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Effect of bottom layer thickness on crystalline quality and surface roughness of ZnO film prepared by multi-step deposition process

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Multi-layered ZnO thin films were prepared through a multi-step deposition process on (0001) sapphire substrates by radio-frequency magnetron sputtering method. For comparison, single-layered ZnO films were fabricated by single-step deposition process. The multi-layered ZnO films consisted of three layers: the bottom layer, the intermediate layer and the top layer. The crystalline quality and surface roughness of the multi-layered films were superior to those of the single-layered films. The effect of bottom layer thickness on the crystalline quality and surface roughness of ZnO film was also studied. As the bottom layer thickness decreased, the intensity of (002) peak in X-ray diffraction spectrum increased and a full-width at half maximum (FWHM) of the (002) peak became narrower, indicating the bottom layer thickness had a significant effect on the crystalline quality. The surface smoothness of the film was also improved with decreasing the bottom layer thickness. The optical bandgap was in substantial agreement with that of bulk ZnO with decreased bottom layer thickness.

Key words: ZnO thin film, RF sputtering, Multistep deposition, Bottom layer thickness, Crystalline quality, Surface smoothness.

Introduction

ZnO is an attractive wide band gap semiconductor material with its band gap of 3.3 eV and large exciton binding energy of 60 meV at room temperature. Its wide band gap makes it suitable for optoelectronic devices such as ultraviolet light emitting diodes and laser diodes [1, 2]. Recently, ZnO has attracted much attention for use as a transparent conductive film for the electrode in solar cells and displays due to its n-type characteristic [3, 4].

The optical and electronic properties of ZnO films have been shown to be highly sensitive to the crystalline quality of the films. Therefore, the growth of ZnO film with high crystalline quality and smooth surface is necessary for the high optoelectronic performance of device. So far, much effort has been made to obtain ZnO films with high crystalline quality. It has been recently reported that the crystalline quality of ZnO films was improved by employing a ZnO buffer layer, which was grown at low temperatures in the range of 300 - 500 °C on Si and sapphire substrates [5-7].

On the other hand, recent studies have shown that the crystalline quality and surface flatness of thin films were improved by enhancing the interlayer transport of adatoms during deposition. Efficient interlayer mass transport leads to two dimensional growth, resulting in the improvement of the crystalline quality and surface flatness of thin films. For efficient interlayer mass transport, atoms deposited on top of islands have to be able to descend from the islands, which can be achieved by increasing the adatom mobility on top of the islands. To realize this concept, we changed the substrate temperature during deposition. The adatom mobility would increase gradually with a gradual increase in the temperature during deposition, inducing the enhancement of adatom mobility.

In this paper, we report the effect of a multi-step deposition process, in which each layer was grown at progressively higher temperatures, on the crystalline quality and surface smoothness of ZnO film. The effect of the bottom layer thickness on the crystalline quality and optical properties of ZnO film is also discussed.

Radio-frequency (RF) magnetron sputtering has advantages in terms of large area deposition and low cost. Thus RF magnetron sputtering is widely used in industry for the deposition of various films. A number of studies have been also performed on ZnO films deposited by RF magnetron sputtering [7-10]. Considering the application in industry, RF magnetron sputtering was employed to deposit ZnO films in this study.

Experimental

Three series of ZnO films were prepared through temperature changed multi-step deposition process. The deposition of the multi-layered ZnO films was carried out in three stages. Consequently, the ZnO films are composed of three ZnO layers: the bottom layer, the intermediate layer and the top layer. Each

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Table 1. Deposition procedure of the samples prepared by single-step and multi-step deposition process

sample	deposition procedure
a	400 °C, 200 mm
b	500 °C, 200 mm
c	600 °C, 200 mm
d	400 °C, 20 mm / 500 °C, 90 mm / 600 °C, 90 mm
e	400 °C, 40 mm / 500 °C, 80 mm / 600 °C, 80 mm
f	400 °C, 60 mm / 500 °C, 70 mm / 600 °C, 70 mm

layer was deposited at 400 °C, 500 °C and 600 °C, respectively. For comparison, three other series of ZnO films were fabricated by conventional single-step deposition process at constant temperatures of 400 °C, 500 °C, and 600 °C, respectively. In order to investigate the effect of the bottom layer thickness on the crystalline quality and surface smoothness of the ZnO film, the bottom layer thickness was changed in the range of 20 - 60 nm. The total film thickness of all the samples was estimated to be about 200 nm by a stylus profiler. The deposition procedure of each sample is summarized in Table 1. Samples (a), (b), and (c) were prepared with a thickness of 200 nm by a single-step process at constant temperatures of 400 °C, 500 °C, and 600 °C, respectively. Samples (d), (e), and (f) consisted of three layers. In the case of sample (d), the thicknesses of the bottom layer, the intermediate layer and the top layer were 20 nm, 90 nm and 90 nm, respectively. Sample (e) was composed of a 40 nm thick bottom layer, an 80 nm thick intermediate layer and an 80 nm thick top layer. The thicknesses of the bottom layer, intermediate layer and the top layer in sample (f) were 60 nm, 70 nm and 70 nm, respectively.

Sapphire with (0001) orientation and sintered ZnO (99.99%) were used as a substrate and a target, respectively. The substrates were cleaned ultrasonically in acetone and ethanol, and dried by dry nitrogen before deposition. The sputtering chamber was evacuated by turbo-molecular pump to a background pressure of less than 5.0×10^{-6} torr. During the deposition, the chamber pressure, sputtering power and target-substrate distance were fixed to be 2.5×10^{-3} torr, 150 W and 10 cm, respectively. Ar was used as a gas for sputtering.

The crystalline structures of the ZnO films were investigated by X-ray diffractometer using Cu-K_{α} radiation operated at 40 kV and 30 mA. The surface morphology of the films was observed by atomic force microscopy (AFM). AFM images were obtained in air in tapping mode. A sharpened Si cantilever with a spring constant of 42 N/m and a resonance frequency of 250 - 360 kHz was used. The AFM measurement was performed at a scan rate of 1 Hz. Optical transmittance was measured by a UV-vis-NIR spectrophotometer in the wavelength range of 200 - 600 nm, from which the optical band gap of the films were determined.

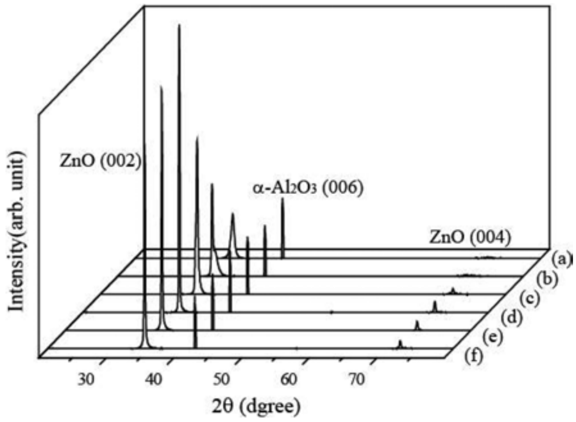

Fig. 1. XRD patterns of the ZnO films prepared by single-step and multi-step deposition process with different deposition procedures.

Results and Discussion

Fig. 1 shows the XRD patterns of the samples. The patterns can be well indexed to the hexagonal wurtzite structure of ZnO. Only ZnO (002) and (004) diffraction peaks were observed in the spectrum of the samples, which indicates the ZnO films were grown with c-axis orientation perpendicular to the substrate. The intensity of the (002) peak for the three-layered ZnO films is stronger than that for single-layered ZnO films, which means that the multi-step deposition process is very effective for improving in crystalline quality of ZnO thin film. On the other hand, for the three-layered ZnO films, the intensity of the (002) peak in the XRD spectrum increases with the decrease in the bottom layer thickness, indicating that the bottom layer thickness affects the crystallization of ZnO film. The strongest intensity of the (002) peak is observed for the sample with the 20 nm thick bottom layer.

Fig. 2 shows the FWHMs of the (002) diffraction peaks for the samples. The FWHMs of samples (a), (b), (c), (d), (e) and (f) were found to be 0.58 °, 0.28 °, 0.28 °, 0.18 °, 0.22 ° and 0.24 ° respectively. For the single-layered ZnO films, the FWHM value became smaller with increasing the deposition temperature. Comparing the single-layered ZnO films with the three-layered ZnO films, the FWHMs of the three-layered ZnO films were smaller than those of the single-layered ZnO films. In addition, for three-layered ZnO films, the FWHM was getting smaller as the bottom layer thickness decreased. The smallest FWHM was obtained for sample 1 with the bottom thickness of 20 nm. The smaller FWHM indicates that the film possesses the superior crystallinity. The FWHM results show that the ZnO film with a 20 nm thick bottom layer has the best crystalline quality. From the XRD result, it is concluded that the crystalline quality of ZnO film is significantly influenced by the bottom layer thickness. On the other hand, for the single-layered ZnO films, the (002) diffraction peaks consist

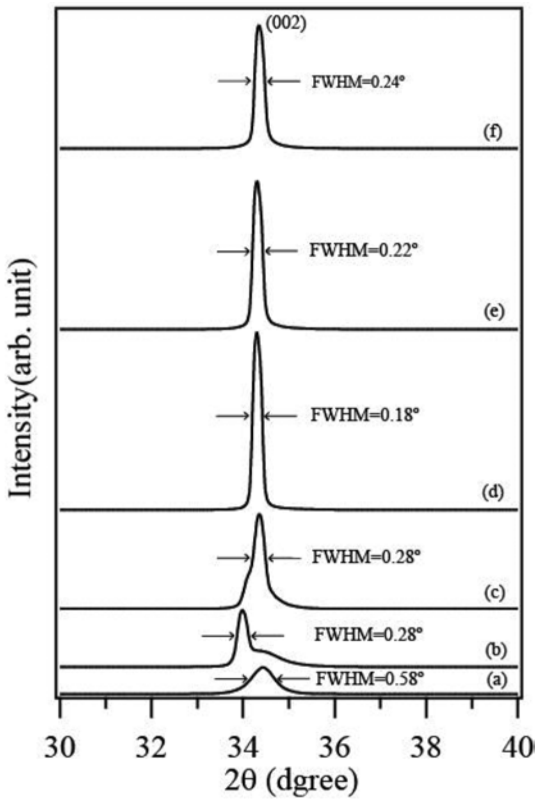

Fig. 2. FWHMs of the ZnO film prepared by single-step and multi-step deposition process with different deposition procedures.

of two superimposed peaks. The (002) peak shape consisting of two or more superimposed peaks with an asymmetric distribution has usually been observed for ZnO films with poor crystallinity [11, 12]. Thus the shape of the (002) peak exhibits that the single-layered ZnO films have poor crystallinity. The single (002) diffraction peaks with a symmetric distribution are observed in the XRD patterns of the three-layered ZnO films, indicating that the ZnO films have a high degree of crystallinity.

Fundamentally, when an atom adsorbs onto the growing film surface, the atom diffuses randomly on the surface. When the atom diffuses to an energetically favorable site, the atom will be incorporated into the site. Ledge and kink sites are considered to be the energetically favorable sites. The ledge and kink sites exist at the edges of islands. On the other hand, as the island size decreases, the atoms landing on the islands may jump easily onto the lower layer and are incorporated into energetically favorable sites such as ledges and kinks existing at the edges of the islands [13, 14], resulting in the growth of ZnO film with high crystalline quality and surface smoothness. Accordingly, by increasing the bottom layer thickness, the island size increases due to the grain coalescence, resulting in the deterioration in the crystalline quality and the surface smoothness.

Fig. 3 shows the AFM images of samples (a), (c), (d), (e) and (f). The AFM images were taken on an area of 1×1 m^2. The root-mean-square (RMS) roughness of samples (a), (c), (d), (e) and (f) are 1.20, 0.73, 0.43, 0.48, 1.10 nm, respectively. For the single-layered ZnO films, the surface smoothness of the ZnO films was improved with the increased deposition temperature, which was due to the enhancement in the mobility of surface atoms at high substrate temperature [15]. In addition, the surface smoothness of the ZnO films was significantly improved by employing the multi-step deposition process, and further improved by decreasing the bottom layer thickness in the multi-step deposition process. Sample (d) with the smallest bottom thickness of 20 nm had the smoothest surface. The surface roughness of ZnO film increased with increasing bottom layer thickness, which is explained in terms of an island-size-dependence on interlayer diffusion. As the

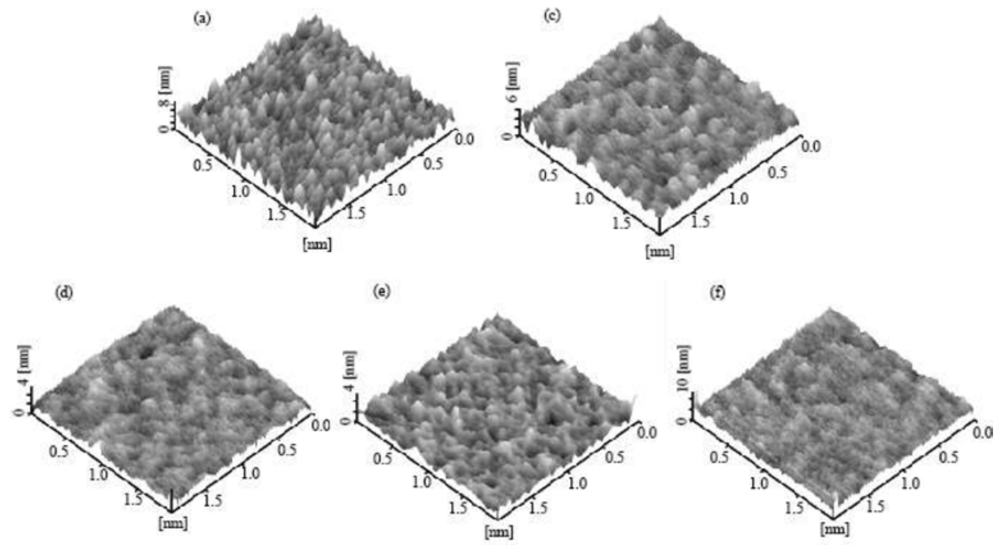

Fig. 3. AFM images of the ZnO films prepared by single-step and multi-step deposition process with different deposition procedures.

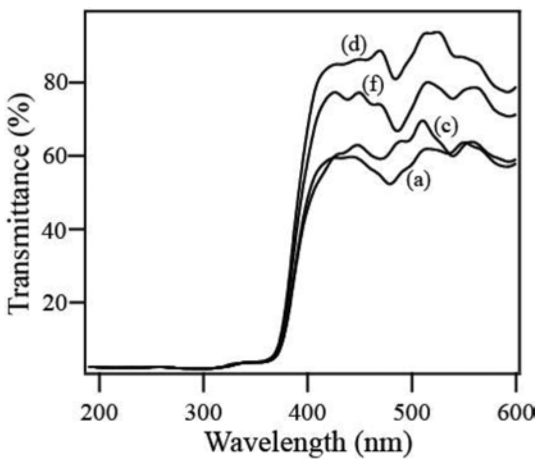

Fig. 4. Optical transmittance spectra of the ZnO films prepared by single-step and multi-step deposition process with different deposition procedures.

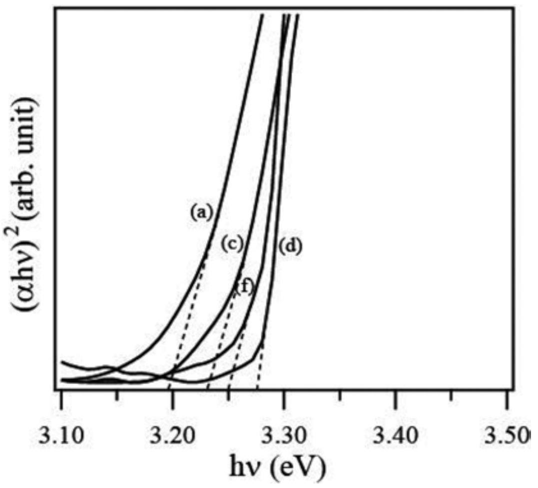

Fig. 5. Plots of $(\alpha h\nu)^2$ vs $h\nu$ of the ZnO films prepared by single-step and multi-step deposition process with different deposition procedures.

bottom layer thickness increased, the island size increased due to the grain coalescence. Then the atoms absorbed onto the islands could not easily jump off the islands, leading to the formation of new islands on the existing islands [16, 17]. This resulted in the increase in the surface roughness.

Fig. 4 shows the optical transmittance measured for samples (a), (c), (d) and (f) as a function of wavelength in the 200 - 600 nm range. The transmittance of the multi-layered ZnO films is higher than that of the single-layered ZnO films. The multi-layered ZnO films showed an average optical transmittance of over 70%, while the single-layered ZnO films showed an average transmittance of approximately 60% in the visual region. Moreover, for the multi-layered ZnO films, the transmittance increased to 80% with decreasing bottom thickness, which is also indicative of the improved crystalline quality.

The optical band gaps of the samples are shown in Fig. 5. The band gaps were estimated to be 3.20 eV, 3.23 eV, 3.28 eV and 3.25 eV for samples (a), (c), (d) and (f). The band gaps were calculated by plotting $(\alpha h\nu)^2$ vs $h\nu$ from the transmittance spectra using an $\alpha h\nu = A(h\nu\text{-}Eg)^{1/2}$ relationship, in which is the absorption coefficient and $h\nu$ is the photon energy, and extrapolating the straight line portion of this plot to the energy axis [18]. The band gap of sample (d) is very close to that of bulk ZnO (3.3 eV) at room temperature, which suggests that the sample (d) has the highest crystalline quality.

Conclusions

Compared to ZnO films deposited by single-step deposition process, ZnO film with higher crystalline quality and smoother surface was fabricated by using a multi-step deposition process. For the multi-layered ZnO films, the bottom layer thickness has an important effect on the crystalline quality and the surface roughness of the film. As the bottom layer thickness decreased, the intensity of the (002) peak in the XRD spectrum increased and the FWHM of the (002) peak decreased, indicating the improvement in the crystalline quality of the film. The surface roughness of the film was also improved with the decrease in the bottom layer thickness.

References

1. Z.K. Tang, G.K.L Wang, P. Yu, M. Kawasaki, A. Ohtomo, H. Koinuma, Y. Segawa, Appl. Phys. Lett. 72 (1998) 3270.
2. F.K. Shan, G.X. Liu, W.J. Lee, G.H. Lee, I.S. Kim, B.C. Shin, Appl. Phys. Lett. 86 (2005) 221910.
3. D. Kim, I. Yun, H. Kim, Curr. Appl. Phys. 10 (2010) S459.
4. Y.R. Park, E.K. Kim, D. Jung, T.S. Park, Y. S. Kim, Appl. Surf. Sci. 254 (2008) 2250.
5. V. Khranovskyy, R. Minikayev, S. Trushkin, G. Lashkarev, V. Lazorenko, U. Grossner, W. Paszkowicz, A. Suchocki, B.G. Svensson, R. Yakimova, J. Cryst. Growth 308 (2007) 93.
6. J. Zhao, L. Hu, Mater. Sci. Semicond. Process. 12 (2009) 233.
7. S.H. Jeong, I.S. Kim, S.S. Kim, J.K. Kim, B.T. Lee, J. Cryst. Growth 264 (2004) 110.
8. J.B. You, X.W. Zhang, Y.M. Fan, Z.G. Yin, P.F. Cai, N.F. Chen, Appl. Surf. Sci. 255 (2009) 5876.
9. D. Sato, Y. Kashiwaba, K. Haga, H. Watanabe, B.P. Zhang, Y. Segawa, Vacuum 74 (2004) 601.
10. C. Lee, A. Park, Y.J. Cho, W.I. Lee, H.W. Kim, Vacuum 82 (2008) 1364.
11. S.L. King, J.G.E. Gardeniers, I.W. Boyd, Appl. Surf. Sci. 96-98 (1996) 811.
12. H.K. Kim, M. Mathur, J. Elect. Mater. 22 (1993) 267.
13. G. Ehrlich, F. G. Hudda, J. Chem. Phys. 37 (1996) 1039.
14. R.L. Schwoebel, E.J. Shipsey, J. Appl. Phys. 37 (1966) 3682.
15. W. Water, S.Y. Chu, Mater. Lett. 55 (2002) 67.
16. G.H. Lee, B.C. Shin, B.H. Min, Mater. Sci. Eng. B 95 (2002) 137.
17. R. Kunkel, B. Poelsema, L.K. Verheij, G. Comsa, Phys. Rev. Lett. 65 (1990) 733.
18. M. Caglar, Y. Caglar, S. Aksoy, S. Ilican, Appl. Surf. Sci. 256 (2010) 4966.