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(0 0 2)-oriented growth and morphologies of ZnO thin films prepared by sol-gel method

DONGYUN GUO[1,*], YANG JU[1], CHENGJU FU[2], ZHIXIONG HUANG[2], LIANMENG ZHANG[2]

[1]Department of Mechanical Science and Engineering, Nagoya University, Nagoya 464-8603, Japan
[2]School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, China

Zinc acetate was used as a starting material to prepare Zn-solutions from solvents and ligands with different boiling temperature. The ZnO thin films were prepared on Si(1 0 0) substrates by spin-coating method. The effect of baking temperature and boiling temperature of the solvents and ligands on their morphologies and orientation was investigated. The solvents and ligands with high boiling temperature were favorable for relaxation of mechanical stress to form the smooth ZnO thin films. As the solvents and ligands with low boiling temperature were used to prepare Zn-solutions, the prepared ZnO thin films showed (0 0 2) preferred orientation. As n-propanol, 2-methoxyethanol, 2-(methylamino)ethanol and monoethanolamine were used to prepare Zn-solutions, highly (0 0 2)-oriented ZnO thin films were formed by adjusting the baking temperature.

Keywords: *ZnO thin film; sol-gel method; boiling temperature; orientation; morphology*

1. Introduction

Zinc oxide (ZnO) is an n-type semiconductor with a wide direct band gap of 3.37 eV and a large exciton binding energy (60 meV). ZnO thin films have been widely applied in high technology such as optoelectronic devices, solar cells, piezoelectric transducers and gas sensors [1–7]. Many techniques have been utilized to prepare ZnO thin films, such as metal organic chemical vapor deposition, pulsed laser deposition, sputtering, hydrothermal, sol-gel method, etc. [8–18]. Due to the low cost and simple equipment, sol-gel method has been extensively applied to prepare ZnO thin films. During the sol-gel process, the (0 0 2)-oriented growth and morphology of ZnO thin films, which are important for their electrical and optical properties, are influenced by many factors.

Ohyama et al. [14, 15] prepared ZnO thin films by dip-coating method and studied the effects of heat-treatment conditions, ligands, withdrawal speed of the substrate and film thickness on crystallographic orientation and morphology of ZnO thin films. The highly (0 0 2)-oriented ZnO thin films were obtained on silica glass substrates by preheating at 300 °C and post-heating at 600 °C to 800 °C with a 2-methoxyethanol-monoethanolamine-$Zn(CH_3COO)_2 \cdot 2H_2O$ solution. They suggested that solvents, such as methanol, ethanol and propanol, with lower boiling temperature than that of 2-methoxyethanol, strongly hindered preferred (0 0 2) orientation of ZnO thin films. When the preheating temperature was too high (>300 °C), vaporization of the solvents and thermal decomposition of zinc acetate took place abruptly and simultaneously with the crystallization, disturbing the unidirectional crystal growth. On the contrary, when the preheating temperature was too low (<300 °C), complete vaporization and thermal decomposition of zinc acetate didn't occur at the preheating step but occurred at the postheating step. The abrupt solvent vaporization and acetate decomposition occurred at the postheating step, which disturbed the unidirectional crystal growth. However, Santos et al. [19] dissolved $Zn(CH_3COO)_2 \cdot 2H_2O$ in methanol and obtained

*E-mail: guodongyun@gmail.com

(0 0 2)-oriented ZnO thin films on glass substrates at a low pre-heating temperature of 120 °C and annealing temperature of 350 °C. Guo et al. [18] used the 2-methoxyethanol-monoethanolamine-$Zn(CH_3COO)_2{\cdot}2H_2O$ solution to prepare ZnO thin films on glass and Si substrates. As the ZnO thin films were baked at 210 °C and annealed at 400 °C, highly (0 0 2)-oriented ZnO thin film was obtained because of solid-state oriented aggregation of the adjacent ZnO nuclei. These results indicate that the further investigation should be done to clearly understand the (0 0 2)-oriented growth of ZnO thin films prepared by sol-gel method.

Recently, Segawa et al. [20] observed a porous wrinkled morphology of ZnO thin films prepared by sol-gel method. The formation of the wrinkled structure increased the roughness of the ZnO thin films, which deteriorated their electrical and optical properties. Maiti et al. [21] indicated that the formation of wrinkled surface was due to the presence of monoethanolamine in the precursor. Hou et al. [22] suggested that the formation of wrinkled structure was related to the release of mechanical stress, which was generated during the baking process. By adjusting the preheating conditions in the spin-coating process, the formation of wrinkled structure could be avoided. It implied that the boiling temperature of the solvents and ligands seriously affected the morphology of ZnO thin films. It is necessary to understand the relationship between the boiling temperature and morphologies of ZnO thin films.

In this study, solvents and ligands with different boiling temperatures were used to prepare Zn-solutions, and the ZnO thin films were deposited on Si substrates by spin-coating method. The effect of boiling temperature and pre-heating temperature on (0 0 2)-oriented growth and morphologies of ZnO thin films was investigated.

2. Experimental

All the chemicals were analytic grade reagents used without further purification. $Zn(CH_3COO)_2{\cdot}2H_2O$ was used as the starting material. Methanol, ethanol, n-propanol and 2-methoxyethanol were used as the solvents, and 2-(methylamino)ethanol, monoethanolamine and diethanolamine were used as the ligands. Their atmospheric boiling temperatures are listed in Table 1. Fig. 1 shows the experimental procedure for preparation of ZnO thin films. A desired amount of $Zn(CH_3COO)_2{\cdot}2H_2O$ was dissolved in the solvent and ligand at 60 °C for 30 min to get the transparent and homogeneous solutions. The molar ratio of ligand to $Zn(Ac)_2{\cdot}2H_2O$ was kept at 1. The concentration of all Zn-solutions was 0.4 $mol{\cdot}L^{-1}$. Table 2 lists the details of all solutions. The ZnO thin films were spin-coated on Si(1 0 0) substrates at 4000 rpm for 30 s. The wetting films were baked on a hot-plate at different temperatures for 10 min. The spin-coating and baking processes were repeated for 3 times. The final films were annealed in a furnace at 400 °C for 60 min in air ambient.

X-ray diffraction (XRD) patterns of the ZnO thin films were measured by a Rigaku D/MAX-IIIA X-ray diffractometer with CuKα radiation. Morphologies of the ZnO thin films were observed with a field emission scanning electron microscope (FESEM, JSM-7000FK, JEOL, Ltd.).

Table 1. Atmospheric boiling temperature of the solvents and ligands.

		Boiling temperatures [°C]
Solvent	Methanol	64.7
	Ethanol	78
	n-propanol	97
	2-methoxyethanol	124
Ligand	2-(methylamino)ethanol	159
	Monoethanolamine	170
	Diethanolamine	268

3. Results

3.1. Zn-solutions with 2-(methylamino)ethanol and different solvents

The ZnO thin films using the Zn-solutions with 2-(methylamino)ethanol and different solvents were spin-coated on Si(1 0 0) substrates and baked at different temperatures (140 °C to 170 °C) for 10 min. The final ZnO thin films

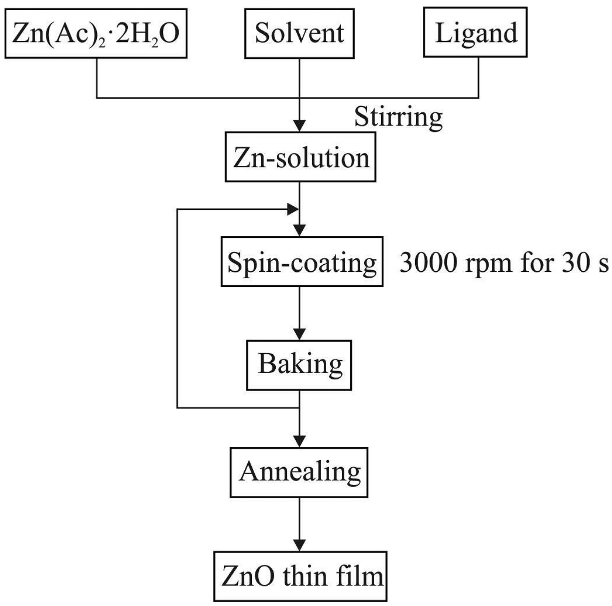

Fig. 1. Process flow chart for preparation of ZnO thin films.

Table 2. The details of solutions.

No. of solution	Ligand	Solvent
1	2-(methylamino)ethanol	Methanol
2		Ethanol
3		n-propanol
4		2-methoxyethanol
5	Monoethanolamine	Methanol
6		Ethanol
7		n-propanol
8		2-methoxyethanol
9	Diethanolamine	Methanol
10		Ethanol
11		n-propanol
12		2-methoxyethanol

were annealed at 400 °C for 60 min. Fig. 2 shows the XRD results of these ZnO thin films. When the ZnO thin films were baked at 140 °C, the (1 0 0), (0 0 2) and (1 0 1) diffraction peaks with low intensity were observed (JCPDS# 36-1451). With increasing the baking temperature, the intensity of (0 0 2) peak became stronger. The highly (0 0 2)-oriented ZnO thin film was obtained using n-propanol at the baking temperature of 150 °C, while the highly (0 0 2)-oriented ZnO thin films were obtained using 2-methoxyethanol at the baking temperature of 150 °C and 160 °C.

Fig. 3 shows the surface morphology of ZnO thin film using Zn-solutions with 2-(methylamino)ethanol and ethanol, baked at 160 °C. The porous wrinkled microstructure was observed and distributed over the whole film surface. Fig. 4 displays the surface microstructure of the ZnO thin films. All samples marked with the dashed line in Fig. 4 show the wrinkled microstructures, as shown in Fig. 3. The ZnO thin films using the n-propanol solvent had the wrinkles at the baking temperature of 140 °C. As the baking temperature increased, the wrinkles disappeared, and the smooth and dense surface was formed. The ZnO thin films obtained using 2-methoxyethanol solvent had smooth and dense surfaces. The grain size of all ZnO thin films almost didn't change with varying the baking temperature.

3.2. Zn-solutions with monoethanolamine and different solvents

The ZnO thin films using the Zn-solutions with monoethanolamine and different solvents were spin-coated on Si(1 0 0) substrates and baked at different temperatures (150 °C to 170 °C) for 10 min. The final ZnO thin films were annealed at 400 °C for 60 min. The XRD results are shown in Fig. 5. All the films show (0 0 2) orientation. With increasing the baking temperature from 150 °C to 170 °C, the intensity of (0 0 2) peaks increased. When the n-propanol and 2-(methaylamino)ethanol were used as solvents and the films were baked at 170 °C, highly (0 0 2)-oriented ZnO thin films were formed.

Fig. 6 shows the surface morphologies of ZnO thin films obtained using the Zn-solutions with monoethanolamine and different solvents. All the ZnO thin films marked with the dashed line in Fig. 6 have the wrinkled network surface, and the other ZnO thin films have dense and smooth surfaces.

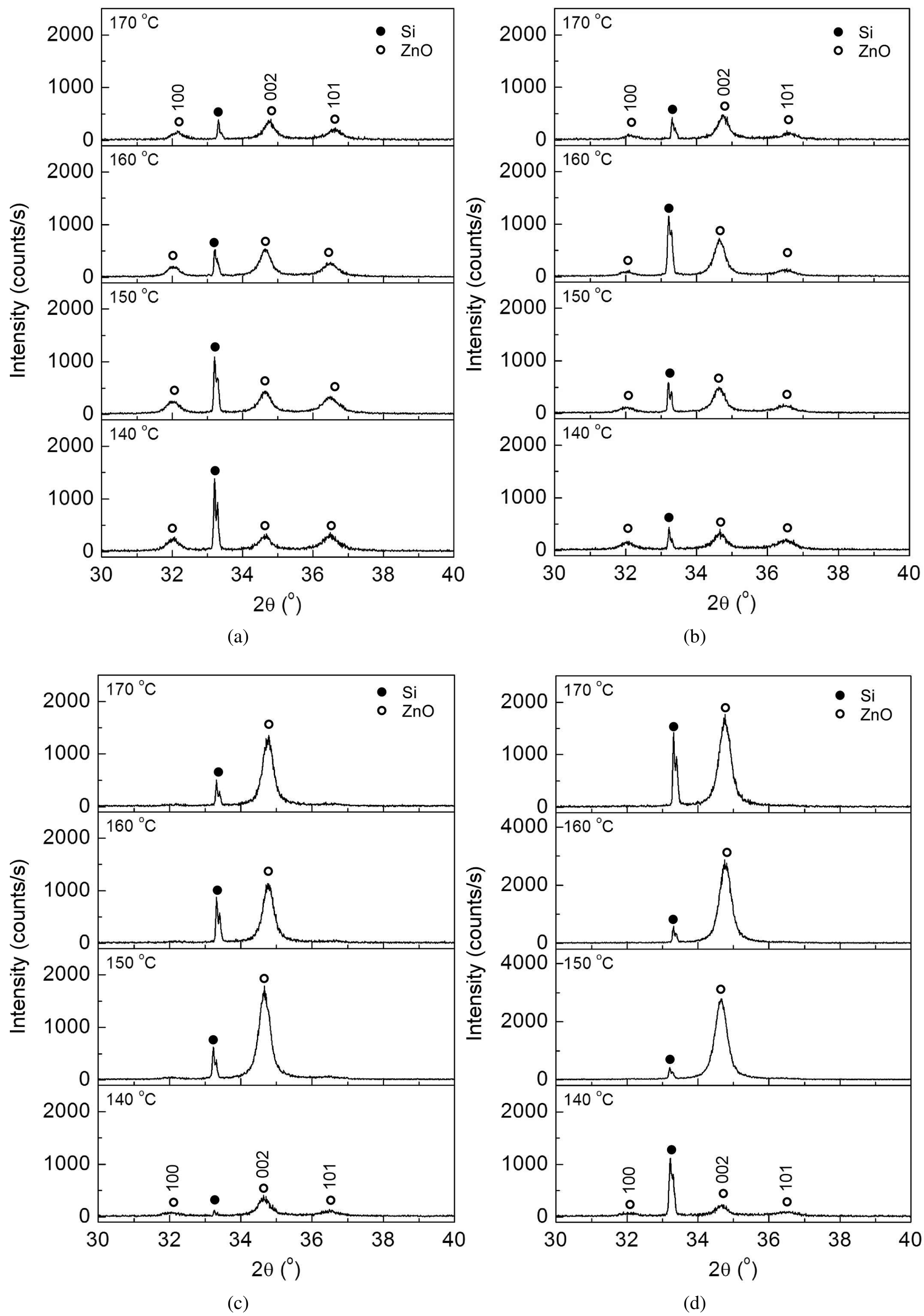

Fig. 2. XRD patterns of ZnO thin films obtained using Zn-solutions with 2-(methylamino)ethanol and different solvents: (a) methanol, (b) ethanol, (c) n-propanol and (d) 2-methoxyethanol baked at different temperatures.

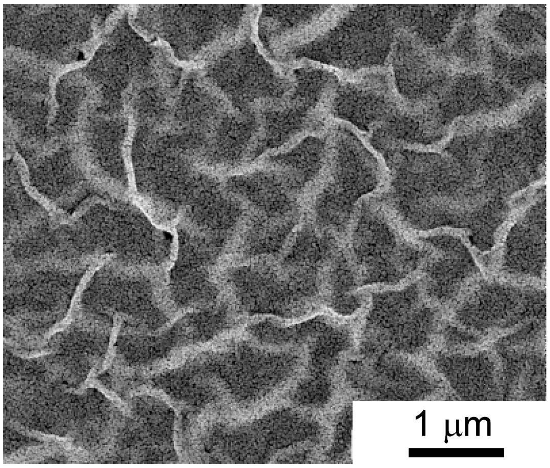

Fig. 3. Surface morphology of ZnO thin film using Zn-solution with 2-(methylamino)ethanol and ethanol baked at 160 °C.

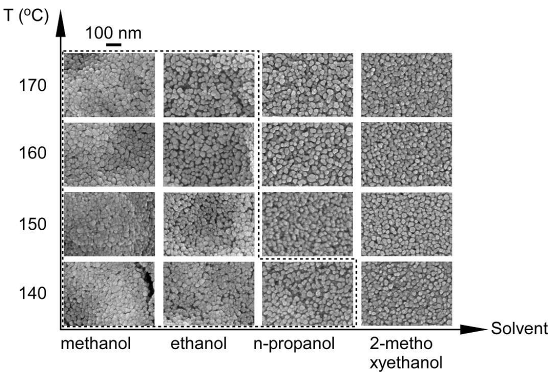

Fig. 4. Surface morphologies of ZnO thin films using Zn-solutions with 2-(methylamino)ethanol and different solvents: (a) methanol, (b) ethanol, (c) n-propanol and (d) 2-methoxyethanol baked at different temperatures.

3.3. Zn-solutions with diethanolamine and different solvents

The ZnO thin films using the Zn-solutions with diethanolamine and different solvents were spin-coated on Si(1 0 0) substrates and baked at different temperatures (260 °C to 270 °C) for 10 min. The final ZnO thin films were annealed at 400 °C for 60 min. Fig. 7 shows the XRD results of the ZnO thin films. The (1 0 0), (0 0 2) and (1 0 1) diffraction peaks with weak intensity are observed, and all the ZnO thin films show random orientation. Their morphologies are displayed in Fig. 8. The ZnO thin films marked with the dashed line in Fig. 8 have wrinkled surface.

4. Discussion

The preparation of ZnO thin film by sol-gel method mainly involved the following processes: (1) The Zn-solution was prepared and then the wetting film was spin-coated on Si substrate; (2) The wetting film was baked for evaporation of the solvent and ligand and decomposition of zinc-organic; (3) The ZnO thin film was annealed to crystallize [18]. The boiling temperature of the solvents and ligands seriously influenced the quality of ZnO thin films in the processes (1) and (2). As methanol was used as a solvent, all prepared ZnO thin films showed porous wrinkled surfaces. Since its boiling temperature is only 64.7 °C, it has already volatilized during the spin-coating process. It was likely to cause the mechanical stress and form the porous wrinkled microstructure, as suggested by Hou et al. [22]. The boiling temperatures of ethanol and 2-(methylamino)ethanol are 78 °C and 159 °C, respectively. As they were used to prepare the Zn-solution, the prepared ZnO thin films also had wrinkled surfaces. When the 2-(methylamino)ethanol was replaced by monoethanolamine or diethanolamine with a higher boiling temperature, the ZnO thin films with smooth surface were obtained by adjusting the baking temperature. For the n-propanol solvent, the ZnO thin films with smooth surface could be formed. As the 2-methoxyethanol was used as a solvent, all prepared ZnO thin films had smooth surfaces. These results indicated that the formation of wrinkled surfaces was related to the evaporation rate of solvents and ligands. As the wetting film was baked, the evaporation rate of solvent and ligand with high boiling temperature was slower than that of the solvent and ligand with low boiling temperature, which was favorable for the relaxation of mechanical stress to obtain the ZnO thin film with smooth surface.

As methanol and ethanol were used as solvents to prepare Zn-solutions with 2-(methylamino)ethanol or monoethanolamine, respectively, the prepared ZnO thin films exhibited

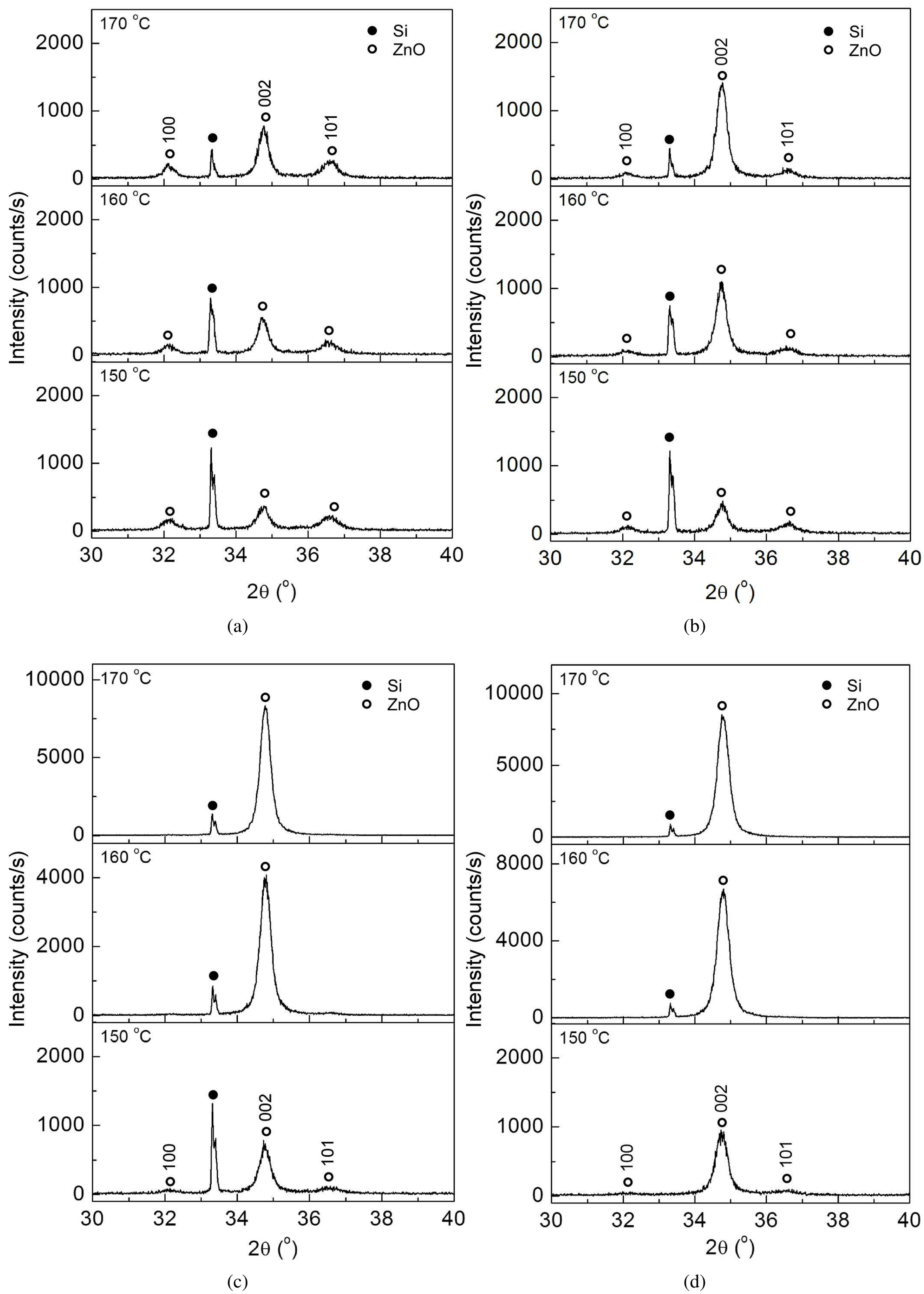

Fig. 5. XRD patterns of ZnO thin films using Zn-solutions with monoethanolamine and different solvents: (a) methanol, (b) ethanol, (c) n-propanol and (d) 2-methoxyethanol baked at different temperatures.

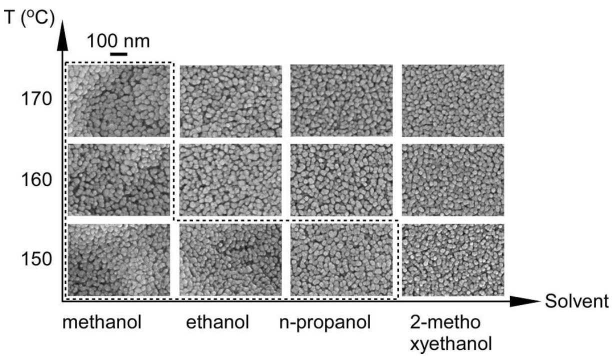

Fig. 6. Surface morphologies of ZnO thin films using Zn-solutions with monoethanolamine and different solvents: (a) methanol, (b) ethanol, (c) n-propanol and (d) 2-methoxyethanol baked at different temperatures.

(0 0 2)-preferred orientation by adjusting the baking temperature. However, other peaks from (1 0 1) and (1 0 0) planes were also observed. Ohyama et al. [14, 15] suggested that the solvents with low boiling temperature disturbed the aligned grain growth in the film, which hindered the highly (0 0 2)-oriented growth of ZnO thin films. When the n-propanol and 2-methoxyethanol were used as solvents to prepare Zn-solutions with 2-(methylamino)ethanol, highly (0 0 2)-oriented ZnO thin films were formed at the baking temperature of 150 °C to 160 °C. The appropriate baking temperature was near the boiling temperature of 2-(methylamino)ethanol (159 °C). As 2-(methylamino)ethanol was replaced with monoethanolamine to prepare Zn-solutions with n-propanol or 2-(methylamino)ethanol, highly (0 0 2)-oriented ZnO thin films were prepared at the baking temperature of 160 °C to 170 °C, which was also near the boiling temperature of monoethanolamine (170 °C). However, as the diethanolamine was used as a ligand to prepare Zn-solutions, the prepared ZnO thin films didn't show a preferred orientation at all, and the intensity of diffraction peaks was very weak. Due to the high boiling temperature of diethanolamine (268 °C), the carbonaceous materials resulting from incomplete combustion of diethanolamine remained in the films when ZnO crystallization occurred, which hindered the preferred grain growth along the (0 0 2) orientation. These results indicated that the boiling temperature of the solvents and ligands seriously affected the (0 0 2)-oriented growth of ZnO thin films.

Guo et al. [18] reported that the ZnO nuclei could be formed by the hydrolysis and/or thermal decomposition of zinc acetate. At low baking temperature, the hydrolysis predominated. At high baking temperature, the thermal decomposition became dominant. In our study, when 2-(methylamino)ethanol and monoethanolamine were used as ligands to prepare ZnO thin films, the baking temperature was low, which was suitable to form the ZnO nuclei by hydrolysis of zinc acetate. When diethanolamine was used as a ligand, the baking temperature was high, which favored the formation of ZnO nuclei by thermal decomposition of zinc acetate. These results indicated that the ZnO nuclei formed by hydrolysis of zinc acetate were favorable for the growth of (0 0 2)-oriented ZnO thin film.

5. Conclusions

The ZnO thin films were prepared by sol-gel method. Their morphologies and oriented growth were seriously affected by the boiling temperature of the solvents and ligands. The solvents and ligands with high boiling temperature were favorable for the relaxation of the mechanical stress to obtain smooth ZnO thin films. As the solvents and ligands with low boiling temperature were used to prepare the Zn-solutions, the prepared ZnO thin films showed (0 0 2) preferred orientation, which indicated that the ZnO nuclei formed by hydrolysis of zinc acetate were favorable for the growth of (0 0 2)-oriented ZnO thin film. As n-propanol, 2-methoxyethanol, 2-(methylamino)ethanol and monoethanolamine were used to prepare the Zn-solutions, highly (0 0 2)-oriented ZnO thin films were formed by adjusting the baking temperature.

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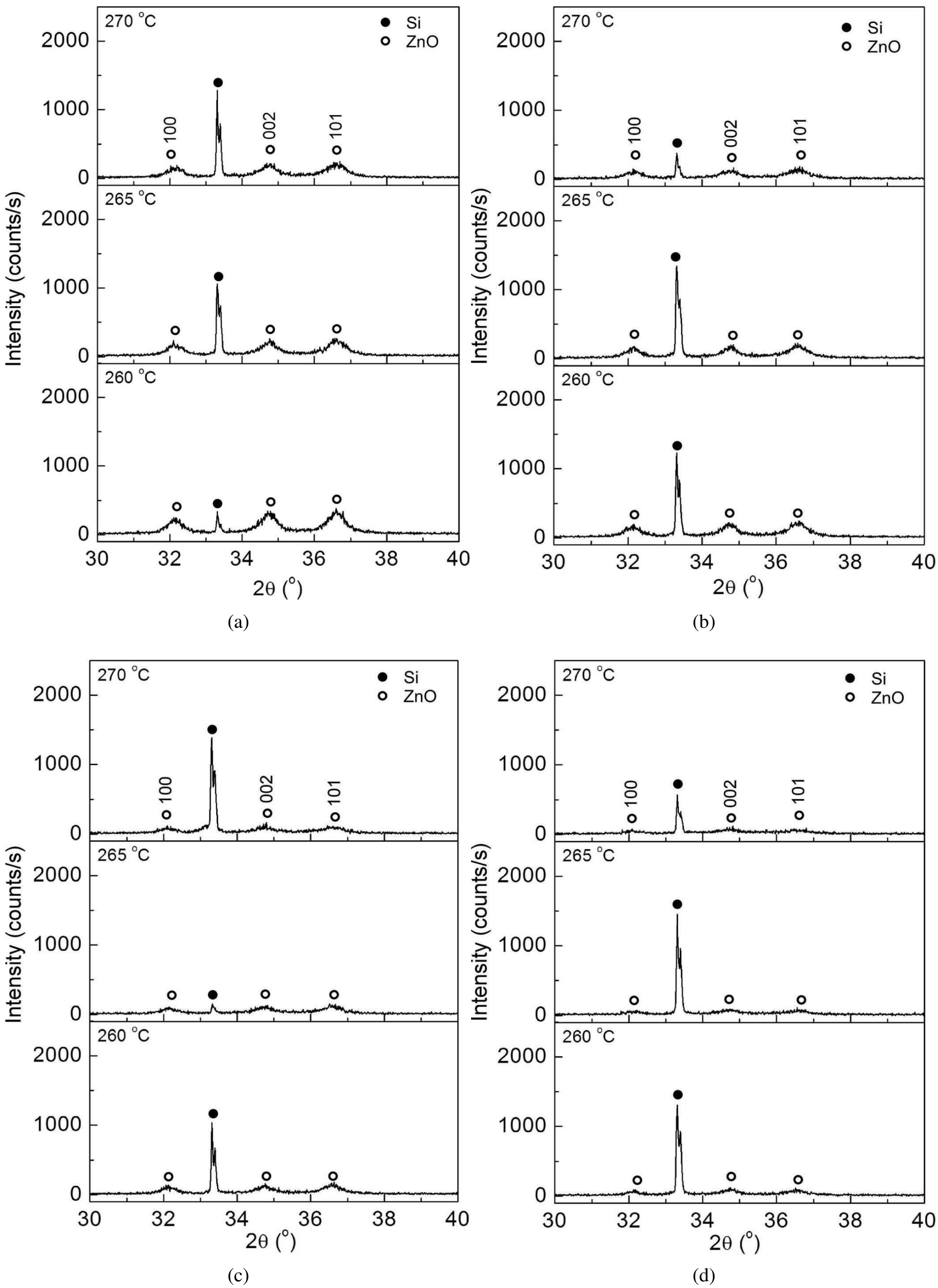

Fig. 7. XRD patterns of ZnO thin films using Zn-solutions with diethanolamine and different solvents: (a) methanol, (b) ethanol, (c) n-propanol and (d) 2-methoxyethanol baked at different temperatures.

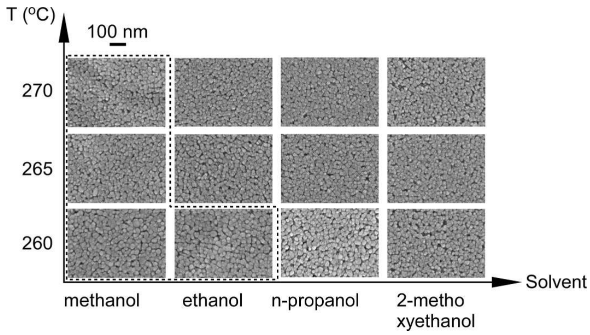

Fig. 8. Surface morphologies of ZnO thin films using Zn-solutions with diethanolamine and different solvents: (a) methanol, (b) ethanol, (c) n-propanol and (d) 2-methoxyethanol baked at different temperatures.

References

[1] Ozgur U., Alivov Y.I., Liu C., Teke A., Reshchikov M.A., Dogan S., Avrutin V., Cho S.J., Morkoc H., *J. Appl. Phys.*, 98 (2005), 041301.

[2] Klingshirn C., *ChemPhysChem*, 8 (2007), 782.

[3] Wang Z.L., *J. Phys.-Condens. Mat.*, 16 (2004), R829.

[4] Ohji K., Toha T., Wasa K., Hayakawa S., *J. Appl. Phys.*, 47 (1976), 1726.

[5] Ellmer K., *J. Phys. D Appl. Phys.*, 34 (2001), 3097.

[6] Hilgendorff M., Spanhel L., Rothenhausler C., Muller G., *J. Electrochem. Soc.*, 145 (1998), 3632.

[7] Hau S.K., Yip H.L., Baek N.S., Zou J., O'Malley K., *Appl. Phys. Lett.*, 92 (2008), 253301.

[8] Jin B.J., Im S., Lee S.Y., *Thin Solid Films*, 366 (2000), 107.

[9] Mirica E., Kowach G., Evans P., Du H., *Cryst. Growth Des.*, 4 (2004), 147.

[10] Shin K.S., Park H.J., Kumar B., Kim K.K., Ihn S.G., Kim S.W., *J. Mater. Chem.*, 21 (2011), 12274.

[11] Govender K., Boyle D.S., Kenway P.B., O'Brien P., *J. Mater. Chem.*, 14 (2014), 2575.

[12] Hu X., Masuda Y., Ohji T., Kato K., *Thin Solid Films*, 518 (2009), 638.

[13] Podlogar M., Richardson J.J., Vengust D., Daneu N., Samardzija Z., Bernik S., Recnik A., *Adv. Funct. Mater.*, 22 (2012), 1.

[14] Ohyama M., Kozuka H., Yoko T., *Thin Solid Films*, 306 (1997), 78.

[15] Ohyama M., Kozuka H., Yoko T., Sakka S., *Jpn. J. Ceram. Soc.*, 104 (1996), 296.

[16] Guo D., Sato K., Hibino S., Takeuchi T., Bessho H., Kato K., *J. Mater. Sci.*, 49 (2014), 4722.

[17] Lee J.H., Ko K.H., Park B.O., *J. Cryst. Growth*, 247 (2003), 119.

[18] Guo D., Sato K., Hibino S., Takeuchi T., Bessho H., Kato K., *Thin Solid Films*, 550 (2014), 250.

[19] Santos A.M.P., Santos E.J.P., *Thin Solid Films*, 516 (2008), 6210.

[20] Segawa H., Sakurai H., Izumi R., Hayashi T., Yano T., Shibata S., *J. Mater. Sci.*, 46 (2011), 3537.

[21] Maiti U.N., Ghosh P.K., Nandy S., Chattopadhyay K.K., *Physica B*, 387 (2007), 103.

[22] Hou Y., Soleimanpour A.M., Jayatissa A.H., *Sensor. Actuat. B-Chem.*, 177 (2013), 761.

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