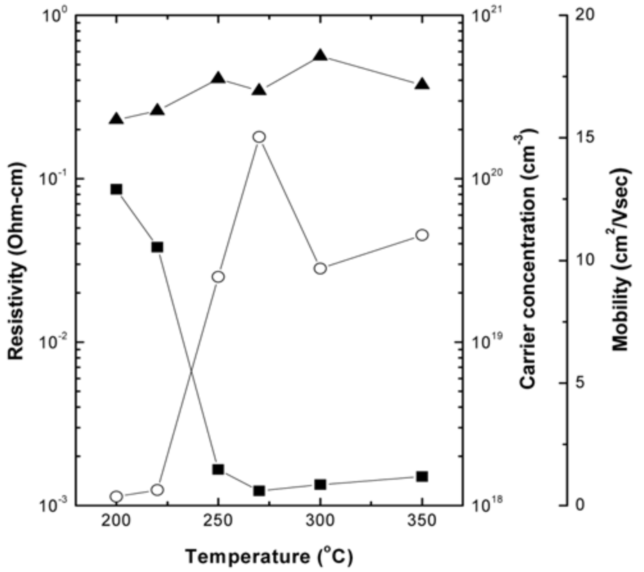

Fig. 3. Resistivity (■), Hall mobility (○) and carrier concentration (▲) as functions of temperature for AZO films prepared by ultrasonic-mist deposition with 2.5 at% aluminum doping.

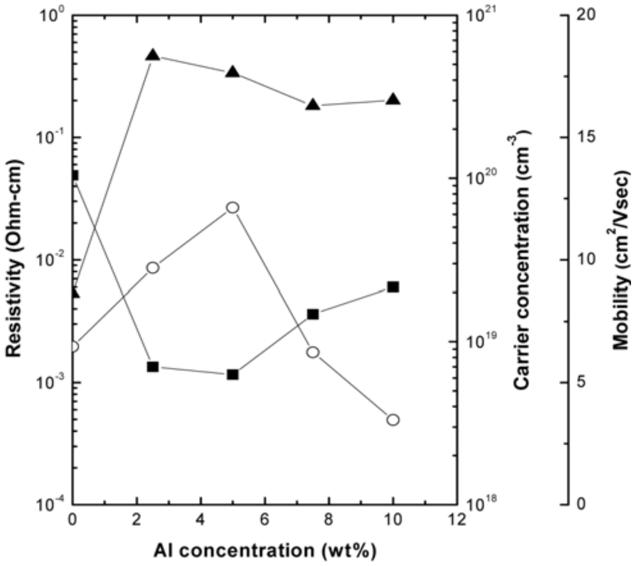

Fig. 4. Resistivity (■), Hall mobility (○) and carrier concentration (▲) as functions of aluminum concentration for AZO films prepared by ultrasonic-mist deposition at a temperature of 300 °C.

As the doping concentration of aluminum increases, the electrical resistivity is found to decrease as shown in Fig. 4. The resistivity reaches the minimum close to 1.0×10^{-3} Ω·cm around at 4 at% aluminum doping concentration and then increases again at higher doping concentrations due to the decrease in both the carrier concentration and mobility. As the doping concentration increases above 3 at%, the carrier concentration starts to decrease from the maximum of 7×10^{-20} cm^{-3} possibly due to the aggregation of aluminum impurities. The mobility shows similar behavior on the variation of the doping concentration. Since there exists a maximum carrier concentration at the aluminum concentration of 3 at%, the excessive aluminum doping might cause the aggregation or accumulation of aluminum impurities at the grain boundaries and subsequently could result in the decrease in the carrier mobility.

Fig. 5 shows the optical transmittance spectra of AZO films on glass substrates for various doping concentrations. Here, in the measurement, we used a glass substrate as a reference sample. It is clearly seen that the transmittance in the visible range was more than 70%, showing good transparency. As shown in the figure, the absorption edge shifts to a shorter wavelength region as the aluminum doping concentration increases. This shift can be attributed to an increase in the carrier concentration and blocking of low energy transitions, which causes a Burstein-Moss effect [21]. This blue-shift means that the optical band gap of AZO films increases with increasing carrier concentration. The optical band gap is defined as the minimum energy needed to excite an electron from the valence band to the conduction band. In pure undoped crystals the optical gap equals the energy separation between the band edges. On heavy doping, the donor electrons occupy states at the bottom of the conduction band, since the Pauli principle prevents states from being doubly occupied, the optical band gap is given by the energy difference between the states with Fermi momentum in the conduction and valence band. This type of blocking of low energy transitions is known as the Burstein-Moss effect [22,23]. It should be mentioned here that the optical transmittance is low for pure ZnO film compared with those of AZO films and it increases as the doping concentration increases. As reported in the literature [10], the films with lower doping concentrations had more granular microscopic structure, while those with higher doping concentration had more columnar microscopic structure, so that the films with lower doping concentrations showed hazier appearance due to increased internal light scattering. Optical transmittance of the AZO films with 2.5 at% aluminum doping was found to decrease as the growth temperature increased, as shown in Fig. 6. We think that at higher temperatures the acetylacetonate precursors decompose prior to arriving at the heated substrate, resulting in contaminated AZO films with lower transmittance.

Even though we have not shown the results in this study, we have also carried out ultrasonic-mist deposition experiments for AZO films using zinc acetate and aluminum acetylacetonate sources for comparison. It has been found from the experiments that the growth of AZO films occurs at similar temperatures, but the resistivity turns

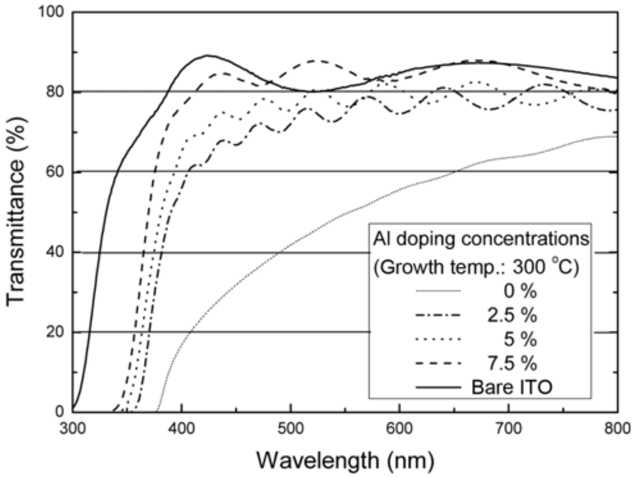

Fig. 5. Optical transmittance spectra of AZO films for different aluminum concentrations.

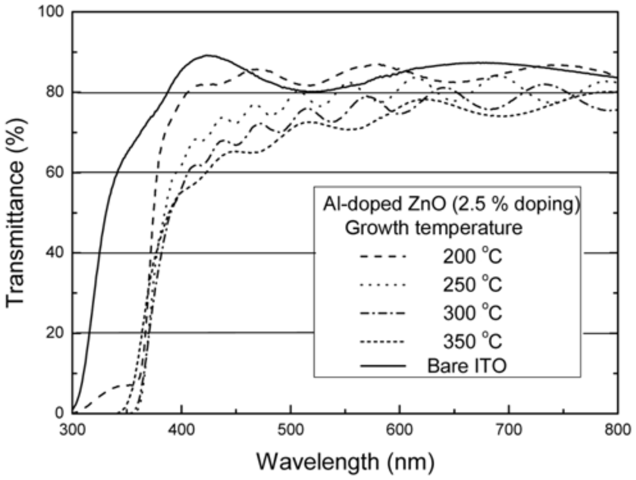

Fig. 6. Optical transmittance spectra of AZO films for different growth temperatures.

Table 1. The optimal operating conditions and properties of grown AZO films in comparison to commercial ASAHI U-type SnO_2 : F films (numbers in parentheses) [22]

Optimal operating conditions	
Zinc source	Zinc acetylacetonate
Aluminum source	Aluminum acetylacetonate
Carrier gas	nitrogen
Growth temperature	270 °C
Aluminum doping concentration	4.0 at%
Deposition time	40 min
Film properties	
Average total transmittance (400-800 nm)	75% (79.5%)
Film thickness	1.0 μm (0.9 μm)
Sheet resistance	15 Ω/□ (13 Ω/□)
Resistivity	1.2 mΩ·cm (1.2 mΩ·cm)
Surface roughness (RMS)	20.4 nm (34.7 nm)

out to be much higher than the case using zinc acetylacetonate by a factor of ten. We think that the low resistance and resistivity of AZO films is responsible to the zinc source material which is zinc acetylacetonate.

The optimal growth condition of the AZO films for the ultrasonic-mist deposition and the resulting film properties are listed in Table 1. We believe that the sheet resistance and resistivity are the lowest among all reported data in the previous literature at a low deposition temperature of 270 °C. The carrier concentration and mobility were also found higher than those reported elsewhere. We have compared the film properties with those of Asahi U-type SnO_2 : F film (numbers in parenthesis) in the table. As can be seen in the table, the properties were found almost identical to the commercial TCO film. The ultrasonic-mist deposition process used in this study is considered an advantageous method for preparing good TCO films at low cost. Also, since the process can be applied to roll-to-roll deposition and scalable to large-area, we think that this process is suitable for fabricating TCO films for flexible solar cell applications.

CONCLUSIONS

We have grown highly conductive and transparent aluminum-doped ZnO films using ultrasonic-mist deposition process at low temperatures. The electrical and optical properties of grown AZO films are found the best among reported in the literature. We attribute the results to the source materials, which are zinc acetylacetonate and aluminum acetylacetonate. The ultrasonic-mist deposition of AZO films carried out in this study would be a useful process to prepare TCO films for flexible solar cell applications since the growth temperature is low enough to use flexible substrates and the process is scalable to roll-to-roll and large area.

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