Fabrication of transparent conductive zinc oxide films by chemical bath deposition using solutions containing Zn\(^{2+}\) and Al\(^{3+}\) ions

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Transparent ZnO films were fabricated on glass substrates by a chemical bath deposition method using zinc acetate solutions also containing AlCl\(_3\). A predominant effect of the Al\(^{3+}\) addition seemed to be suppression of the growth of ZnO crystals and change of the crystallographic orientation of ZnO films. The c-axis and the a-axis of the ZnO films came to stand parallel and vertical to the substrate, respectively, by increasing the Al\(^{3+}\) concentration. A post ultraviolet irradiation to the films led to a decrease in the sheet resistance from the order of 10\(^6\) to 10\(^4\) Ω·sq.\(^{-1}\) without changing the morphology or the crystallinity. This might be related to the photocatalytic effect of ZnO to decompose residual organics in the films and increase the number of carriers. The ZnO film obtained from the solution with 1.0 mol% AlCl\(_3\) showed the lowest sheet resistance of 2.5 x 10\(^4\) Ω·sq.\(^{-1}\).

1. Introduction

Transparent conductive oxides (TCOs) are used in optoelectronic devices such as flat panel displays, thin-film solar cells, and touch screens. ZnO, In\(_2\)O\(_3\), and SnO\(_2\) have been used as the basic materials of TCOs due to their high mobility of electrons in the conduction band derived from overlapping metal s-orbitals. Among them, ZnO is an attractive material because it consists of anionic species. However, there have been few reports focusing on the influence of cationic species on the growth and orientation of ZnO films in the solutions.

There are many reports about the fabrication methods of ZnO films such as sputtering, pulsed laser deposition, and chemical vapor deposition. However, these methods require extraordinary deposition conditions of high energy consumption and high production costs. Compared to these methods, liquid-phase processes are usually conducted at ordinary temperatures and pressures using simple equipment, and they thus have attracted attention of many researchers as an environmentally friendly process. Using liquid-phase processes, ZnO films with controlled nanostructures have been produced under relatively mild conditions aiming at practical applications.

Recently, the liquid-phase processes of Al-doped ZnO films have attracted a renewed attention to facilitate TCO films of lower resistivity with economical manner. Actually, the sol–gel method, the solvothermal method, and the chemical solution method have been pursued to fabricate ZnO:Al films of higher quality. In these methods, it is of fundamental importance to control the crystal growth in solutions to obtain desired film microstructure. However, there have been few reports focusing on the influence of cationic species on the growth and orientation of ZnO films in the solutions.

Our approach to the fabrication of ZnO films is based on the chemical bath deposition (CBD). We have demonstrated recently that the morphology of solution-processed ZnO materials can be highly controlled by using a surfactant having a cationic head group, cetyltrimethylammonium chloride (CTAC). That is, the formation reaction of ZnO in zinc acetate solutions with CTAC leads to the evolution of unique morphologies as nanostructured particles or oriented thick films with high transparency. In the present work, we further added aluminum chloride (AlCl\(_3\)) to zinc acetate solutions with CTAC to investigate the influence of foreign metal cations on the growth of ZnO films. It was also expected that Al\(^{3+}\) ions could possibly be doped in ZnO films. A significant role of Al\(^{3+}\) was then found in the modulation of film textures through changes in a growth rate and an orientation direction of ZnO films. The resultant ZnO films kept high transparency of around 80% in the visible light region and their sheet resistance, which was dependent on the solution composition, could be decreased from the order of 10\(^6\) to 10\(^4\) Ω·sq.\(^{-1}\) by a post ultraviolet (UV) irradiation. Our results would give an insight into the effect of Al\(^{3+}\) on the solution-processed ZnO films in terms of the microstructural evolution, which had not been explored so far.

2. Experimental procedure

2.1 Fabrication of buffer ZnO thin film by sol–gel method

Zn(CH\(_3\)COO)\(_2\)·2H\(_2\)O (0.75 M) was dissolved in 2-methoxyethanol containing a same concentration of monoethanolamine. The resultant solution was dropped on a borosilicate glass sub-
strate (Matsunami Glass Ind., Ltd.) 1 mm in thickness, followed by spin-coating at 1000 rpm for 10 s and continuously at 3000 rpm for 50 s. The coated substrate was heat-treated at 300°C for 0.5 h in air. A buffer ZnO thin film thus deposited on the substrate was used in the CBD method, as described below.

2.2 Fabrication of ZnO film by CBD method

Zn(CH\textsubscript{2}COO\textsubscript{2}).2H\textsubscript{2}O, AlCl\textsubscript{3}.6H\textsubscript{2}O, and cetyltrimethylammonium chloride (CTAC; 0.4 M) were dissolved in an ethanol/H\textsubscript{2}O (96/4 vol%) mixed solution under ultrasonic treatment for 0.25 h. A concentration of metal ions was fixed at 0.15 M, while a Zn:Al ratio was varied between 100:0, 99.5:0.5, 99.0:1.0, and 98.0:2.0 in mol. The glass substrates coated with the buffer ZnO layer were immersed in the CBD solutions filled in screw-cap bottles. The bottles were placed in an oven and kept at 90°C for 0.5 h in air. A buffer ZnO thin film thus obtained from the solution with 2.0 mol % AlCl\textsubscript{3} shows relatively weaker diffraction peaks, as compared to the other films, indicative of lower crystallinity and/or a smaller crystallite size.

To investigate a precise orientation nature, we conducted a wide range reciprocal space map (wide range RSM) measurement. Figure 2 shows the wide range RSM of the ZnO films obtained from the solutions with 0–2.0 mol % AlCl\textsubscript{3}. A horizontal axis and a vertical axis correspond to the diffraction angle of 2θ and the inclination angle of ψ, respectively. Diffraction intensity is indicated as differences of colors. It is seen that the relative intensity of the whole diffraction tends to decrease with increasing the AlCl\textsubscript{3} concentration of the solutions. This is because the film thickness is gradually decreased with increasing the AlCl\textsubscript{3} concentration, as shown in FESEM images of the films (see Fig. 3). The (002) and the (100) peak, which are observed at around ψ = 50° for the ZnO film from the solution without AlCl\textsubscript{3}, move toward 90 and 0°, respectively, with increasing the AlCl\textsubscript{3} concentration. This movement implies that the c-axis and the a-axis come to stand parallel and vertical to the substrate, respectively, by increasing the AlCl\textsubscript{3} concentration in the solutions.

3. Results and discussion

3.1 Structure and morphology of films

Figure 1 shows XRD patterns, which were measured by the out-of-plane condition in 2θ/θ, of the films deposited in the solutions with 0–2.0 mol % AlCl\textsubscript{3} at 90°C for 6 h. The respective patterns agree with the ICDD diffraction pattern of ZnO (ICDD 36-1451) in terms of the peak position. On the other hand, the relative intensity of the peaks is different from that of the ICDD pattern, indicating that the deposited films might have a specific crystallographic orientation. The ZnO film obtained from the solution without AlCl\textsubscript{3} shows three main peaks of (002), (101), and (102). When 0.5 and 1.0 mol % of AlCl\textsubscript{3} was added to the solution, the relative intensity of the (002) and (102) peaks decreases and simultaneously that of the (100) and (110) peaks increases. The ZnO film obtained from the solution with 2.0 mol % AlCl\textsubscript{3} shows relatively weaker diffraction peaks, as compared to the other films, indicative of lower crystallinity and/or a smaller crystallite size.

To investigate the effect of the Al\textsuperscript{3+} ions on the ZnO crystal growth. From these considerations, it was assumed that the addition of the Al\textsuperscript{3+} ions in the solutions would have a remarkable effect for suppressing the crystal growth of ZnO.

3.2 Effect of Al\textsuperscript{3+} on film formation

To investigate the effect of the Al\textsuperscript{3+} ions on the film formation, we prepared two other films with repeated deposition or prolonged deposition in the solution with 2.0 mol % AlCl\textsubscript{3}: one is the film obtained by four-times repetition of the deposition for 6 h (24 h in total) where a fresh solution was used each time; the other is that obtained by one-time deposition for 24 h. Figures 4(a–c) show FESEM images of ZnO films obtained by the four-times repetition of the deposition for 6 h and one-time deposition for 24 h from the solution with 2.0 mol % AlCl\textsubscript{3} at 90°C. As seen from the cross-sectional view, the thickness of the respective films is 600 nm (four-times repetition) and 2.5 μm (one-time deposi-
Also the grain size of the film by the four-times repetition is smaller than that of the one-time deposition.

Wang et al. investigated the influence of cationic species on the crystal growth of ZnO in the hydrothermal process. In case of $M^{3+}$ (M = In or Al), $M(H_2O)_2(OH)_4$ formed in the aqueous solution would be incorporated into the Zn face of ZnO, or $M^{3+}$ dissociated from $M(H_2O)_2(OH)_4$ would be adsorbed on the O face of ZnO. If the $Al^{3+}$ ions were adsorbed on the crystal plane of the ZnO lattice, they could be doped into the ZnO lattice to generate carriers. The solvent employed in the present work is the ethanol/H$_2$O (96/4 vol%) mixed solution and has a lower dielectric constant than H$_2$O. Therefore, it is probable that the ionic species are more unstable in the solution and favor the incorporation and/or adsorption to the growing crystal. In the film formation, the film should grow thicker if the effect of the $Al^{3+}$ ions are diminished after being consumed by doping into the ZnO lattice or adsorbing on the grain boundary as a certain kind of aluminum compounds at an early stage of the crystal growth. This explanation can be applied to the 2.5-μm thick ZnO film obtained by the one-time deposition for 24 h.

XRD patterns in Fig. 5 show that the film obtained by the four-times repetition of the deposition has the strongest peak of (100). On the other hand, the film obtained by the one-time deposition

![Fig. 2. The wide range RSM (the 2θ/θ measurement at θ angle between 0 and 90°) of the ZnO films obtained from the solution with AlCl$_3$ of (a) 0 mol%, (b) 0.5 mol%, (c) 1.0 mol%, and (d) 2.0 mol% at 90°C for 6 h.](image)

![Fig. 3. FESEM images [(a–d) surface and (e–h) cross-section view] of the ZnO films obtained from the solution with AlCl$_3$ of (a, e) 0 mol%, (b, f) 0.5 mol%, (c, g) 1.0 mol%, and (d, h) 2.0 mol% at 90°C for 6 h.](image)

<table>
<thead>
<tr>
<th>Batch amount of Al$^{3+}$ (mol %)</th>
<th>0</th>
<th>0.5</th>
<th>1.0</th>
<th>2.0</th>
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<tbody>
<tr>
<td>pH</td>
<td>7.69</td>
<td>7.71</td>
<td>7.66</td>
<td>7.54</td>
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Table 1. The pH of the CBD solution with 0–2.0 mol% AlCl$_3$
has the strongest (101) peak. Thus the duration and the repetition of the deposition also affect the crystallographic orientation of the films, considering that the amount of the effective Al\(^{3+}\) ions would continue to change during the film-formation process as suggested by the above FESEM observation. From the wide range RSM (Fig. 6), the leaning of the c-axis is still observed for both the samples. In Fig. 6(a) of the film obtained by the four-times repetition of the deposition, the \(\psi\) value at the \{002\} plane is around 70°–80° and that at the \{100\} plane is around 0°. This wide range RSM is basically similar to that of Fig. 2(d) except the diffraction intensities and therefore the repetition of the deposition for 6 h results in the similar orientation of the film. In contrast, the film obtained by the one-time deposition for 24 h, as shown in Fig. 6(b), indicates that the \(\psi\) value at the \{002\} plane is around 60° and that at the \{100\} plane is around 30°–40°, similarly to the film obtained from the solution without AlCl\(_3\) [Fig. 2(a)]. This implies that the orientation of the films is subject to change only when the effective Al\(^{3+}\) ions exist in the solution.

In summarizing the effect of the Al\(^{3+}\) ions, they work to modulate the microstructure of the ZnO films during the CBD process by suppressing the growth of the ZnO crystals and also changing the crystallographic orientation of the growing films. As described later, this modulation also seems to influence physical properties of the films.

### 3.3 Effect of post UV irradiation on film properties

We confirmed that no appreciable change was observed for the crystallographic orientation, the morphology, and the thickness of the films, which had been deposited in the solutions with 0–2.0 mol % AlCl\(_3\) at 90°C for 6 h, after the post UV irradiation for 0.5 h.

Figure 7 shows UV–Vis-IR spectra of the films, deposited in the solutions with 0–2.0 mol % AlCl\(_3\) at 90°C for 6 h, before and after the UV irradiation for 0.5 h. The transmittance in the visible region is about 80%, which was not changed before and after the UV irradiation. The appearance of the undulating interference from the respective spectra indicates the optical uniformity of the films 0.26–1.25 \(\mu\)m in thickness. A decrease in the transmittance in the NIR region after the UV irradiation corresponds to enhanced reflection of the films. In general, the transmittance in the NIR region is reduced in accordance with an increase in the number of carriers in TCOs due to the plasma reflection.\(^{31}\) The present result therefore suggests that the UV irradiation is effective to increase the carriers in the CBD-derived ZnO films. It is also seen in Fig. 7 that a degree of the change in the NIR transmittance becomes smaller as the Al\(^{3+}\) concentration of the solution increases. This is related rather to the larger change in the film thickness than to the difference in the carrier concentration among the samples. Optical energy band-gap \(E_g\) values determined from the absorption edge of the transmittance spectra are listed in Table 2. The \(E_g\) values are increased by the UV irradiation in any
of the samples, also indicative of an increase in the number of carriers (electrons). This can be interpreted as the well-known Burstein-Moss effect.32) From the above experimental fact, it is conceivable that the number of carriers increases by the UV irradiation. This phenomenon may be related to a photocatalytic effect on the film surface.

Figure 8 shows FT-IR spectra of the films, deposited in the solution without AlCl₃ at 90°C for 6 h, before and after the UV irradiation for 0.5 h. It is clearly seen that absorption by –CH₃ or –COOH groups, possibly ascribed to the adsorbed acetate anions, are considerably decreased after the UV irradiation. The removal of such residual organics by the UV-light decomposition is not possible since the high-pressure mercury lamp used in the present work did not include high-energy bright lines necessary for it. Instead, the decomposition can be promoted by the photocatalytic effect of ZnO as follows. First, UV photons are absorbed by ZnO through the band-gap transition, generating electron–hole pairs. Second, the generated electrons or holes react with O₂ or H₂O in air to form active oxygen species.33) Then the residual organics in the films are decomposed by the active oxygen species, leaving oxygen vacancies in the ZnO lattice through the thermal desorption of carbon or hydrogen species.34) The cleavage of Zn–O bonds (photolysis) by the charge transfer from O²⁻ to Zn²⁺ also contributes to the formation of oxygen vacancies.35) The number of electrons in the conduction band can be increased by increasing the number of oxygen vacancies.

Table 3 summarizes the sheet resistance of the films before and after the UV irradiation. Before the UV irradiation, the sheet resistance of the respective films is on the order of 10⁶ Ω·sq⁻¹. The UV irradiation is effective to decrease the sheet resistance to the order of 10⁴ Ω·sq⁻¹. The lowest sheet resistance is 2.5 × 10⁴ Ω·sq⁻¹ for the ZnO film from the solution with 1.0 mol % AlCl₃ after the UV irradiation. As to the dependence on the Al³⁺ concentration, the sheet resistance decreases with increasing the Al³⁺ concentration up to 1.0 mol % and then increases at 2.0 mol % in the films after the UV irradiation. This trend corresponds to that of transparent conductive Al-doped ZnO films prepared by the sol–gel method.36) However, a simple comparison between the sol–gel-derived and the CBD-derived films is quite difficult because the actual Al³⁺ content could not be determined in the latter. In general, the chemical composition of doped compounds or solid solutions are examined by energy dispersive X-ray spectrometry (EDX) or X-ray photoelectron spectroscopy (XPS). For the Al-doped ZnO...
films, these techniques are useful when the Al$^{3+}$ doping level lies between 1 and 6 at%.$^{37}$-$^{39}$ Actually we attempted to detect Al$^{3+}$ by EDX and XPS, but no signal from Al$^{3+}$ was obtained even for the film from the solution with 2.0 mol% AlCl$_3$. It is then assumed that the amount of the Al$^{3+}$ ions, even if they are doped in the ZnO lattice, is considerably small. The consideration on the explain the Al$^{3+}$ in (i) associated with the (ii); that is, the effect of the UV irradiation tallographic orientation, crystallinity, and grain-boundary resistivity in the present work. The optical transmittance of the ZnO films is estimated to be limited to a minimum level in the present case. It is obvious that the Al$^{3+}$ addition causes the change in the thickness, the morphology, and the crystallographic orientation in the CBD-derived films. Therefore we tentatively provide two appropriate mechanisms underlying the decrease in the sheet resistance in the present films: (i) the increase in the number of carriers by the UV irradiation and (ii) the change of the crystallographic orientation, crystallinity, and grain-boundary resistivity. The present experimental results support the mechanism (i) associated with the (ii); that is, the effect of the UV irradiation is sensitive to the microstructure of the films, which is in turn influenced by the Al$^{3+}$ addition. Consequently the structural change of the ZnO films by the Al$^{3+}$ addition is more plausible to explain the Al$^{3+}$-dependency of the sheet resistance.

4. Conclusions

Transparent ZnO films with a unique crystallographic orientation nature were obtained on buffer-coated glass substrates from the CBD solutions containing Al$^{3+}$ ions. The effect of the Al$^{3+}$ addition was remarkably observed as the change of the crystal-growth rate and the crystallographic orientation of the ZnO films. The wide range RSM revealed that the c-axis and the a-axis of the ZnO films came to stand parallel and vertical to the substrate, respectively, by increasing the AlCl$_3$ concentration of the solutions. The optical transmittance of the ZnO films was about 80% in the visible region. The post UV irradiation decreased the sheet resistance of the ZnO films from the order of $10^5$ to $10^3$ $\Omega$·sq$^{-1}$. The film obtained from the solution containing 1.0 mol% AlCl$_3$ showed the lowest sheet resistance (2.5 × $10^3$ $\Omega$·sq$^{-1}$) in the present work.

References