J Mater Sci (2011) 46:3537–3543
DOI 10.1007/s10853-011-5263-8

Low-temperature crystallization of oriented ZnO film using seed layers prepared by sol–gel method

**Hiroyo Segawa · Hideaki Sakurai · Reiko Izumi ·
Toshiharu Hayashi · Tetsuji Yano ·
Shuichi Shibata**

Received: 9 August 2010 / Accepted: 6 January 2011 / Published online: 21 January 2011

Abstract Transparent zinc oxide (ZnO) films were coated on seed layers prepared by the sol–gel method by chemical solution deposition method. Firstly, seed layers were prepared from zinc acetate and monoethanolamine, 2-methoxyethanol by the sol–gel method on a silicon substrate or a slide glass. Next, the substrate coated with a seed layer was immersed in zinc nitride solution with hexamethylenetetramine, and ZnO films were obtained. The transmittance of the ZnO films depended on the morphology and crystallinity of the seed layers. When the seed layer were dried on a hot plate, the seed layer had flat surface and transparent ZnO film could be obtained on the seed layers dried at temperatures above 200 °C. When the seed layer was prepared from zinc acetate dihydrate dried in a petri dish, the seed layer were smooth without cracks and the transparent ZnO films were obtained at temperature below 100 °C.

Introduction

Zinc oxide (ZnO) is known to be a versatile material with a wide band gap and a high exciton binding energy. In particular, ZnO films have attracted much attention for variety of applications as transparent electrodes for display and so on [1, 2]. Highly oriented film can be used as a transducer for surface acoustic wave devices because of the piezoelectric properties [3]. Besides, the films can find applications in gas sensors [4, 5], solar cells [6], and optical waveguide devices [7]. When ZnO will be coated on plastic substrates, the ZnO films have potential applications for flexible devices.

Chemical or physical deposition method has been employed to fabricate ZnO thin films. Wet chemical process such as the sol–gel method [8–11], the electrodeposition [12], and the electroless deposition [13] has advantages to obtain films at low temperature by low cost. In the case of the sol–gel method, the ZnO films with (002) orientation could be obtained by heating at temperatures above 400 °C, when mixture of zinc acetate, amine and 2-methoxyethanol was used for the precursor [8]. The kinds of amine affected the crystallization of the ZnO gel films and the addition of monoethanolamine (MEA) was most effective in forming the oriented ZnO films [8]. In the sol–gel preparation, both preheating at 200–300 °C and postheating at 500–600 °C were used to obtain ZnO films with highly orientation [9, 11], because the gel films might be relaxed structural by the preheating before crystallization [8]. It is difficult to obtain crystalline ZnO films with highly orientation at temperatures below 300 °C by the sol–gel method. Then, the ZnO films could not be generally fabricated on plastic substrates by the sol–gel method. However, it was reported that ZnO nanoparticles could be obtained from zinc acetate and ethanol at 120 °C under solvothermal condition [14]. This

H. Segawa (✉)
Exploratory Nanomaterials Research Laboratory, National Institute for Materials Science, 1-1 Namiki, Tsukuba-shi, Ibaraki 305-0044, Japan
e-mail: Segawa.Hiroyo@nims.go.jp

H. Sakurai · R. Izumi · T. Hayashi
Central Research Institute, Naka Research Center, Mitsubishi Materials Corporation, 1002-14 Mukohyama, Naka-shi, Ibaraki 311-0102, Japan

T. Yano · S. Shibata
Department of Chemistry and Materials Science, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8550, Japan

suggests that ZnO nucleus can be formed in the sol prepared from zinc acetate at temperatures below 200 °C which corresponded to the temperature to crystallize from zinc acetate to ZnO [15].

On the other hand, ZnO nanorods oriented to *c*-axis have been obtained by the hydrothermal method on the ZnO seed layers which were prepared by the sol–gel method [16–18]. In the hydrothermal method or chemical solution deposition, the formation of ZnO occurs at low temperatures below 100 °C. By the two-step process; preparation seed layers by the sol–gel method and preparation of ZnO rods by the hydrothermal process, dense films with high orientation could be obtained by controlling the concentration of the precursors for the hydrothermal process [19]. In this case, the seed layer was prepared by heating at 200 °C which was too high to prepare on plastic substrates.

In this work, transparent ZnO films were fabricated at the temperature below 100 °C, at which organic substrates can keep the properties without the degradation or colorization, by the chemical solution deposition on seed layers coated by the sol–gel method. The drying temperature of seed layers and concentration of precursors for seed layers were investigated.

Experimental procedures

ZnO seed layers were prepared from zinc acetate precursors containing $Zn(CH_3COO)_2$ (ZnAc; 99.99%, Sigma-Aldrich Co.) or $Zn(CH_3COO)_2 \cdot 2H_2O$ (ZnAcH; 99.9%, Wako Pure Chemical Industries, Ltd.) by the sol–gel method. The ZnAc or ZnAcH was added to 2-methoxyethanol and MEA (Wako Pure Chemical Industries, Ltd.). The molar ratio of ZnAc or ZnAcH and MEA was 1:1 and the zinc concentration for 2-methoxyethanol was set from 0.25 to 1.2 M. The mixture was stirred at 60 °C for 30 min to yield a clear homogeneous solution. After stirring, the solution was spin-coated at 500 rpm for 5 s and 3000 rpm for 30 s on (100) plane of a silicon substrate or a slide glass. After that, the seed layers were dried at different temperature (100–250 °C) (a) on a hot plate for 1 h or (b) in a petri dish by an oven for 1 day.

ZnO films were fabricated on the seed layer by the chemical solution deposition method. 0.1 M $Zn(NO_3)_2$ aqueous solutions were prepared from $Zn(NO_3)_2 \cdot 6H_2O$ (99.9%, Wako Pure Chemical Industries, Ltd.) and hexamethylenetetramine (HMT; Wako Pure Chemical Industries, Ltd.) of which molar ratio was 1:1. The aqueous solution was stirred at room temperature for 30 min to obtain a clear solution. The substrates with the seed layer were immersed in the solution at 80 °C for 3 h. The films were washed by water to remove excessive depositions and were dried by N_2 gas blowing.

The seed layers and films were observed by a scanning electron microscopy (SEM; JEM-2010F, JEOL, Tokyo, Japan). The crystal structures of the samples were characterized using an X-ray diffractometer (XRD; D8 Advance, Bruker AXS GmbH., Tokyo, Japan) with Cu Kα ($\lambda = 15418$ Å) radiation. XRD patterns of seed layers were measured from $2\theta = 10°$ to $40°$ at $0.01°$ intervals by a fixed X-ray incident angle of 0.4°. XRD patterns of ZnO films were recorded to evaluate the orientation from $2\theta = 25°$ to $75°$ at $0.01°$ intervals by θ–2θ scanning technique. UV–VIS spectra of the films on the slide glasses were measured by a spectrometer (V-570, JASCO, Tokyo, Japan) to examine the transmittance.

Results

SEM images of the seed layers on silicon substrates are shown in Fig. 1. Figure 1a–c shows the surface of the seed layers, which were prepared from 1.2 M ZnAc precursor and were dried on the hot plate at (a) 100 °C, (b) 150 °C, and (c) 250 °C for 1 h, respectively. In Fig. 1a, the surface was not homogeneous and was not covered. In Fig. 1b, the seed layer covered whole the surface, however, the seed layer was not flat and was wavy. The seed surface dried on the hot plate at temperatures from 125 to 175 °C showed the same morphology. In Fig. 1c, the surface of the seed layer looks like smooth. The seed layer dried at 200 °C had also similar to that at 250 °C. In the case of drying on a hot plate, the smooth seed layers were obtained by the drying at temperatures above 200 °C which is starting temperature of crystallization of ZnO [15]. Figure 1d–f shows the SEM images of seed layers dried in the petri dish at 100 °C. The seed layers were prepared from precursors with (d) 1.2 M ZnAc, (e) 0.5 M ZnAc, and (f) 0.5 M ZnAcH. Figure 1d-2, e-2, and f-2 shows the 40° images from upper side. In Fig. 1d–f, the all surfaces looked like smooth. This represents that the smooth surface of the seed layers were obtained at 100 °C when the seed layers were dried in the petri dish. In Fig. 1d-1 to f-1, expanded images were inserted, respectively. From the comparison of the expanded images and the 40° images from upper side, cracks were observed in Fig. 1d and e, but cracks were not observed in Fig. 1f. The size of cracks on the surface in Fig. 1d was larger than that in Fig. 1e. The thickness of the seed layer increased slightly with increasing the Zn concentration. In the case of 0.5 M ZnAc, the substrate might not be completely covered with the seed layer. The smoothest surface of the seed layer was obtained when 0.5 M ZnAcH were used as the precursor.

XRD patterns of the seed layers are shown in Fig. 2. The XRD patterns of the seed layers prepared on the hot plate at (a) 100 °C, (b) 125 °C, and (c) 150 °C, respectively, are

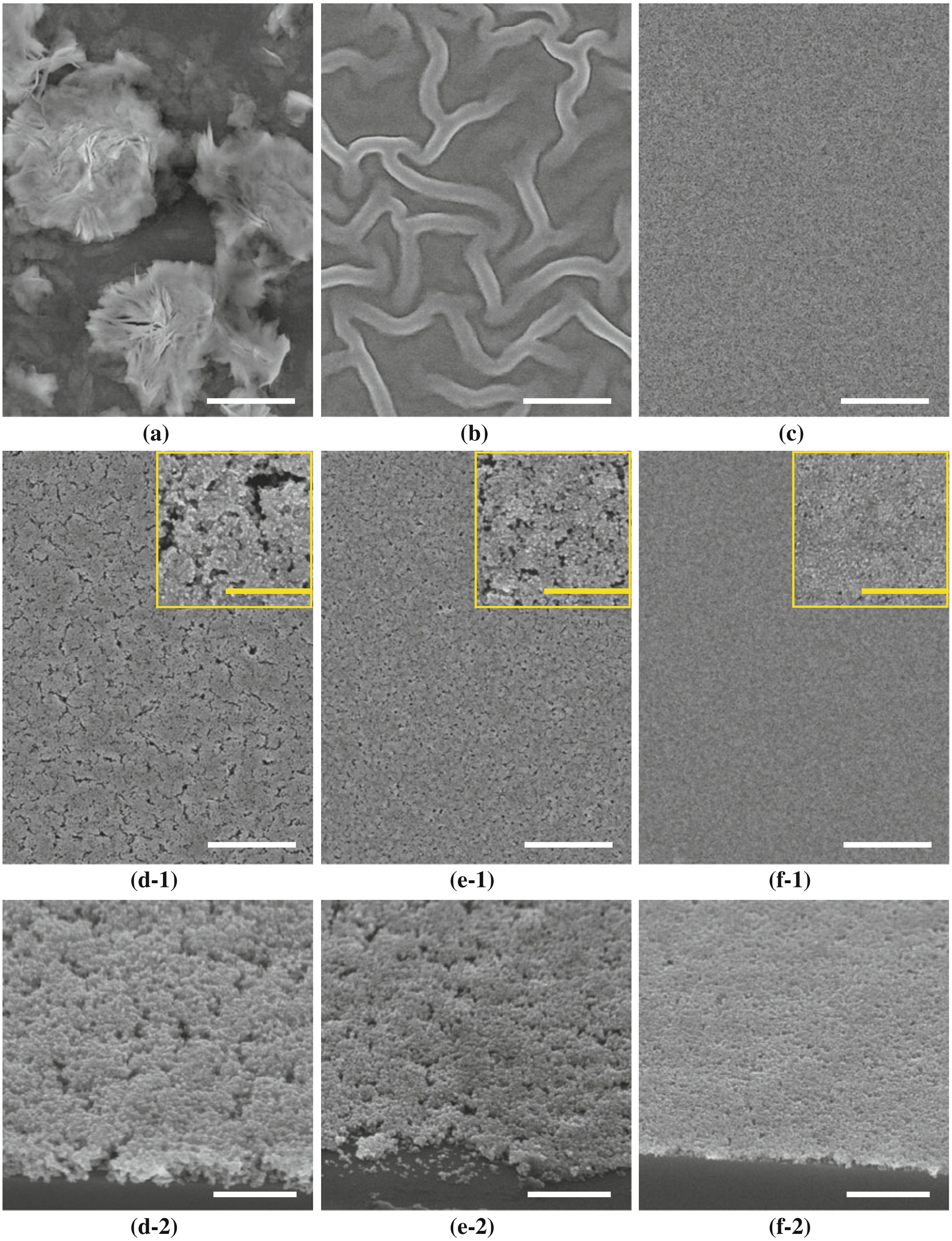

Fig. 1 SEM images of seed layers prepared on the hot plate at **a** 100 °C, **b** 150 °C, **c** 250 °C, and those prepared at 100 °C in a petri dish from precursors **d** 1.2 M ZnAc, **e** 0.5 M ZnAc, and **f** 0.5 M ZnAcH. The *bars* are 2 μm, and the *bars* in the expanded image are 400 nm. **d-2**, **e-2**, and **f-2** show the 40° images from *upper side*

shown. The XRD patterns of the seed layer dried at 100 °C showed peaks assigned to ZnAcH (JCPDS: #33-1464). The peaks became weak with increase of the drying temperature and disappeared at 150 °C. The XRD patterns of seed layers dried at 125 and 150 °C had peaks assigned to ZnO (JCPDS: #36-1451). The XRD patterns of the seed

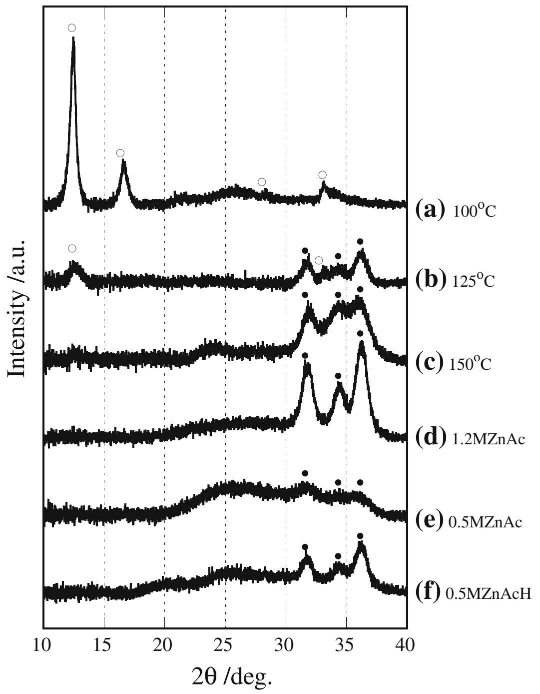

Fig. 2 XRD patterns of seed layers prepared from 1.2 M ZnAc and dried on a hot plate at **a** 100 °C, **b** 125 °C, and **c** 150 °C, and prepared from **d** 1.2 M ZnAc, **e** 0.5 M ZnAc, and **e** 0.5 M ZnAcH dried in a petri dish at 100 °C. *Open circle* ZnAc·$2H_2O$ (JCPDS#33-1464), *filled circle* ZnO (JCPDS#36-1451)

layers dried at 100 °C in the petri dish are shown in Fig. 2d–f. The seed layers were prepared from the precursors with (d) 1.2 M ZnAc, (e) 0.5 M ZnAc, and (f) 0.5 M ZnAcH, respectively. There were not peaks assigned to ZnAcH and the all peaks were assigned to ZnO when the seed layers were dried in the petri dish. The peaks assigned to ZnO of 1.2 M ZnAc and 0.5 M ZnAcH were sharp and the sizes of crystallite calculated from (101) peaks according Scherrer's equation are 88 and 86 Å, respectively. This means that the seed layers prepared from precursors of 1.2 M ZnAc and 0.5 M ZnAcH had high crystallinity.

Figure 3 shows typical SEM images of the surface and cross-section of ZnO films. In Fig. 3a and b, the films were coated on the seed layers which were prepared from 1.2 M ZnAc and were dried on the hot plate at (a) 150 °C and (b) 250 °C, respectively. When the seed layer was dried on the hot plate at 150 °C, the surface of the film was wavy as shown in Fig. 3a-1. From the cross-section image shown in Fig. 3a-2, it was found that the ruggedness was formed because rods were standing vertically on the wavy seed layers. The morphology of the ZnO films hardly depended on the Zn concentration and kinds of Zn sources. Similar films were obtained on the seed layers dried on the hot plate at temperatures from 125 to 175 °C. In Fig. 3b-1, the film surface was flat and hexagonal rods with sides about 200 nm long were close together. The morphology of the ZnO films did not depend on the Zn concentration and the kinds of the Zn sources, when the seed layers were prepared at the temperature above 200 °C. The cross-section showed that the hexagonal rods are standing vertically and densely on the seed layer, of which thickness is about 80 nm, in Fig. 3b-2. Figure 3c shows the image of the film which was prepared from the 0.5 M ZnAcH and dried in the petri dish at 100 °C. The shape of the film looked like similar to that on the seed layer prepared on the hot plate at 250 °C shown in Fig. 3b, and the sides of hexagonal rods were longer than it. The similar morphology was obtained, when the seed layers were prepared by drying in the petri dish at 100 °C, even if the thickness of the seed layers differed slightly. This suggests that the morphology of the ZnO is not affected by the thickness of the seed layer. These represents that the surface shape and orientation of the ZnO films depended on the morphology of the seed layer. The flat ZnO film could be formed on the seed layers dried on the hot plate at temperatures above 200 °C or in the petri dish at 100 °C.

Figure 4 shows transmittance spectra of the ZnO films on the seed layers dried (a) on the hot plate and (b) in the petri dish. In Fig. 4a, the transmittance spectra of the film on the seed layers prepared from 1.2 M ZnAc. When the seed layers were prepared on the hot plate, the films on the seed layers dried at 200 or 250 °C had transmittance of over 80% in the UV–VIS range. The films coated on the seed layers dried at 125 or 150 °C, of which surfaces was wavy, did not show good transmittance and looked like opaque. In Fig. 4b, the transmittance of the film on the seed layer were highly ordered; 0.5 M ZnAcH > 0.5 M ZnAc > 1.2 M ZnAc. The ZnO films on the seed layers prepared from ZnAcH showed higher transmittance than those from ZnAc. Taking the SEM images shown in Fig. 1d–f into account, the transmittance of the film became high, when the surface of the seed layers was smooth.

Figure 5 shows XRD patterns of the ZnO films, which were prepared on the seed layers were dried (a) on the hot plate and (b) in the petri dish. The patterns were normalized for (002) peak except for that of a ZnO film on the seed layer prepared at 150 °C in Fig. 5a. In Fig. 5a, the films on the seed layers dried on the hot plate at 200 or 250 °C showed (002) and (004) ZnO diffraction peaks, indicating that the films were strongly *c*-axis oriented. The films on the seed layers dried at temperatures from 125 to 175 °C showed strong (002) peaks and the other peaks were assigned to ZnO. The product on the seed layer dried at 100 °C did not form a film and the XRD patterns showed peaks assigned to two kinds compounds; ZnO was originated from the aqueous solution and ZnAcH was directly originated from the seed layers. In the case of the drying in

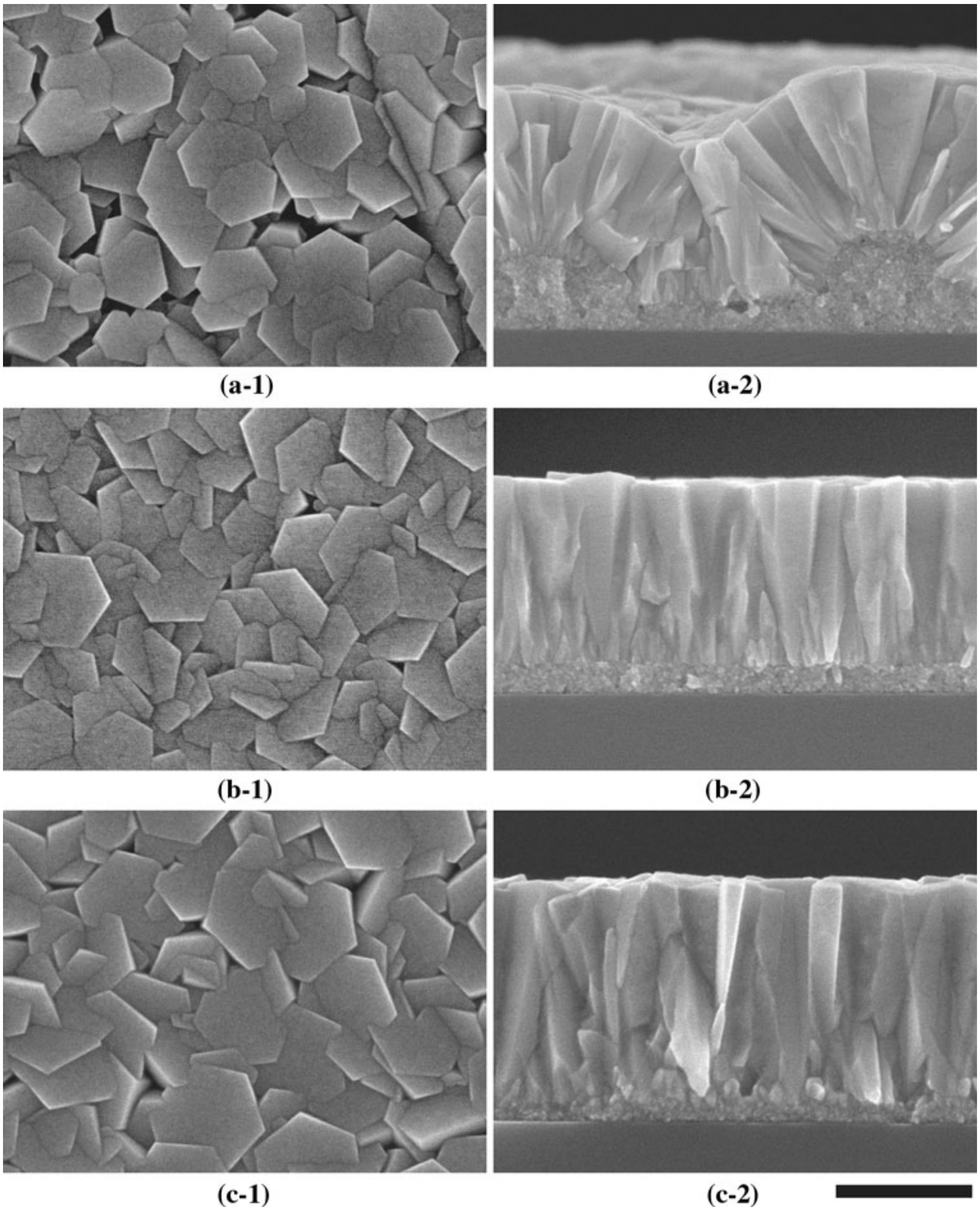

Fig. 3 SEM images of ZnO films coated on the seed layers prepared from 1.2 M ZnAc and dried at **a** 150 °C, **b** 250 °C and prepared from **c** 0.5 M ZnAcH at 100 °C. The *bars* are 400 nm

the petri dish at 100 °C, the XRD patterns had peaks assigned to ZnO. The (002) and (004) diffraction peaks were strong for all patterns, and the other peaks were observed. The peak intensity of the other peaks depended on the kind of the precursors, indicating that the orientation of the ZnO film depended on the precursor and ordered 1.2 M ZnAc $\approx$ 0.5 M ZnAcH > 0.5 M ZnAc.

Discussion

The transparent ZnO films could be successfully obtained at 100 °C which is applicable temperature for preparation on a plastic substrate, when the seed layers prepared from the precursors containing with ZnAcH were dried in the petri dish. In this section, the effects on the formation of transparent ZnO film of drying process and kinds of precursors of seed layers are discussed.

In previous study, the precursors containing ZnAc were considered not to be crystallized at temperatures below 200 °C, because the decomposition temperature of ZnAc is at 260 °C [15], and the boiling temperature of MEA and 2-methoxyethanol is 170 and 125 °C, respectively. It was reported that the crystallization of ZnO in the film prepared from ZnAcH–2-methoxyethnol–MEA solutions began at 200–300 °C [8]. In this study, the crystallization of ZnO

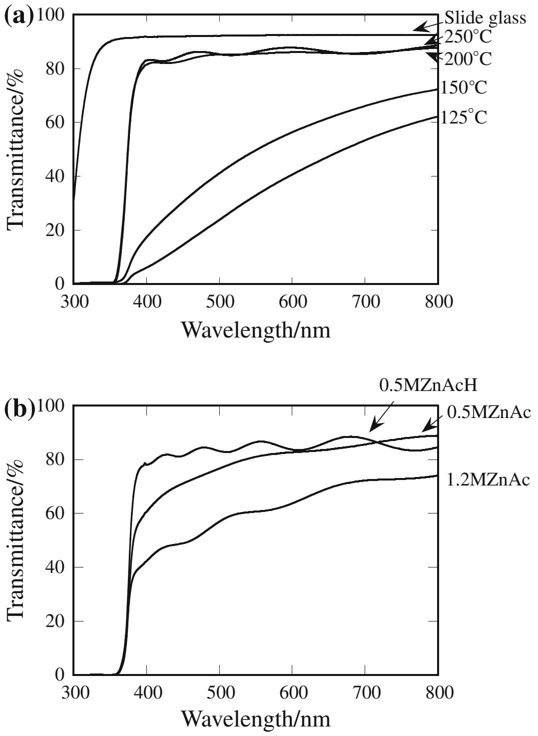

Fig. 4 Transmittance spectra of the ZnO films coated on seed layers dried **a** on the hot plat prepared from 1.2 M ZnAc and **b** in the petri dish at 100 °C

was observed on the hot plate at 125 °C or in the petri dish at 100 °C.

The crystallization of ZnO seed layers occurred at temperatures below 100 °C as shown in Fig. 2. In the sol, the ZnO would be formed by the hydrolysis of ZnAc as follows:

$$\mathrm{ZnAc} + \mathrm{H_2O} \leftrightarrow \mathrm{ZnO} + 2\mathrm{CH_3COOH}. \qquad (1)$$

When the seed layer was dried on the hot plate at 100 °C, ZnAcH was formed as shown in Fig. 2a. This means that the ZnAc would react with water in air, solvent, or absorption water in ZnAc, although H_2O was not contained. At 100 °C, the acetic acid of which boiling point is 118 °C hardly evaporates from the gel film, and ZnO could not be formed in the seed layer. At temperatures above 150 °C, the equilibrium shown in Eq. 1 would be moved to right side due to the evaporation of acetic acid, resulting in that the ZnO seed layers were obtained. In the case of the drying in the petri dish using the oven, the ZnO seed layers were fabricated at even 100 °C. The acetic acid would be dried gradually according Eq. 1 during the holding at 100 °C for 1 day in the petri dish, although the boiling temperature is above 100 °C.

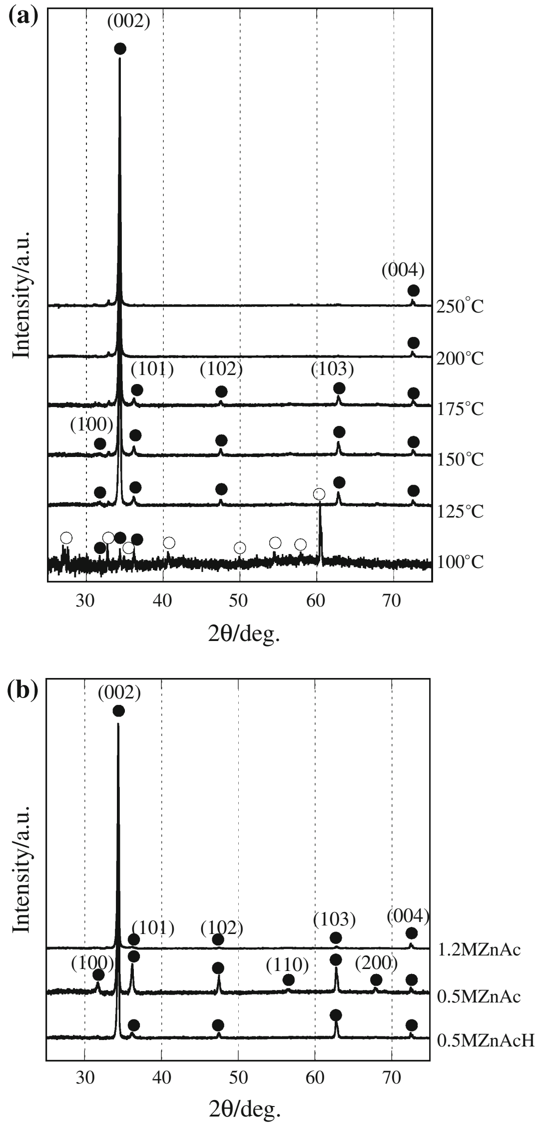

Fig. 5 XRD patterns of ZnO films coated on seed layers dried **a** on the hot plat prepared from 1.2 M ZnAc and **b** in the petri dish at 100 °C. *Filled circle* ZnO (JCPDS#36-1451)

The flat seed layers could not be obtained by drying on the hot plate at temperatures below 175 °C but obtained by drying in the petri dish at 100 °C. In comparison with the drying process, the evaporation speed of the solvent on the hot plate was faster than that in the petri dish at same temperature. During the drying of the films, the stress would be generated in the film due to the difference in the thermal expansion between the substrate and the gel film. The stress in the film dried on the hot plate was larger than that in the petri dish because of the difference of the evaporation speed. Thus, the wave was formed on the seed layers dried on the hot plate due to shrinkage of the surface of films. In the case of the drying in the petri dish, the evaporation of the seed layer was very slow and the stress was relaxed during the drying, resulting in that the flat seed layers could be obtained at 100 °C.

In the case of drying in the petri dish, the transmittance of ZnO films on the seed layer prepared from ZnAcH were higher than those from ZnAc. It was found that the transparent ZnO film can be obtained when the seed layers are flat and high crystallinity. From the SEM image of the seed layers as shown in Fig. 1, the crack size of seed layer prepared from ZnAc dried in the petri dish was larger than that from ZnAcH. The transmittance of the ZnO films increased with decrease of the crack size. In the case of ZnAc, the ZnO films on the seed layer prepared from 0.5 M ZnAc had more crystals with different types from (002) than those from the others as shown in Fig. 5b. Taking the morphology on the surfaces into account, the orientation of the ZnO films might be affected to the complete coverage by the seed layers. The transmittance and orientation of the ZnO film would be improved when the seed layers had good crystallinity without cracks with submicrometer size, which corresponded to the wavelength in the range of UV–VIS.

These results represented that the transparent and high oriented ZnO films could be coated at temperatures below 100 °C, at which ZnO were coated even on plastic substrate such as a polypropylene, under controlling the morphology and the crystallinity of seed layer.

Conclusions

In summary, highly oriented ZnO films were fabricated by the chemical solution deposition at temperatures below 100 °C. Firstly, seed layers were prepared from zinc acetate by the sol–gel method, and dried. Next, the seed layers were immersed in the zinc nitrate aqueous solution. When the seed layers were obtained from the precursors contained with zinc acetate dehydrate and dried in the petri dish at 100 °C, the seed layers were flat and the transparent ZnO films with (002) highly ordered were obtained on the seed layer. By the controlling the precursor and drying process of the seed layer, ZnO transparent film could be obtained at the temperature below 100 °C. The transparent ZnO films coated on plastic substrate will be applicable for flexible devices such as displays.

References

1. Chen M, Pei ZL, Sun C, Gong J, Huang RF, Wen LS (2001) Mater Sci Eng B 85:212
2. Kruz A, Brakecha K, Puetz J, Aegerter MA (2006) Thin Solid Films 502:212
3. Srivastava JK, Agarwal L, Bhattacharyya AB (1989) Electrochem Soc 136:3414
4. Xiangfeng C, Dongli J, Djurišic AB, Leung YH (2005) Chem Phys Lett 401:426
5. Agarwal G, Speyer RF (1998) J Electrochem Soc 145:2920
6. Hara K, Horiguchi T, Kinoshita T, Sayama K, Sugihara H, Arakawa H (2000) Solar Energy Mater Solar Cells 64:115
7. Mais N, Reithmaier JP, Forchel A, Kohls M, Spanhel L, Müller G (1999) Appl Phys Lett 75:2005
8. Ohyama M, Kozuka H, Yoko T, Sakka S (1996) Ceram Soc Jpn 104:296
9. Ohyama M, Kozuka H, Yoko T (1997) Thin Solid Films 306:78
10. Li H, Wang J, Liu H, Yang C, Xu H, Li X, Cui H (2004) Vacuum 77:57
11. Kim YS, Tai WP, Shu SJ (2005) Thin Solid Films 491:153
12. Pauporté T, Lincot D (2000) Electrochim Acta 45:3345
13. Raviendra D, Sharma JK (1985) J Appl Phys 58:838
14. Du H, Yuan F, Huang S, Li J, Zhu Y (2004) Chem Lett 33:770
15. Liu TQ, Sakurai O, Mizutani N, Kato M (1986) J Mater Sci 21:3698. doi:10.1007/BF02403024
16. Vayssaieres L, Keis K, Lindquist S, Hagfeldt A (2001) J Phys Chem B 105:3350
17. Vayssieres L (2003) Adv Mater 15:464
18. Hirano S, Takeuchi N, Shimada S, Masuya K, Ibe K, Tsunaka H, Kuwabara M (2005) J Appl Phys 98:094305
19. Hirano S, Masuya K, Kuwabara M (2004) J Phys Chem B 108:4576