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Effect of homo-buffer layers on the optical properties of ZnO thin films grown by pulsed laser deposition on Si (100)

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Abstract The influence of homo-buffer layers deposited at high-temperature (HT) or low-temperature (LT) and post-annealing process on the structure and photoluminescence properties of ZnO films grown by pulsed laser deposition on Si (100) was studied by X-ray diffraction (XRD), atomic force microscope (AFM) and photoluminescence spectrum (PL). It is found that the optical property of the films can be improved greatly because the stress between the films and the substrates could be reduced by using buffer layers. By using LT buffer layer, high-quality ZnO films with only one strong ultraviolet emission (UV) can be obtained, but the post-annealing process in air will make the optical property of the film deteriorate.

1 Introduction

ZnO-based material is a good candidate for optoelectronic devices due to its large band-gap of 3.3 eV at room temperature and large excitonic binding energy of 60 meV. It is one of the most promising materials for transparent and conductive oxide thin films, e.g., it is a candidate of optoelectronic devices for the ultraviolet (UV) region [1–3]. UV light sources have many important applications, such as high-density optical recording, light sources for phosphors excitation, medical equipment, and treatments of environmental pollution materials [4, 5].

As it well known, the room temperature photoluminescence spectra of ZnO thin films always include near-band-edge emission (NBE) and deep-level emission, and the deep-level emissions are related to defects, such as oxygen deficiency and zinc interstitials. Many efforts have been devoted to improve the quality of the ZnO thin films, so the intrinsic NBE emission can be enhanced and the deep-level emission can be suppressed. Now, the common substrates used to grow ZnO thin films are sapphire with a- and c-plane orientation, GaN, glass, Si and so on. Among all, silicon is a promising substrate because it is cheap, conductive and easy to cleave. In particular, it can be integrated with advanced Si microelectronics technology, so it is valuable to grow ZnO thin films on Si substrate. But the crystal structure of silicon is cubic and it has large lattice and thermal expansion coefficient mismatch with ZnO films, which will cause the direct growth of ZnO films with only one intrinsic photoluminescence emission to be a difficult task.

Amano et al. [6] and Nakamura [7] had suggested that the quality of the films could be improved greatly by prior deposition of a buffer layer on the substrate. Attempts have been made to utilize different buffer layers, such as GaN, Zn, ZnS, CaF_2, and ZnO [8–15], but the homo ZnO buffer layer is better than others. On the same time, the choice and control of the experimental conditions are also important to obtain high-quality ZnO thin films, because the stress in the film will influence its density of dislocations and optical properties. In this paper, we studied the influence of a low-temperature (LT) homo-buffer layer and a high-temperature (HT) homo-buffer layer and post-annealing process on the structure and photoluminescence properties of ZnO films grown by pulsed laser deposition (PLD) on Si (100) substrates.

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2 Experimental procedure

A KrF excimer laser operating at 248 nm was used for ablation of a commercially available ZnO (99.99% purity) target. The laser energy and repetition rate were 150 mJ and 5 Hz, respectively. In this study, polished Si (100) single-crystal substrates were used and ultrasonic cleaned in acetone and ethanol without etched in HF. The chamber was first turbopumped to a base pressure of 10^{-7} Torr, and then oxygen gas was backfilled into the chamber through a mass flow controller. The chamber was kept at a constant pressure of 200 mTorr during all the deposition process and the distance between the target and the substrate was kept at 5 cm. The buffer layer temperature (T_b) was set at 300 or 550 °C and the deposition time is 3 min. After deposition of the buffer layers, the subsequent main ZnO layers were deposited at the deposition temperature (T_f) of 550 or 300 °C, and the deposition process was retained for 27 min.

All the deposition time is 30 min, so the role of the buffer layer can be studied under the same film thickness. Between the deposition of the buffer layers and the main layers, no annealing process was done. The thickness of the buffer layer was about 10 nm. In order to explore the effect of the buffer layers, a film without buffer layer was also deposited at 550 °C for 30 min. After deposition, the films were cooled down to room temperature, keeping the oxygen pressure unchanged. To study the effect of the post-annealing on the optical property of the film, another sample DT1 was deposited under the same conditions of the sample D1 but annealed at 600 °C in air for 1 h in a furnace. The sample's name and the experiment conditions are labeled in Table 1.

A Philips X'pert PRO X-ray diffractometer (XRD) and the Park Scientific Instruments designed Autoprobe CP type atomic force microscope (AFM) were used to characterize the crystallization and the microstructure of the synthesized films. The optical properties of the final ZnO thin films were characterized by a He–Cd laser with the 325 nm line as excitation source. All spectra were measured at room temperature.

Table 1 Samples name and the experiment conditions

Sample	T_b (°C)	T_f (°C)	T_a (°C)	FWHM	rms roughness (nm)
D1	300	550		0.2085	17.7
D2	550	300		0.2676	54.7
D3		550		0.2076	15.2
D4	300			0.3955	2.85
D5	550			0.2694	3.64
DT1	300	550	600	0.1723	10.9

Note: T_b is the deposition temperature of the buffer layer; T_f is the deposition temperature of the subsequent main ZnO layer; T_a is the annealing temperature

3 Results and discussion

It has been found that the experiment conditions were crucial in determining the quality of the ZnO thin films: too low substrate temperature results in a low surface migration of adatoms, while too high substrate temperature causes the adatoms to reevaporate from the film surface. In addition, when the ZnO films were deposited on vacuum, the as-prepared films always contained a lot of defects. From our past one-step PLD experiment results, the films deposited at substrate temperature of 550 °C and an oxygen pressure of 200 mTorr have the best quality, so most of our samples were deposited under these conditions [16].

Figure 1 shows the XRD θ-2θ spectra of the as-prepared samples D1, D2, D3, and the insert is the XRD spectra of the sample D4 and D5. It can be observed that there is only one strong (0002) diffraction peak of ZnO in the measurement range, which means that all the ZnO films are highly c-oriented. In order to compare the crystallinity, the FWHM values of the samples are showed in Table 1. From the data, it can be seen that the sample D1 and D3 have similar crystallinity and superior to that of the sample D2, because the main deposition layer of the sample D2 was deposited at low-temperature, so the crystallinity was deteriorated greatly. This result can also be obtained when the sample D4 and the sample D5 are compared. From the insert, it can be seen that the (0002) diffraction peak of the sample D4 is broader than that of the sample D5, which means that the grain size of the sample D4 is much smaller than that of the sample D5 because the low deposition temperature will facilitate buffer layer to form more nuclear centers with small size. In particular, the FWHM values of the sample D1 and D3 are almost identical regardless of the first buffer layer, which indicate that there is no degradation of crystallinity of the total films by using a LT buffer-layer. After annealing of the sample D1, the crystallinity of the sample DT1 is improved and the FWHM value is about 0.17 (the XRD θ-2θ spectrum was not shown here).

The AFM images of the two buffer layers are shown in Fig. 2 for comparison. It can be seen that the particles of the sample D4 are uniform and small, but the sample D5 has some large particles, so the root-mean-square (rms) roughness value of the sample D5 is larger than that of the sample D4. Figure 3 shows AFM images of the sample D1, D2, and D3, and the rms roughness values were labeled in Table 1. As it shown in the images, all the films are crack-free regardless of the different experiment conditions. Interesting, the sample D3 without buffer layer are made of

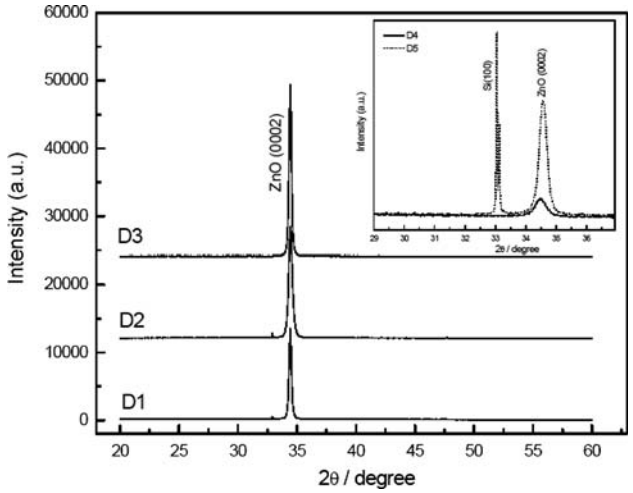

Fig. 1 The XRD θ-2θ patterns of the samples D1, D2, and D3. The insert is the XRD θ-2θ patterns of the samples D4 and D5

slice-like crystals, but there are exist some large pores, which indicates that the surface morphology of the sample D3 is not satisfying. By using buffer layers, the sample D1 and D2 have denser surfaces in comparison with that of the sample D3. In addition, it can be observed that the particle size of the sample D1 is much smaller than that of the sample D2, which indicate that the initial particles of the buffer layer have great influence on the subsequent growth of the films.

Commonly, high substrate temperature will make the average roughness of the films increase, as it can be seen from the samples D4 and D5, but it is discrepant with the result when we compare the sample D1 with the sample D2. Though the main ZnO film of the sample D1 was deposited at high substrate temperature, but the average roughness of the sample was much lower than that of the sample D2 deposited at low substrate temperature. We think it is strongly related to the properties of the buffer layers, because the sample D1 was synthesized using a LT buffer-layer, the LT buffer-layer with small grain size and low roughness will affect the growth of the subsequent main ZnO layer, which will make the subsequent growth on the original nuclear centers formed by depositing a thin buffer layer easier and more homogenous, so the sample D1 is flat and with lower roughness. All these results mean that in order to obtain ZnO thin films with high-quality and low roughness, the LT buffer-layer should be used.

Figure 4 shows the room temperature PL spectra of the sample D1, D2 and D3, respectively. In order to compare the photoluminescence intensity, all the vertical scales are set as the same scale. It is worth noting that there is only one strong ultraviolet emission with a shoulder at low-energy part in all the films, but little or no emission peak is observed in the visible region, which suggests that no deep-

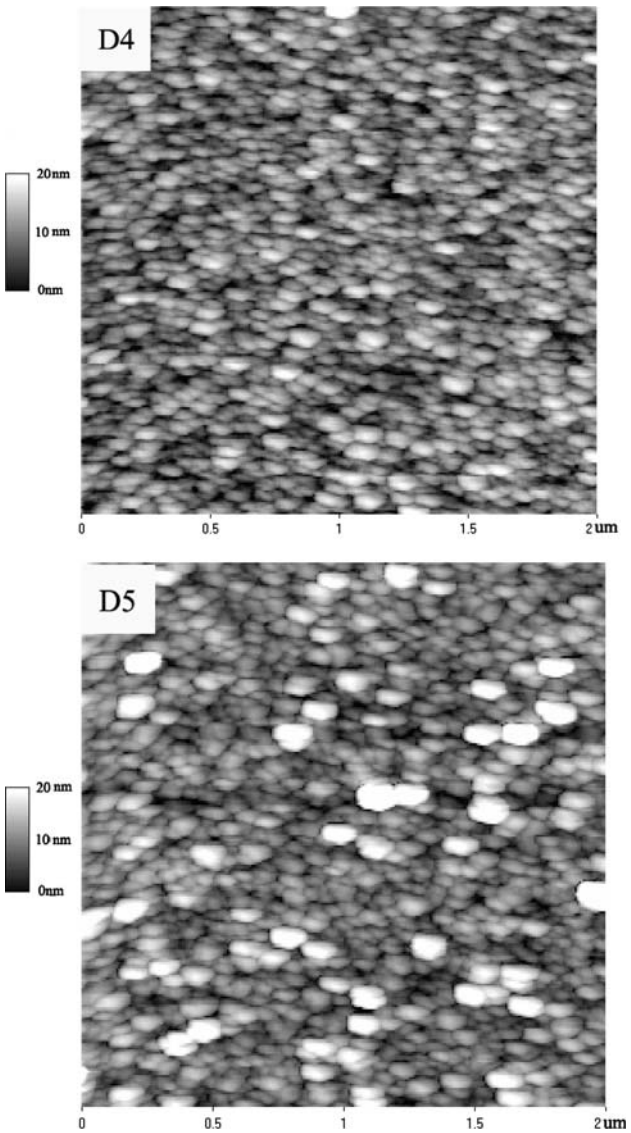

Fig. 2 The AFM images of the samples D4 and D5

level impurities and/or lattice defects are formed in the films. This implies that the as-deposited films are of high-optical quality. From the XRD data, the crystallinity of the sample D1 and D3 is almost identical, but the UV emission intensity of the sample D1 is enhanced about 2.2 times by using a LT buffer-layer. Compare the sample D2 and D3, it can be seen that although the crystallinity of the sample D3 is much better than that of the sample D2, but the UV emission of the sample D2 is also improved significantly. These results indicated that the buffer layers have significant effect on the optical property of the final ZnO films. In addition, by fitting process, the UV emission peaks of the sample D1 and D2 can be divided into two Gaussian emission peaks and both of them are located at the UV region, so we think the asymmetric peaks with a

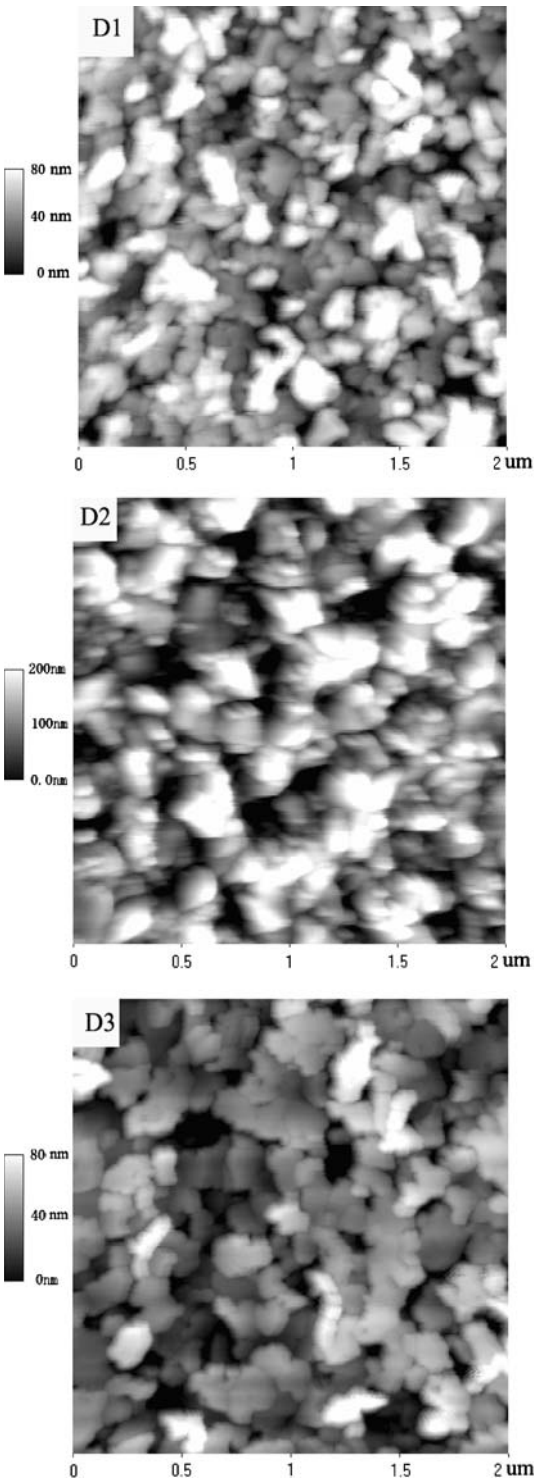

Fig. 3 The AFM images of the samples D1, D2, and D3

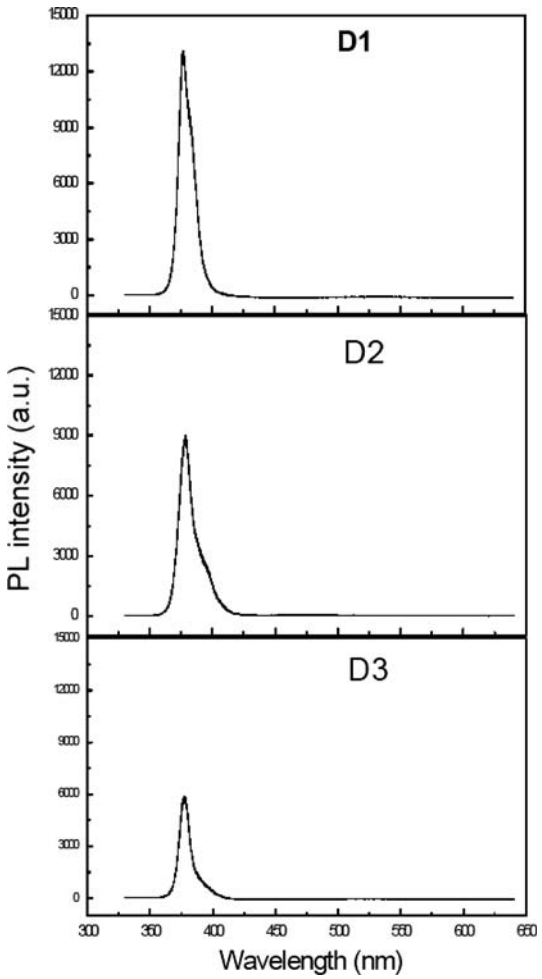

Fig. 4 Room temperature PL spectra of the samples D1, D2 and D3

low-energy tail can be attributed to the contribution of high-order phonon replicas [17].

From the above results, it can be seen that the buffer layers play important roles in the structure and optical properties of the films. When the buffer layer was deposited at low-temperature, the zinc and oxygen atoms can be absorbed easily on the substrate surface, and they can diffuse into the nucleation sites to form ZnO films with small and uniform grains. With increasing of the buffer layer temperature, the grain size becomes larger and uneven as it can be seen from Fig. 2. Therefore, the quality of the final ZnO thin films can be severely affected by the growth of the initial buffer layer.

It has been reported that the PL emission characteristics of ZnO films are strongly dependent on the crystallinity and stoichiometry of the film [18–20]. But when we compare the XRD and PL results of the sample D2 with that of the sample D3, it is suggested that the effect of the crystallinity of the film on the PL emission is not a decisive factor in our experiments, many other effects should be considered, such as stress, because the stress in thin films will influence its density of dislocations and optical properties [21–23]. In this work, by using a LT or HT buffer-layer, the stress between the substrates and the films can be effectively released, so the intensity of the UV emission of the samples D1 and D2 can be improved greatly.

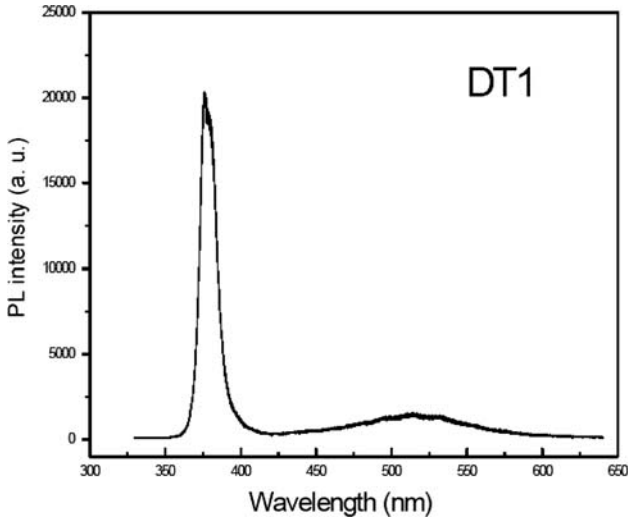

Fig. 5 Room temperature PL spectrum of the sample DT1

Additionally, in order to obtain films with the strongest UV emission, the subsequent growth should be carried through under high substrate temperature, because the enhancement of the migration and diffusion rates will lead to the formation of ZnO films with large crystal grains and smooth surface as it can be seen from Table 1. The films with LT buffer-layer and high crystallinity would have good optical properties.

In order to see the anneal process on the optical property of the ZnO film, the sample D1 with the best crystallinity, surface morphology and optical emission was annealed in air for 1 h, the PL spectrum of the annealed sample DT1 has some change as shown in Fig. 5. Beside the UV emission, there is a board deep-level emission located at 525 nm, which is related to oxygen or Zn defects in the films [24]. It is indicated that the anneal process will make the optical property of the ZnO film declining.

4 Conclusion

Summarizing, ZnO thin films on Si (100) were prepared using a LT buffer-layer or HT buffer-layers to study the role of the buffer layers on the structure, surface morphology and optical properties of the films. It was found that by using a LT buffer-layer, the surface morphology and the UV emission could be improved greatly without sacrifice the crystallinity of the film. It was ascribed to the stress releasing by using the buffer layers. To obtain a film with only one strong UV emission, the post-annealing process in air should be avoided because it would make the PL property of the film deteriorate.

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References

1. D.M. Bagnall, Y.F. Chen, Z. Zhu, T. Yao, S. Koyama, M.Y. Shen, T. Goto, Appl. Phys. Lett. **70**, 2230 (1997)
2. Z.K. Tang, G.K.L. Wong, P. Yu, M. Kawasaki, A. Ohtomo, H. Koinuma, Y. Segawa, Appl. Phys. Lett. **72**, 3270 (1998)
3. H. Cao, Y.G. Zhao, H.C. Ong, S.T. Ho, J.Y. Dai, J.Y. Wu, R.P.H. Chang, Appl. Phys. Lett. **73**, 3656 (1998)
4. T. Nishida, H. Saito, N. Kobayashi, Appl. Phys. Lett. **79**, 711 (2001)
5. D. Morita, M. Sano, M. Yamamoto, T. Murayama, S. Nagahama, T. Mukai, Jpn. J. Appl. Phys. Part 1 **41**, 1434 (2002)
6. H. Amano, N. Sawaki, I. Akasaki, Y. Toyoda, Appl. Phys. Lett. **48**, 353 (1986)
7. S. Takamura, Jpn. J. Appl. Phys. **30**, L1705 (1991)
8. A. Nahhas, H.K. Kim, J. Blachere, Appl. Phys. Lett. **78**, 1511 (2001)
9. Z. Fu, B. Lin, G. Liao, Z. Wu, J. Crystal Growth. **193**, 316 (1998)
10. A. Miyake, H. Kominami, H. Tatsuoka, H. Kuwabara, Y. Nakanishi, Y. Hatanaka, J. Crystal Growth. **214–215**, 294 (2000)
11. K. Koike, T. Komuro, K. Ogata, S. Sasa, M. Inoue, M. Yano, Physica E. **21**, 679 (2004)
12. K. Ogata, S.W. Kim, Sz. Fujita, Sg. Fujita, J. Crystal Growth **240**, 112 (2002)
13. K. Haga, T. Suzuki, Y. Kashiwaba, H. Watanabe, B.P. Zhang, Y. Segawa, Thin Solid Films. **433**, 131 (2003)
14. S.H. Jeong, I.S. Kim, J.K. Kim, B.T. Lee, J. Crystal Growth **264**, 327 (2004)
15. J.F. Yan, Y.M. Lu, Y.C. Liu, H.W. Liang, B.H. Li, D.Z. Shen, J.Y. Zhang, X.W. Fan, J. Crystal Growth **266**, 505 (2004)
16. W.W. Dong, R.H. Tao, Q.L. Su, Z.H. Deng, X.D. Fang, Proc. SPIE **6029**, 60290X-1 (2005)
17. W. Shan, W. Walukiewicz, J.W. Ager, K.M. Yu, H.B. Yuan, H.P. Xin, G. Cantwell, J.J. Song, Appl. Phys. Lett. **86**, 191911 (2005)
18. B.J. Jin, S. Im, S.Y. Lee, Thin Solid Films **366**, 107 (2000)
19. A. Mitra, R.K. Thareja, J. Appl. Phys. **89**, 2025 (2001)
20. S. Im, B.J. Jin, S. Yi, J. Appl. Phys. **87**, 4558 (2000)
21. M. Karger, M. Schilling, Phys. Rev. B. **71**, 075304 (2005)
22. V. Srikant, D.R. Clarke, J. Appl. Phys. **81**, 6357 (1996)
23. H. Amano, M. Iwaya, T. Kashima, M. Katsuragama, I. Akasaki, J. Han, S. Hearne, J. Floro, E. Chason, J. Figiel, Jpn. J. Appl. Phys. Part 2 **37**, L1540 (1998)
24. K. Vanheusden, C.H. Seager, W.L. Warren, D.R. Tallant, J.A. Voigt, Appl. Phys. Lett. **68**, 403 (1996)