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Effect of chelating agents on the preferred orientation of ZnO films by sol-gel process

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Abstract The effect of chelating agents of ZnO precursor solutions on crystallization behavior was investigated. Two different additives, monoethanolamine (MEA) and diethanolamine (DEA), and crystalline Pt (111)/Si and amorphous SiN_x/Si substrates, were used for this study. ZnO film grown on SiN_x/Si from a DEA-chelated precursor solution shows a poorly oriented microstructure with weak crystallization peaks, while ZnO film grown on Pt(111)/Si shows a c-axis preferred orientation. In the case of ZnO films prepared with a MEA-chelated precursor solution, all films show a strong preferred orientation irrespective of substrate type. This result clearly demonstrates the role of the chelating agent on the crystallographic orientation and crystallization behavior of sol-gel processed ZnO films.

Introduction

Extensive studies have been conducted on ZnO films because of their flexible properties for a wide range of applications, including transparent conductive film [1, 2], laser [3], solar cell [4], and acoustic wave devices [5]. Acoustic wave devices based on thin film technology have attracted much attention for filters in telecom applications and transducers in biosensor applications. The driving force for developing the thin film technology is the need to replace the expensive single crystal substrates and thus to provide a flexible choice of substrate materials and mass manufacturability. For utilizing ZnO thin films for such applications, ZnO thin films should be grown to have preferred orientation whose direction shows piezoelectricity. Various coating techniques for ZnO films have been employed, such as sputtering [5, 6], chemical vapor deposition [1], pulsed laser deposition [7], and sol-gel process [2, 8]. Among these, chemical solution deposition (CSD) methods like the sol-gel technique represent an efficient way for easy fabrication of a large-area thin film with low cost, allowing excellent compositional flexibility and easy control of film thickness. To obtain the strong c-oriented structure, solution chemistry, heat treatment condition, and substrate type have been investigated to grow ZnO films by sol-gel process. Solution chemistry, such as the type and the concentration of the starting precursor materials[9], the solvent [10], and the chemical additives [11, 12], is considered to obtain ZnO films with good crystallinity. Although alkanolamine is often added as a chelating agent to improve the homogeneity of the ZnO chemical solution and to increase the solubility of Zn-acetate against humidity from its surroundings, its role on the film orientation and crystallization is rarely reported.

In this study, we investigate the crystallization behavior of sol-gel processed ZnO films depending on types of chelating agents on different silicon-based substrates. As chelating agents, DEA (diethanolamine) and MEA (monoethanolamine) were used, and amorphous silicon nitride grown on silicon substrates and crystalline platinum coated on silicon substrates were also used to understand the interrelationships between these controllable parameters and their relative importance on the crystallization behavior.

Experimental

Zinc acetate dihydrate (Aldrich, $(C_2H_3O_2)_2Zn \cdot 2H_2O$) and 2-methoxyethanol (Aldrich, $C_3H_8O_2$) were used as a Zn

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source and solvent, respectively. The molar concentrations of solutions were varied from 0.1 to 0.5 M. Diethanolamine (DEA) and Monoethanolamine (MEA) were used as chelating agents. The molar ratio of zinc acetate and the chelating agent was fixed to 1:1. After 1 h of stirring at 80 °C, the precursor was cooled down to room temperature, and it was transparent. No precipitates were found in the precursors after 72 h of aging. ZnO films were fabricated onto two different substrates: amorphous silicon nitride grown on Si (SiN_x/Si) and (111) oriented platinum-coated Si (Pt/Si). Spin coating of the precursor solution was performed at 3000 rpm for 30 s. After each spin coating cycle, pyrolysis was performed at 200–400 °C for 10 min. Films after five coatings were then annealed at 500–700 °C for 1 h for crystallization. Each layer after pyrolysis was measured to be about 5 nm, 15 nm, and 28 nm thick at 0.1, 0.3, and 0.5 M concentration, respectively.

Crystallization and orientation of films were evaluated by an X-ray diffractometer (Rigaku D/MAX B) utilizing $Cu_{K\alpha}$ radiation. The thermal properties of ZnO precursor solutions were analyzed using differential scanning calorimeter/thermo-gravimetric analysis (DSC/TG, Rheometric Scientific STA1500), with a heating rate of 10 °C/min. The surface morphology of the films was characterized by a scanning electron microscope (SEM, JEOL JSM-7000F). For the Raman experiment, He–Cd laser (Kimmon Electric) with 441.6 nm of wavelength was used. The laser beam nominal power was 80 mW, and optical microscopy (Zeiss Axiotech) for focusing a spot with around 5 μm in diameter was connected with a thermoelectrically cooled charged coupled device (CCD) detector for imaging. Backscattering geometry was used, and the polarization state of the laser beam was not analyzed for the incident and the scattered light. Frequency resolution was about 0.4 cm^{-1}, and its range was 96–877 cm^{-1}.

Results and discussion

Transparent ZnO precursor sols were obtained from both the MEA and DEA chelating agents that were used to improve the solution stability by preventing rapid reaction between metal alkoxide and water molecules [13]. To evaluate the bonding characteristics of the final precursor solutions depending on types of chelating agents, differential scanning calorimeter/thermo-gravimetric (DSC/TG) analysis was carried out as shown in Fig. 1. The DSC curve of the MEA-chelated precursor shows endothermic peaks at around 115, 235, and 305 °C corresponding to the evaporation of water molecules, 2-methoxyethanol, and strongly bound organic compounds remaining in the precursor, respectively. The total weight loss of the MEA-chelated precursor was about 65% and the most weight loss occurred below 300 °C. In the case of the DEA-chelated precursor, peaks of the DSC curve appeared at 130, 250, and 335 °C, which are associated with the evaporation of water, solvents, and other organic compounds, respectively. The total weight loss for this solution was approximately 60% and occurred until 420 °C. Thus, TG/DSC results show that the crystallization of ZnO films derived by DEA-chelated solution will occur at a higher temperature than those derived by MEA-chelated solution. Additionally, ZnO films derived by MEA-chelated solution will be contracted at a higher degree due to its high weight change during heat treatment. Consequently, it is believed that the thermal behaviors of the two solutions are apparently strongly influenced by the type of chelating agent.

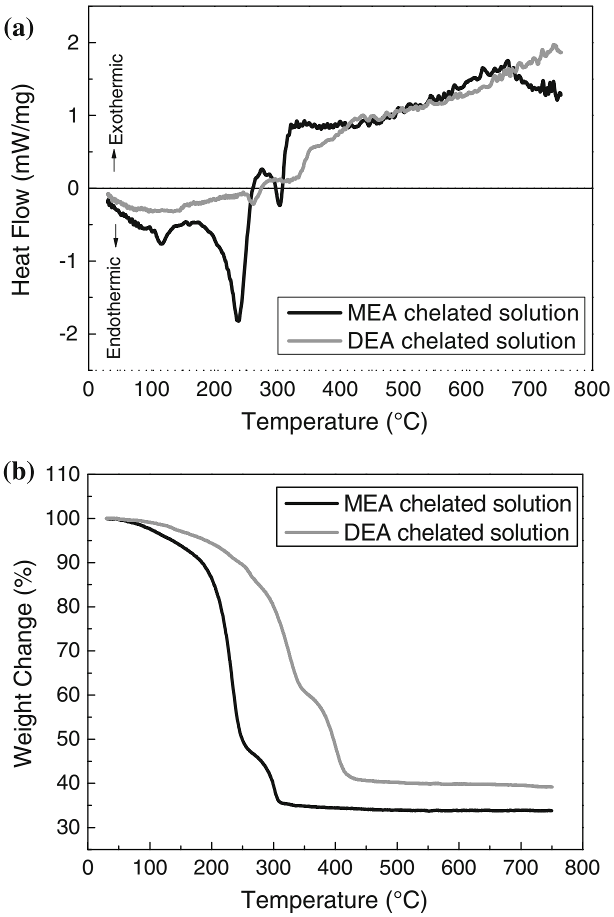

Fig. 1 (**a**) DSC and (**b**) TG curves obtained from the 0.5 M ZnO precursors depending on the chelating agents

The crystallization behavior of ZnO films depending on different precursor solutions and substrates was characterized by XRD analysis as shown in Fig. 2. ZnO films derived with MEA chelating represent strong ZnO(002) peak intensity in both polycrystalline Pt(111)/Si and amorphous SiN_x/Si substrates. ZnO films prepared by the DEA-chelated solution possess a very high degree of (002) peak on Pt(111)/Si substrate, while the film grown on

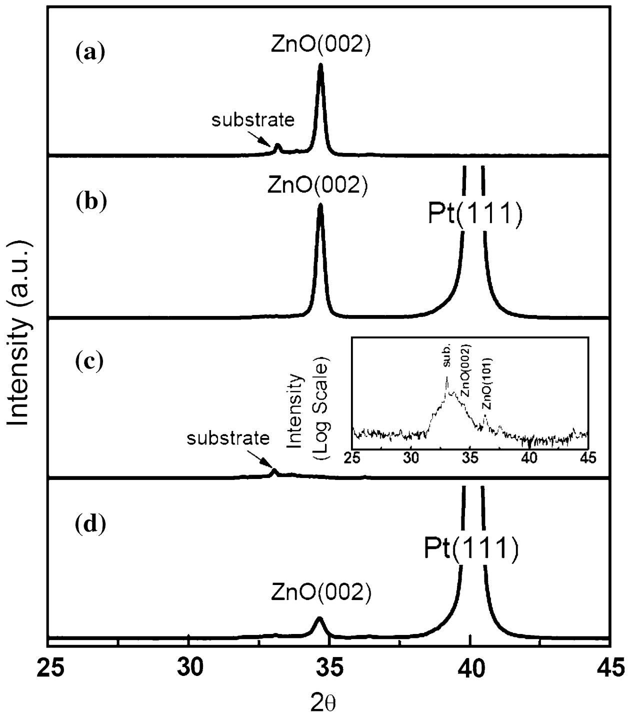

Fig. 2 X-ray diffraction patterns of ZnO films grown on different substrates from sol-gel solutions modified by two different chelating agents: (**a**) MEA-chelated solution and SiN_x/Si substrate, (**b**) MEA-chelated solution and Pt(111)/Si substrate, (**c**) DEA-chelated solution and SiN_x/Si substrate, and (**d**) DEA-chelated solution and Pt(111)/Si substrate. All films were pyrolyzed at 300 °C for 10 min and annealed at 700 °C for 1 h. Solution concentration was 0.5 M, and the thickness of the films was about 140 nm

SiN_x/Si did not show clear ZnO(002) peak. Peaks of ZnO were only observed when a logarithmic scale of the intensity was used, as shown in Fig. 2. This feature was very similar irrespective of the pyrolysis temperature observed, which ranged from 200 to 400 °C, and regardless of the solution concentration of 0.1–0.5 M.

The fact that the peaks of the DEA-chelated precursor shift to higher temperature and that the weight loss of DEA-chelated solution is lower than that of the MEA-chelated solution may demonstrate that the DEA-chelated solution has a stronger chemical bonding to Zn^{2+} ions compared with that of MEA. Moreover, considering the melting point of the chelating agents, DEA, whose boiling point is 270 °C, may promote a higher degree of polymerization compared with MEA (b.p. = 170 °C). Different degrees of polymerization due to the molecules of the chelating agent can affect the crystallization process, which is the transformation of gels or substances in an amorphous pyrolyzed state to crystalline piezoelectric materials. This can be explained in terms of a nucleation and growth process. The addition of chelating agents increases the bonding force of the gel, which can increase the energy barrier for nucleation and growth barrier for crystallization.

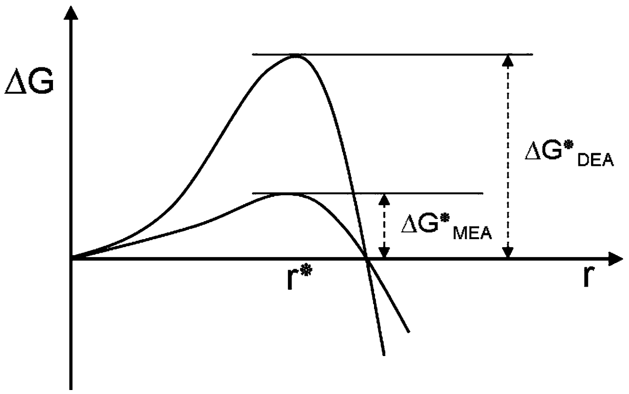

Fig. 3 Schematic diagram of the free energies for ZnO crystallization from the MEA- and DEA-chelated precursor solutions

Since DEA forms stronger bonds compared with that of MEA in gels and/or pyrolyzed structures, the crystallization from a DEA-chelated precursor solution may demand a higher nucleation barrier as described in Fig. 3 Lower energy barriers for MEA solution systems may facilitate the c-axis growth of ZnO, which is the lowest energy direction of the ZnO material, irrespective of the surface configuration of the substrate. On the other side, the crystallization of ZnO films from a DEA-chelated precursor solution can be hindered by the higher energy barrier needed for crystallization. Therefore, the crystallization can be promoted only when the lattice between the ZnO and the substrate matches by reducing the elastic strain energy attributable to the energy barrier [14], as found in the XRD data of ZnO film on Pt(111) in Fig. 2d. This result can explain prior reports on why ZnO films prepared by an MEA-chelated solution system show a strong degree of c-axis orientation on glass substrates [15–17], while the DEA system does not show c-axis orientation [12].

To investigate the crystallinity and the internal stress of the films, Raman spectroscopy was performed, and the result of the E_2 mode is shown in Fig. 4. ZnO has a Wurtzite crystal structure with 6-fold symmetry, which belongs to $C_{6v}{}^4$. By the group theory, ZnO can have A_1, $2B_2$, E_1, and $2E_2$ modes. A_1 and E_1 modes are polar and can be split into LO (longitudinal optical) and TO (transverse optical) modes. $2B_2$ modes are silent. Among them, the A_1(LO) and E_1(LO) modes are related to the free carrier concentration, and E_2(high) mode is related to the stress in the film [18]. The peak position of the E_2 mode shifts upward under a compressive stress state and downward under a tensile stress state in the film [19]. To evaluate the internal stress in the films, the curves were fitted by the Lorentzian function. The determination of the peak position for the stress state in the films was assessed by comparing the peak positions with ZnO single crystals (Eagle Pitcher Inc.), which is shown in the inset of Fig. 4b.

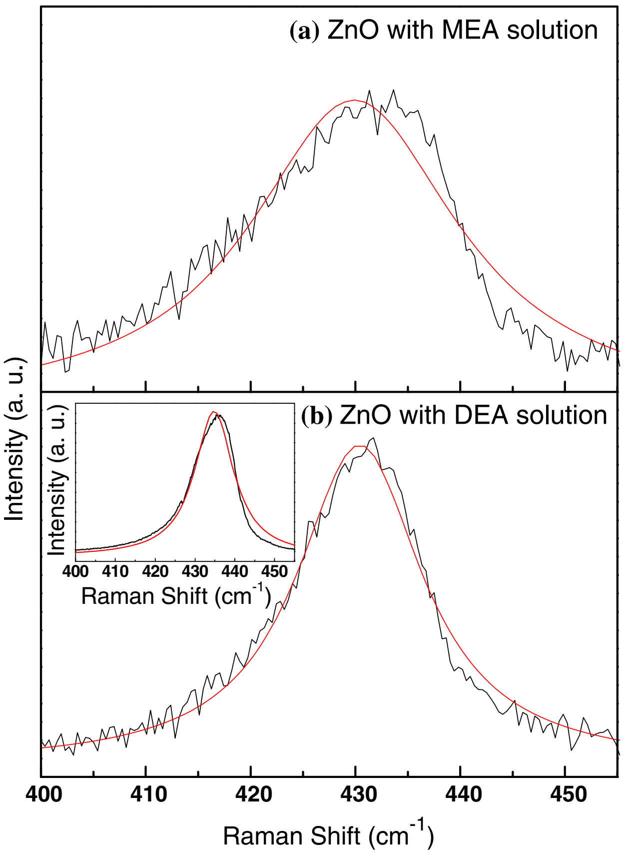

Fig. 4 Raman data of ZnO films fabricated with different sol-gel solutions modified by two different chelating agents: (**a**) MEA-chelated solution on Pt(111)/Si substrate and (**b**) DEA-chelated solution on Pt(111)/Si substrate. All films were pyrolyzed at 300 °C for 10 min and annealed at 700 °C for 1 h. Solution concentration was 0.5 M, and the thickness of the films was about 140 nm. Raman data of ZnO single crystal are shown at the inset of (**b**)

In contrast with the peak position at 434.8 cm^{-1} of the ZnO single crystal, ZnO films by DEA- and MEA-chelated solutions have a peak position at 430.5 cm^{-1} and 430.3 cm^{-1}, respectively, indicating tensile stress in the deposited films. The shift of the XRD peak position to the higher angles in Fig. 2 indicates a tensile stress of the film confirming the Raman results. The tensile stress might be caused by the lattice mismatch and the mismatch of the thermal expansion coefficients between the film and the substrate. However, the slightly more tensile stress of the ZnO film derived by the MEA-chelated solution is probably due to its larger weight loss than the DEA-chelated solution, as shown in the TG/DSC data (Fig. 1), which was caused by the weak chemical bonding in the solution. The detailed stress condition of ZnO films derived by CSD is under an investigation as a function of thickness and chelating agents.

The microstructure of ZnO films was characterized by SEM. ZnO films on amorphous SiN_x on silicon substrates were shown in Fig. 5. SEM images show that the ZnO films show a microstructure consisting of small grains whose size ranges from 70 to 100 nm. The ZnO film derived with MEA shows a dense structure on the amorphous substrate, while the film derived with DEA shows many voids on the surface. The dense structure of the ZnO film may indicate the high crystallinity of ZnO film derived by a MEA-chelated solution even on the amorphous substrate and indicates that the low energy barrier of nucleation and growth facilitates the c-axis preferred orientation of the deposited film, which is in good agreement with the XRD data. Alternatively, voids or pores observed in the ZnO films on SiN_x/Si derived with DEA may be due to poor crystallization resulting from the higher energy barrier.

Conclusion

The effect of chelating agents of ZnO precursor solutions on crystallization behavior has been investigated. Two

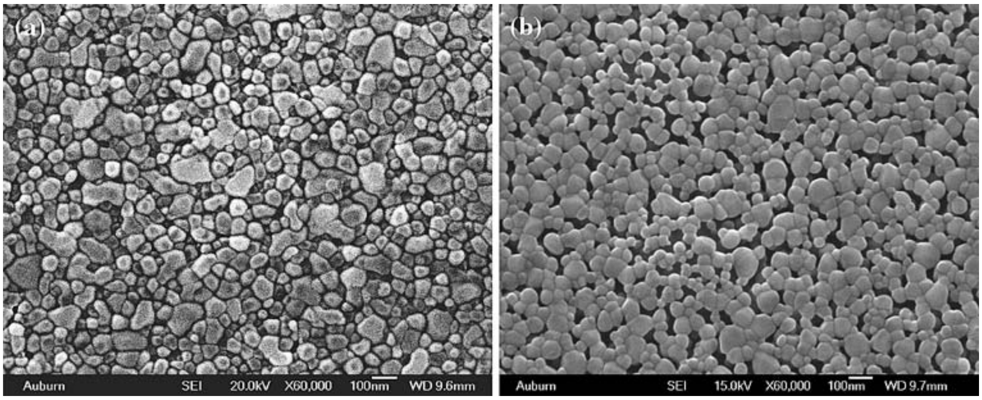

Fig. 5 SEM images of ZnO films prepared from (**a**) MEA-chelated solution on SiN_x/Si substrate and (**b**) DEA-chelated solution on SiN_x/Si substrate. The films were pyrolyzed at 300 °C for 10 min and annealed at 700 °C for 1 h. The solution concentration was 0.5 M and the thickness of the films was about 140 nm

different additives, monoethanolamine (MEA) and diethanolamine (DEA), and polycrystalline Pt (111)/Si and amorphous SiN_x/Si substrates were used for this study. ZnO film grown on SiN_x/Si from a DEA-chelated precursor solution shows poorly oriented structure with weak crystallization peaks, while ZnO film on Pt(111)/Si shows c-axis preferred orientation. In the case of ZnO films prepared by a MEA-chelated precursor solution, all films show strong preferred orientation irrespective of the substrate. The change of the gel/pyrolyzed structure induced by modifying molecules of the solution by incorporating a chelating agent can explain the observed tendency of their crystallization behaviors. This result clearly demonstrates the importance of the chelating agent on the crystallographic orientation and crystallization behavior of ZnO films on silicon-based substrates.

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References

1. Nishino J, Ohshio S, Kamata K (1992) J Am Ceram Soc 75:3469. doi:10.1111/j.1151-2916.1992.tb04452.x
2. Lee JH, Park BO (2003) Thin Solid Films 426:94. doi:10.1016/S0040-6090(03)00014-2
3. Znaidi L, Illia GJAAS, Benyahia S, Sanchez C, Kanaev AV (2003) Thin Solid Films 428:257. doi:10.1016/S0040-6090(02)01219-1
4. Jin M, Feng J, De-heng Z, Hong-lei M, Shu-ying L (1999) Thin Solid Films 357:98. doi:10.1016/S0040-6090(99)00357-0
5. Petrov I, Orlinov V, Misiuk A (1984) Thin Solid Films 120:55. doi:10.1016/0040-6090(84)90173-1
6. Kim KH, Park KC, Ma DY (1997) J Appl Phys 81:7764. doi:10.1063/1.365556
7. Myoung JM, Yoon WH, Lee DH, Yun I, Bae SH, Lee SY (2002) Jpn J Appl Phys 41:28. doi:10.1143/JJAP.41.28
8. Wessler B, Lange FF, Mader W (2002) J Mater Res 17:1644. doi:10.1557/JMR.2002.0242
9. Ohya Y, Saiki H, Tanaka T, Takahashi Y (1996) J Am Ceram Soc 79:825. doi:10.1111/j.1151-2916.1996.tb08512.x
10. Kim YS, Tai WP, Shu SJ (2005) Thin Solid Films 491:153. doi:10.1016/j.tsf.2005.06.013
11. Ohya Y, Saiki H, Takahashi Y (1994) J Mater Sci 29:4099. doi:10.1007/BF00355977
12. Ohyama M, Kozuka H, Yoko T, Sakka S (1996) J Ceram Soc Jpn 104:296
13. Sanchez C, Livage J, Henry M, Babonneau F (1988) J Non-Cryst Solids 100:65. doi:10.1016/0022-3093(88)90007-5
14. Yoon SH, Kim DJ (2007) J Cryst Growth 303:568. doi:10.1016/j.jcrysgro.2006.11.351
15. Fujihara S, Sasaki C, Kimura T (2001) Appl Surf Sci 180:341. doi:10.1016/S0169-4332(01)00367-1
16. Ohyama M, Kozuka H, Yoko T (1997) Thin Solid Films 306:78. doi:10.1016/S0040-6090(97)00231-9
17. Ohyama M, Kozuka H, Yoko T (1998) J Am Ceram Soc 81:1622
18. Asmar RA, Atanas JP, Ajaka M, Zaatar Y, Ferblantier G, Sauvajol JL et al (2005) J Cryst Growth 279:394. doi:10.1016/j.jcrysgro.2005.02.035
19. Huang Y, Liu M, Li Z, Zeng Y, Liu S (2003) Mater Sci Eng B 97:111. doi:10.1016/S0921-5107(02)00396-3