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Preparation of Al-doped ZnO films by aqueous solution process using a continuous circulation reactor

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The fabrication of Al-doped ZnO films by an aqueous solution process using a continuous circulation reactor was studied. By heating ZnO-saturated ammonia solutions containing 2-10 mM $Al(NO_3)_3$ with pH 10.7 at 90 ºC under ambient pressure, polycrystalline ZnO films with Al content of 1-2 at.% were deposited. The carrier concentration of ZnO films increased with increasing Al content, indicating that Al was successfully incorporated into the ZnO crystals. The Al-doped ZnO films had carrier concentrations of 10^{19}-10^{20} cm^{-3} and mobilities of 0.7 to 7 $cm^2\ V^{-1}\ s^{-1}$ after annealing at 300 ºC in air.

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1 Introduction Zinc oxide (ZnO) is a transparent oxide semiconductor with a direct bandgap of ~3.3 eV, and is a promising material for a wide variety of applications such as transparent conducting films, waveguides, and ultraviolet lasers. A number of vapor phase deposition techniques can be employed to fabricate high-quality ZnO films, including sputtering [1], pulsed laser deposition (PLD) [2], and metalorganic chemical vapor deposition (MOCVD) [3]. However, aqueous solution processes such as electrochemical deposition [4], chemical bath deposition (CBD) [5], and hydrothermal synthesis [6] have recently attracted more attention owing to their capability to produce large area ZnO films with low cost and low environmental impact. Recently, Lange's group developed a novel aqueous process using a continuous circulation reactor [7]. This continuous process, taking advantage of retrograde ZnO solubility with temperature in ammonia solutions, is especially attractive because it enables ZnO crystals to grow under steady-state conditions. Unlike batch processes as typified by CBD, the reaction conditions such as the concentrations of solutes and pH do not change during the crystal growth, thereby producing highly-uniform ZnO films at a constant growth rate.

In this study, we investigated the formation of aluminum-doped ZnO films through the continuous aqueous solution process. The doping of Al is most widely performed to produce n-type ZnO films with a low resistivity. Methods for the preparation of Al-doped ZnO films are well established in the vapor phase deposition processes [1-3] and sol-gel process [8,9], and there have been a few reports on Al-doped ZnO films prepared by CBD [10] and successive chemical solution deposition [11], but no detailed report is available for Al-doping in the continuous aqueous solution process. We prepared Al-doped ZnO films using ammonia solutions containing various amounts of $Al(NO_3)_3$, and examined the effect of $Al(NO_3)_3$ addition on the morphology, Al content, and electrical properties of the resulting ZnO films.

2 Experimental procedure Prior to the ZnO growth by the aqueous solution process, a ZnO seed layer was formed on a sapphire substrate (7 × 7 mm^2) by spin-coating using a mixture solution of 2-methoxyethanol, 2-aminoethanol, and zinc acetate with the mol ratio of 10:1:1 [12]. The spin-coating was performed at 3000 rpm, followed by annealing at 300 °C in air for 1 hour, forming a polycrystalline ZnO layer with a thickness of ~130 nm. This seed layer was necessary to grow ZnO films adherent to the substrate.

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The ZnO-saturated ammonia solutions for the growth of ZnO films were prepared by dissolving 0.95 M (= mol L^{-1}) NH_3(aq), 0.05 M NH_4NO_3 and 0.5 mM sodium citrate tribasic dihydrate in distilled water. The sodium citrate was added to enhance the lateral growth of ZnO crystals [13] and thereby to form denser films. If the solutions do not contain citrate ions, ZnO grows in the form of nanorods. As the source of Al ions, $Al(NO_3)_3$ was added into the solution in the concentration range of 0-10 mM. The solutions were equilibrated with an excess amount of ZnO powder in a sealed container under agitation at room temperature (~25 °C) for more than a day. The film growth was carried out using a continuous circulation reactor consisting of two plastic vessels (60 mL each) connected with a silicone tube. The temperature of one of the vessels was kept at room temperature, while the other was heated at 90 °C. The ammonia solution was circulated between the two vessels through the tube and an in-line filter (0.45 μm) by a peristaltic pump at the flow rate of 1 mL min^{-1}. An excess amount of ZnO powder was put in the unheated vessel to keep the concentration of Zn ions constant. The seeded substrate was inserted into the heated vessel, and ZnO film growth was performed for 5 hours.

The crystallinity and morphology of the resulting films were examined with an X-ray diffractometer (Panalytical, X'PertPRO-MPD PW 3040) and an SEM (Hitachi, X900). The Al contents in the ZnO films (Al/(Al+Zn)) were determined by EDX. The electrical properties of the ZnO films were measured with a resistivity/Hall measurement system (Toyo Corporation, ResiTest 8300) using the van der Pauw method at room temperature. For the measurements, Al ohmic electrodes were formed on the ZnO films by vacuum evaporation.

3 Results and discussion ZnO films were deposited from the ZnO-saturated ammonia solutions containing 0-10 mM $Al(NO_3)_3$ by heating at 90 °C. The pH of the solutions was 10.7 at room temperature. Deposition of ZnO occurs because the thermodynamic stability of $Zn(NH_3)_4^{2+}$ ion, which is the dominant species of Zn ions in the solutions at room temperature, decreases with increasing temperature at this pH, and therefore the solubility of ZnO decreases. With pH 10.7 and 1.0 M of total ammonia (that is free and combined) concentration, the solubility of ZnO is thermodynamically calculated to be 0.015 M and 7.5×10^{-5} M at 25 °C and 90 °C, respectively [14]. On the other hand, Al ion dissolves in the form of AlO_2^-, and its solubility should increase with temperature. Thus, the deposition of Al oxide or hydroxide should not occur independently, but it can be expected that Al ions are incorporated into the ZnO crystals during the crystal growth.

Figure 1 shows XRD patterns of the samples prepared from the solutions without and with 10 mM $Al(NO_3)_3$. Both patterns show only the ZnO 0002 reflection at 2θ = 34.5°, indicating that ZnO crystals with a strong *c*-axis preferred orientation were deposited even from the solution containing 10 mM $Al(NO_3)_3$.

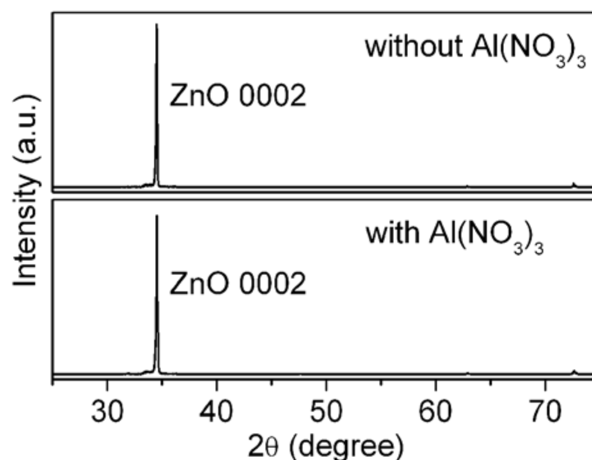

Figure 1 XRD patterns of ZnO films deposited from ammonia solutions without and with 10 mM $Al(NO_3)_3$.

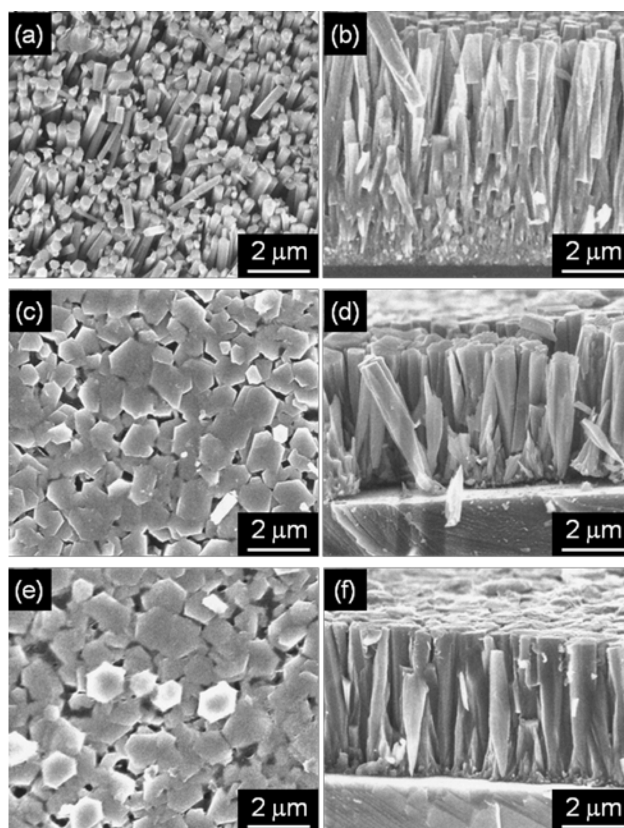

Figure 2 SEM images of ZnO films deposited from the ammonia solutions containing (a, b) 0 M, (c, d) 2 mM, and (e, f) 10 mM $Al(NO_3)_3$. (a, c, e) Top surfaces and (b, d, f) fractured cross-sections.

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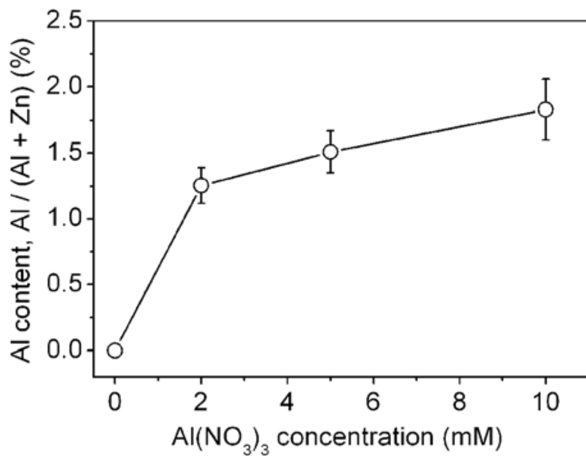

Figure 3 Al content of ZnO films deposited from the ammonia solutions with various concentrations of $Al(NO_3)_3$.

Figure 2 presents SEM images of the top surfaces and fractured cross-sections of the ZnO films deposited from the solutions containing 0, 2 and 10 mM $Al(NO_3)_3$. The SEM images reveal that hexagonal columns of ZnO crystals grew perpendicularly to the substrate from all the solutions. However, the dimensions of the ZnO hexagonal columns vary with the addition of $Al(NO_3)_3$; the diameters and the heights of the ZnO columns from the solution without $Al(NO_3)_3$ are 190-280 nm and 7.7 μm, respectively, while those with 10 mM $Al(NO_3)_3$ are 460-650 nm and 4.8 μm. That is, the growths in the *a*- and *c*-directions are promoted and suppressed, respectively, by the addition of Al ions. This change in the *c*/*a*-growth ratio is attributable to that AlO_2^- ions being preferentially adsorbed on the relatively positively charged (0001) surface of ZnO crystal and suppressing the ZnO growth in the *c*-direction, as citrate ions do [13].

Composition analysis by EDX confirmed that the ZnO films from the solutions with $Al(NO_3)_3$ contained 1-2 at.% of Al, while the Al content of the ZnO without $Al(NO_3)_3$ was below the detection limit (0.1%) (Fig. 3). The Al content in the ZnO film increased with the concentration of Al ions in the solution.

The electrical resistivity of the as-deposited ZnO films was lowered by the addition of $Al(NO_3)_3$ to the solution; while the resistivity of the ZnO film without $Al(NO_3)_3$ was $\sim 10^3$ Ω cm, those with $Al(NO_3)_3$ were ~10 Ω cm (Fig. 4a). The annealing at 300 °C in air decreased the resistivity of all the ZnO films by more than two orders of magnitude. Even after the annealing, the resistivities of the ZnO films from the solutions with $Al(NO_3)_3$ were lower than that of the non-doped ZnO film. The minimum resistivity of 3×10^{-2} Ω cm was obtained when the concentration of $Al(NO_3)_3$ was 5 mM. The sheet resistance of this film with the thickness of 5.8 μm was 53 Ω/sq.

The Hall measurements indicated that the ZnO films have n-type conductions. Figure 4b shows the carrier mobility and carrier concentration of the ZnO films after the annealing. The carrier concentration of the ZnO films increased with increasing concentration of $Al(NO_3)_3$ and reached 2×10^{20} cm^{-3}, which is two orders of magnitude higher than that of the non-doped ZnO film (10^{18} cm^{-3}), offering clear evidence that Al is incorporated into ZnO crystals from the solutions and works as an donor impurity. The mobility did not vary substantially with the addition of $Al(NO_3)_3$ up to 5 mM, and was in the range of 2.5-7 cm^2 V^{-1} s^{-1}. However, the mobility decreased to 0.7 cm^2 V^{-1} s^{-1} by the addition of 10 mM $Al(NO_3)_3$, probably because the ionised impurity scattering became significant [1].

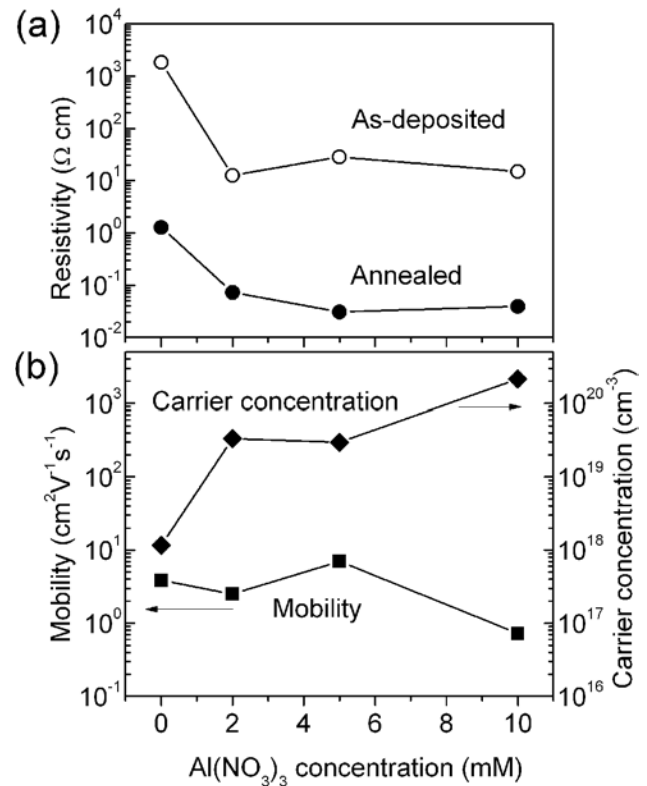

Figure 4 (a) Resistivity, (b) carrier mobility and carrier concentration of ZnO films deposited from the ammonia solutions with various concentrations of $Al(NO_3)_3$.

Although the carrier concentration could be increased by the Al-doping, the resistivity obtained in this study is still higher than those reported for Al-doped ZnO films prepared by the vapor phase deposition processes ($\sim10^{-4}$ Ω cm) [1,2], mainly because the mobility is smaller in the present films. Since the mobility of the non-doped film prepared by the present process was already small, the primary cause of the small mobility should be the presence of high density of structural defects such as grain boundaries.

3 Conclusions Al-doped polycrystalline ZnO films were prepared by an aqueous solution process using a continuous circulation reactor at 90 ºC. By adding 2-10 mM

$Al(NO_3)_3$ to the ammonia solutions, ZnO films containing 1-2 at.% Al were deposited. The carrier mobility of the ZnO films did not vary significantly with the Al addition and ranged from 0.7 to 7 $cm^2 V^{-1} s^{-1}$. However, the carrier concentration increased with increasing concentration of $Al(NO_3)_3$ and reached 2×10^{20} cm^{-3}, which was two orders of magnitude higher than that of the non-doped ZnO film. This result demonstrated that Al was successfully doped into the ZnO films by the aqueous solution process.

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