Preparation of ZnO Films with Preferential Orientation by Sol-Gel Method

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ZnO films were prepared on silica glass substrates by the sol-gel method from Zn(CH3COO)2·2H2O-2-methoxyethanol solutions containing monoethanolamine (MEA) or diethanolamine (DEA). Smooth and transparent ZnO films were obtained by heating at temperatures from 200 to 500°C for 10 min after each coating and finally at the same temperatures for 1 h. The films prepared from coating solutions containing MEA were strongly oriented along the (002) plane. The effects of heating temperature and ethanolamines on the film morphology, grain size distribution and crystallographic orientation are discussed based on X-ray diffraction and scanning electron microscopy.

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1. Introduction

ZnO films have several promising applications in solar cells,1) gas sensors2) and optical waveguide devices and so on. In particular ZnO films oriented along the c-axis have been used as surface acoustic wave (SAW) devices because of the large piezoelectric constant.3) ZnO films have been fabricated by several techniques, such as thermal deposition,4) sputtering,3) chemical vapor deposition5)-7) and spray pyrolysis.8)-10)

The sol-gel method has been extensively used for preparing various kinds of functional oxide films, such as TiO2,11),12) BaTiO3,13) LiNbO3,14) ITO,15) Li2B4O716) films. Okamura et al.17) prepared n-ZnO/p-Si heterojunction by the sol-gel method using zinc diethoxide as the starting material, studying the gap states of the ZnO films. Tsuchiya et al.18) and Tang and Cameron19) prepared Al-doped ZnO films from zinc nitrate or acetate, studying the electrical conductivity of the films. Ohya et al.20) and Takahashi et al.21) prepared non-doped or doped ZnO films from zinc acetate and zinc di-n-propoxide using diethanolamine as an additive, studying the photoconductivity of the films. They also found that the non-doped films are slightly c-axis oriented. As far as we know, however, no report has been presented on highly oriented, sol-gel-derived ZnO films, and on the effect of the preparation conditions on preferred orientation.

In the present study, we report the sol-gel preparation of highly oriented ZnO films on the silica glass substrates from Zn(CH3COO)2·2H2O-2-methoxyethanol-alkanolamine solutions. The effects of heating temperature and alkanolamine addition on the morphology, homogeneity, crystallographic orientation of the resultant ZnO coating films are examined.

2. Experimental

2.1 Preparation

Figure 1 shows the experimental procedure for preparing ZnO films. In the present study, 2-methoxyethanol was used as solvent, instead of 2-propanol, which was employed in a work by Takahashi et al.21) Since zinc acetate has very low solubility in 2-

![Flow chart showing procedure for film preparation.](image-url)
methoxyethanol, monoethanolamine (MEA) or diethanolamine (DEA) was further added to obtain clear solutions. Then two kinds of starting solutions for dip-coating were prepared; solution A and solution B contain MEA and DEA, respectively. Zn(CH₃COO)₂·2H₂O was dissolved in 2-methoxyethanol mixed with alkanolamine (MEA or DEA), and the resultant solution was allowed to stand at 60°C for 30 min under stirring. The molar ratio of alkanolamine to zinc acetate was fixed at 1.0, the same molar ratio as that employed by Takahashi et al., and the concentration of zinc acetate was fixed at 0.6 mol·L⁻¹.

Films were obtained by dipping silica glass substrates in the coating solutions and subsequently pulling them up at a constant speed (3.5 cm·min⁻¹). After each coating, the films were immediately subjected to heat treatment at temperatures from 200 to 800°C for 10 min. This procedure was repeated 2 times. After the third coatings, the films were heated at the same temperatures for 1h.

2.2 Characterization
X-ray diffraction (XRD) of the ZnO films was measured by a Rigaku RAD II A X-ray diffractometer using Cu Kα radiation. The surface and cross-sectional morphology of the films were observed by a Hitachi S-800 scanning electron microscope (SEM).

3. Results
3.1 Surface and cross-sectional morphologies
The films from solution A were transparent when heated at temperatures below 500°C, while the films heated above 600°C were translucent. Figure 2 shows the SEM photographs of the films from solution A. Figures 2(a), (b), (c) and (d) show the surface morphologies of the solution A-derived films heated at 300, 500, 600 and 800°C, respectively. Particulate structure is evident in all films. The particle size increases with heating temperature, and aggregation of the particles and large distribution of the particle size are observed in the films heated at 600 and 800°C. Figures 3(a), (b), (c) and (d) show the cross-sectional morphologies of the solution A-derived films heated at 300, 500, 600 and 800°C, respectively. Small particles piled up on the substrate are observed in the film heated at 300°C. In the film heated at 500°C one layer of particles which are very homogeneous in size and aligned lying perpendicular to the substrate are observed. The particles in the films heated above 600°C, however, are grown and arranged randomly, and the surface of the films is very rough. This coarse microstructure may explain why

Fig. 2. SEM photographs of the surface of the ZnO films prepared from solution A. The films were heated at (a) 300, (b) 500, (c) 600 and (d) 800°C.

Fig. 3. SEM photographs of the cross section of the ZnO films prepared from solution A. The films were heated at (a) 300, (b) 500, (c) 600 and (d) 800°C.

Fig. 4. SEM photographs of the surface of the ZnO films prepared from solution B. The films were heated at (a) 300, (b) 500, (c) 600 and (d) 800°C.
the films heated above 600°C are not transparent, but translucent. In contrast, all films obtained from solution B were smooth and transparent except the film heated at 300°C, which was light brown in color. Figures 4(a), (b), (c) and (d) show the surface morphologies of the films heated at 300, 500, 600 and 800°C, respectively. No aggregated particles are present and the particle size distribution is small. Figures 5(a), (b), (c) and (d) show the cross-sectional morphologies of the solution B-derived films heated at 300, 500, 600 and 800°C, respectively. Small particles piled up on the substrate are observed in the films heated at 300 and 500°C. Particles are grown above 600°C, forming one layer of particles aligned perpendicular to the substrate.

3.2 X-ray diffraction

Figure 6 shows X-ray diffraction patterns of the films from solution A. Crystallization of ZnO is found to begin above 200°C. The peak intensity of (002) plane increases with increasing heating temperature up to 500°C and no peaks other than this can be observed, indicating the preferred grain growth along the (002) plane. The (002) peak intensity, however, rapidly decreases above 600°C and other peaks appear.

Figure 7 shows X-ray diffraction patterns of the films from solution B. Preferred orientation along the (002) plane is not observed at all, differing from the solution A-derived films. Two diffraction peaks due to (100) and (101) planes appear even in the film heated at 300°C. Although a peak due to (002) plane is observed in the films heated above 400°C, the peak intensity only slightly increases with increasing heating temperature, extremely weak compared to the films from solution A.

4. Discussion

The amino groups and/or the hydroxyl groups of alkanolamines are known to coordinate the metal atoms of alkoxides, improving the solubility and stability against hydrolysis of the alkoxides. This is also the case with zinc acetate as demonstrat-
ed in literatures\(^{18,20,21}\) and in the present study; addition of more than 0.5 mole of alkanolamine to 1 mole of zinc acetate provided a clear solution. There are two possible ways for MEA, a bidentate ligand, to coordinate the zinc atoms; one is to act as a chelating ligand and the other is to bridge two zinc atoms. Although \(^1\)H NMR and Raman spectroscopic measurements were performed on the solutions, it was very difficult to make this point clear in the present work.

ZnO films fabricated from zinc acetate solutions appear to have a tendency to grow preferentially along the (002) plane. For example, Caillaud et al.\(^{10}\) reported that ZnO films prepared from an aqueous solution of zinc acetate by spray pyrolysis exhibited a preferred orientation of the c-axis perpendicular to the alumina-based substrate. Major et al.\(^{24}\) obtained similar result by using zinc acetate and 2-propanol as solvent and glass substrate. It should be noted here, however, that other peaks such as (101) and (100) planes were also observed in the films fabricated by spray pyrolysis on the substrate that was heated at 300–450°C. It seems that water and 2-propanol, solvents with low boiling points, disturb the aligned grain growth in the film. Takahashi et al. observed preferred orientation of the c-axis perpendicular to the substrate in the sol-gel ZnO films derived from a solution of zinc acetate, 2-propanol and DEA.\(^{23}\) The preferred orientation, however, was again imperfect, suggesting that 2-propanol, a solvent of lower boiling point than 2-methoxyethanol, hinders strongly preferred orientation. In contrast, the use of 2-methoxyethanol and MEA, solvents of higher boiling points, resulted in strongly preferred orientation of ZnO crystals as in the present study.

One possible explanation of the effect of the solvent boiling point on ZnO crystallization is that a solvent of higher boiling point would evaporate more slowly on heating, allowing the structural relaxation of the gel film before crystallization. Taking account of the boiling point of 2-methoxyethanol (125°C) and the crystallization temperature of acetate-derived ZnO film (200°C),\(^{10}\) crystallization is thought to occur after vaporization of 2-methoxyethanol. Since 2-methoxyethanol has a higher boiling point than 2-propanol and water, the structural relaxation of the ZnO gel film can be allowed by the slower vaporization of the solvent, providing denser precursor films. It is easily expected that aligned crystal growth can take place more readily in denser precursor films than porous ones. The effect of MEA on the molecular scale structure of the gel, of course, should be also taken into account. MEA, which has a boiling point of 170°C and is thought to coordinate zinc metal atoms, would remain in the film even at crystallization temperature. Modification of the molecular scale structure is then another possible effect of MEA on the crystallization behavior.

As far as the heat treatment temperature is concerned, heat treatment of solution A-derived films at 500°C resulted in transparent ZnO films with strongly preferred orientation, whereas that above 600°C resulted in translucent films with less preferred orientation. When gel films are placed in a furnace of higher temperatures, they experience higher heating rates. At higher heating rates, solvents evaporate more abruptly, leaving less time for the gel to undergo structural relaxation. In other words, gel films are generally more porous when heated at a higher rate as suggested by Logan et al.\(^{25}\) In the present case, the precursor gel film would be denser at crystallization temperature when introduced into a 500°C furnace, resulting in dense, transparent film with strongly preferred orientation. On the other hand, the precursor gel film would be more porous at crystallization temperature when introduced into a 600°C furnace, leading to more porous films consisting of grains with random size and orientation. In another experimental work,\(^{26}\) we have prepared ZnO films from a zinc acetate solution of a similar composition by repeating dip-coating and preheat-treatment at 200–500°C and finally heating the preheated films at 500°C. Refractive index of the film thus obtained was found to increase from 1.776 to 1.838 when the preheating temperature decreased from 500 to 200°C. This experimental fact reveals that films subjected to lower preheating temperatures experience structural relaxation there and become denser.

The above consideration suggests that the structural relaxation of the precursor gel before crystallization is necessitated for obtaining dense, homogeneous films with strongly preferred orientation. This can be achieved by employing solvents of relatively high boiling points of about 200°C and heating the film at lower rates or preheating at lower temperatures of 200–300°C.

The solution B-derived ZnO film did not show preferred orientation at all. The film heated at 300°C was light brown in color. Taking into account that the boiling point of DEA is 270°C, carbonaceous materials resulting from incomplete combustion of DEA remain in the films when ZnO crystallization occurs, hindering the preferred grain growth along the (002) plane. Another feature of the solution B-derived ZnO films are their transparency, which was not lost even when the films were subjected to heat treatment above 600°C. This suggests that the structure of alkanolamine–zinc acetate complexes formed in the coating solutions is somewhat different between DEA and MEA. This is easily expected by noting that MEA is a bidentate ligand, while DEA is a terdentate one.

5. Conclusion

ZnO films were prepared from Zn(CH\(_3\)COO)\(_2\)·2H\(_2\)O–2-methoxyethanol-monoethanolamine (MEA) or diethanolamine (DEA) solutions by repeated dip-coating and heat treatment. It was found that the
films prepared from the solution containing MEA exhibit strongly preferred orientation of ZnO c-axis perpendicular to the substrate surface when heated at 500°C. Both heat treatment at higher temperatures and addition of DEA to the solution deteriorated preferred orientation. The effects of alkanolamines and heat treatment temperature on the ZnO crystallization have been discussed on the basis of the structural relaxation, molecular structure and impurity phase in the films.

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References