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Effects of low-temperature-grown ZnO buffer layer and Zn/O ratio on the properties of high-temperature-overgrown ZnO main layer on Si substrate by MBE

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Abstract

The undoped ZnO thin films grown on Si (1 1 1) substrates by plasma-assisted molecular beam epitaxy (P-MBE) were reported. The effects of growth temperature, the thickness of low temperature ZnO buffer layer and Zn/O ratio on the quality of high-temperature-overgrown ZnO main layer were studied by atomic force microscopy (AFM), X-ray diffraction (XRD) and room-temperature photoluminescence (PL) spectra. These results showed that it was difficult to directly obtain high quality ZnO films on Si substrate. By introducing a thin ZnO buffer layer at 350 °C, *c*-axis preferred orientation ZnO films with improved optical properties were obtained at 750 °C. However, the thickness of ZnO buffer layer and Zn/O ratio in the ZnO main layer greatly influenced the quality of high-temperature-overgrown ZnO main layer.

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1. Introduction

In recent years, ZnO has been attracted considerable attention as one of the most promising materials for ultraviolet light-emitting devices [1–3]. Our groups have successfully fabricated ZnO LED on sapphire by MBE method [3]. However, sapphire introduces complexity to device fabrication process since it is an electrically insulation material and difficult to cleave. The growth of high quality ZnO on Si substrate was of great importance. However, it was difficult to obtain high quality ZnO on Si substrate due to the existence of an oxide layer on Si surface. Some attempts have been made by using AlN [4], MgO [5,6], GaN [7,8] buffer layer and nitridation of Si substrate [9] to solve the oxidation of Si substrate. These techniques introduced foreign atoms in the samples; so low-temperature ZnO buffer layers attracted more attention [10–14]. As for the fabrication method, different methods such as pulsed laser deposition [6,11], magnetron sputtering [8,12], MOCVD [4,7] and MBE [5,9] were used. Among these methods, MBE method is most promising due to high vacuum and good reproducibility. Furthermore, MBE system was often equipped with ECR or RF source to activate O atoms. Xiu et al. [10] have reported that high-quality of ZnO was grown on Si substrate with low-temperature ZnO buffer by MBE method, the full-width at half-maximum (FWHM) of (0 0 2) diffraction peak for ZnO in XRD spectra together with the FWHM of UV peak in their PL spectra showed a much broaden peak. The possible reason was that the thickness of ZnO buffer

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layer and Zn/O ratio in the high-temperature ZnO main layer was not optimized in their experiment.

In this paper, the effects of growth temperature, the thickness of low-temperature ZnO buffer layer and the Zn/O ratio on the quality of ZnO main layer were investigated.

2. Experiment procedure

ZnO thin films were grown on Si (1 1 1) substrates by plasma-assisted MBE (P-MBE). The zinc source was supplied by evaporation of metal zinc with a purity of 99.9999%. The oxygen gas activated by a radio-frequency (RF) plasma source was used as oxygen source. Before growth, the Si (1 1 1) substrates were ultrasonic cleaned with trichloroethylene followed by acetone and ethanol. Then it was etched with H_2SO_4: $HNO_3 = 1:1$, HCl: H_2O: $H_2O_2 = 3:1:1$ and HF: $H_2O = 1:20$ for 5 min, respectively. In order to investigate the effects of growth temperature on the quality of ZnO thin films, a series of samples marked as A, B, C, D and E were grown directly on Si substrates at 350, 450, 550, 650 and 750 °C, respectively. At the beginning of the growth, the Zn beam was firstly irradiated on Si substrate before the irradiation of O beam. In order to investigate the thickness of low-temperature ZnO buffer layers on the quality of high-temperature–overgrown ZnO main layer, a ZnO buffer layer with the thickness of 180 nm (sample F), 90 nm (sample G) and 30 nm (sample H) were firstly grown at 350 °C, then with the shutters of Zn beam and O beam open, the growth temperature was increased to 750 °C with a step of 0.3 °C/sec. When the temperature achieved 750 °C, the growth of ZnO main layer began without annealing process. The growth rate was kept constant (about 6 nm/min at 350 °C, 4 nm/min at 750 °C) As the Zn/O ratio was another important parameter for the growth of high quality ZnO thin films on Si substrate, the effect of Zn/O ratio in the high-temperature-overgrown ZnO main layer on the quality of ZnO were also investigated. For this study, three samples marked as samples H, I and J were investigated. These three samples had the same growth conditions except the different Zn/O ratio in the high-temperature ZnO main layer. Sample H was grown at approximate stoichiometric condition; Samples I and J were grown at Zn-rich and O-rich condition, respectively.

3. Results and discussion

(1) Direct growth on Si substrate

Fig. 1 shows the XRD spectra of sample A, B, C, D, and E, which was grown at 350, 450, 550, 650, and 750 °C, respectively. It can be seen that sample A showed only a broad FWHM of ZnO (0 0 2) peak. With the increase of growth temperature, other orientation related to ZnO such as (1 0 0), (1 0 1), (1 0 2) and (1 1 0) appeared. It indicated that the orientations of the crystal became random; it was possibly due to the serious oxidation of Si substrate and

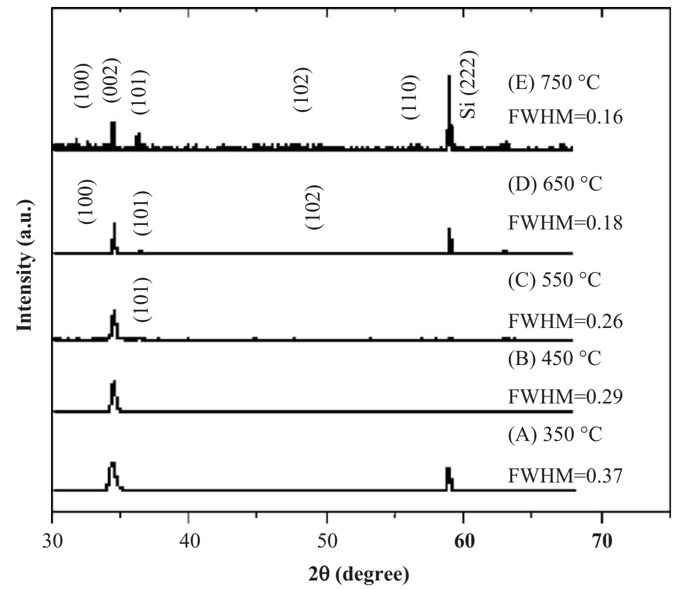

Fig. 1. XRD spectra of sample A, B, C, D and E, which was grown at 350, 450, 550, 650, and 750 °C, respectively.

formed amorphous silicon oxide at high temperature. At the same time, the FWHM of (0 0 2) peak decreased from 0.37° for sample A to 0.29°, 0.26°, 0.18°, 0.16° for sample B, C, D and E, respectively. The decrease of FWHM of (0 0 2) peak was related to the migration and diffusion rates of zinc and oxygen atoms. At low temperature, the zinc and oxygen atoms have no enough energy to migrate to normal lattice site, which lead to a broaden of (0 0 2) peak and small grain size. With the increase of temperature, small grains have enough energy to combine together and form larger grains, which lead to the decrease of the FWHM of (0 0 2) peak [10].

Fig. 2 shows the normalized room-temperature PL spectra of these five samples. In this figure, it can be seen that the spectra was consisted of near band UV emission (at high energy) and deep-level emission (at low energy). The deep-level was associated with structural defects. It can be seen that with the increasing of growth temperature, the intensity of deep-level emission decreased. The FWHM of UV emission peak for sample A, B, C, D and E was 124, 104, 104, 95 and 102 meV, respectively.

According to the above analysis, it was found that low temperature growth was benefit to avoid the oxidation of Si substrate and obtain *c*-axis preferred orientation, while high temperature growth was benefit to improve the optical quality and increase the grain size.

(2) The thickness of the low-temperature ZnO buffer layer

In order to obtain both high crystal and optical quality of ZnO films, a low temperature (350 °C) ZnO buffer layer was grown before the growth of ZnO epitaxial layer at 750 °C. However, the thickness of the buffer layer greatly influenced the quality of high-temperature-overgrown ZnO main layer. For this study, three samples (F, G and H) with

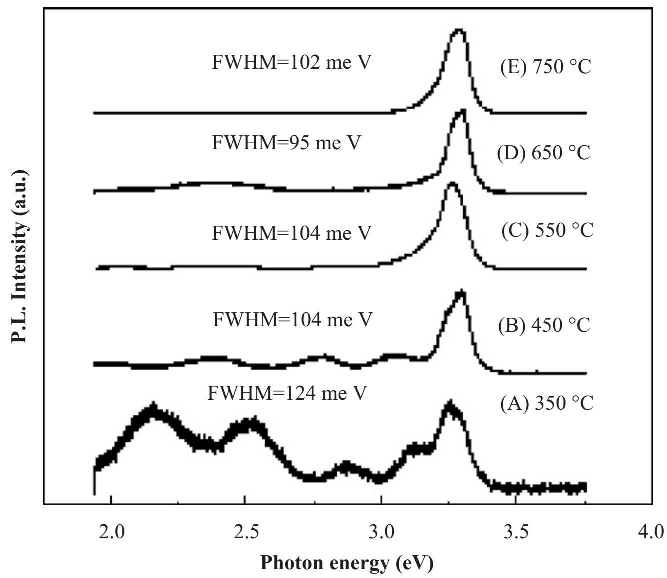

Fig. 2. PL spectra of sample A, B, C, D and E, which was grown at 350, 450, 550, 650, and 750 °C, respectively.

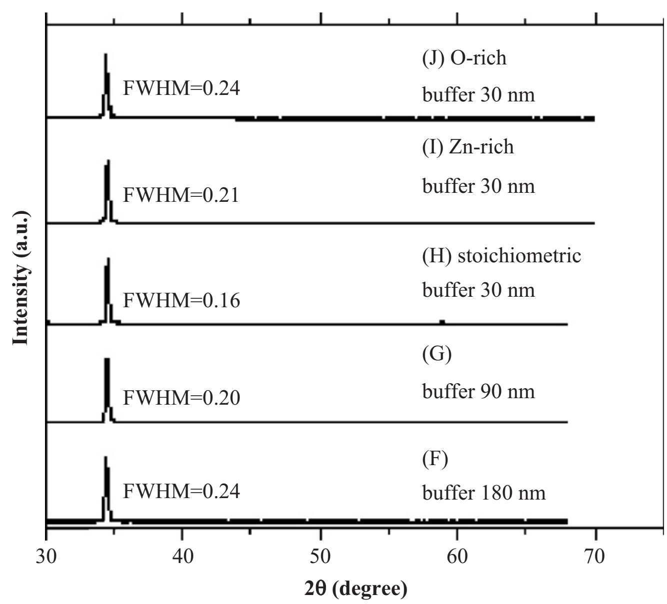

Fig. 3. XRD spectra of sample F, G, H, I and J. Sample F and G were grown with the buffer layer thickness of 180 and 90 nm, respectively. Sample H, I and J were grown with the buffer layer thickness of 30 nm at stoichiometric, Zn-rich and O-rich condition, respectively.

the buffer layer thickness of 180, 90 and 30 nm, respectively, were investigated. Curves (F, G and H) in Fig. 3 shows the XRD patterns of these three samples. It was found that only (0 0 2) peak related to ZnO was observed after introducing a low-temperature ZnO buffer layer. With the decrease of the buffer's thickness, the FWHM of (0 0 2) peak decreased from 0.24°, to 0.20° and 0.16°. These values of FWHM were quite smaller than that report by Xiu et al., in which high quality of ZnO films were grown on Si substrate with a low-temperature ZnO buffer by electron cyclotron resonance-assisted MBE [10].

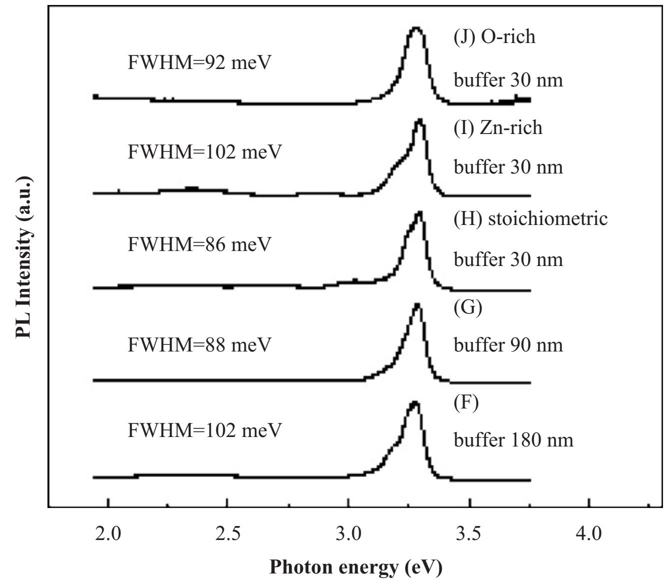

Fig. 4. PL spectra of sample F, G, H, I and J. Sample F and G were grown with the buffer layer thickness of 180 and 90 nm, respectively. Sample H, I and J were grown with the buffer layer thickness of 30 nm at stoichiometric, Zn-rich and O-rich condition, respectively.

At the same time, the PL spectra for this series of samples showed a strong near-band emission and a very weak deep-level emission, which was seen in Fig. 4 (curve F, G and H). The FWHM of UV emission peak for sample F, G and H was 102, 88 and 86 meV, respectively. These FWHM values were also smaller than that reported by Xiu et al. [4]. By comparing the quality of ZnO films in this seize of samples, the sample with buffer layer thickness of 30 nm (sample H) has a best crystal and optical quality in our experiments. It must be pointed that the Zn/O ratio in sample H was kept at a proximately stoichiometric condition in our experiments. In the following, we would find that the quality of the sample grown at stoichiometric condition was better than that grown at Zn-rich and O-rich condition. This is possible the reason that caused the difference between our results and Xiu's [10].

(3) Zn/O ratio in the high-temperature-overgrown ZnO main layer

Curves H, I and J in Fig. 3 shows the XRD results for the samples (H, I and J) with different Zn/O ratio, it was observed that with the decrease of Zn/O ratio, the FWHM of ZnO (0 0 2) peak firstly decreased from 0.21° to 0.16°, then increased to 0.24°. Furthermore, It can also be found that the FWHM of (0 0 2) peak for ZnO sample grown under O-rich conditions (sample J) was broader than that of ZnO sample grown under stoichiometric (sample H) or Zn-rich condition (sample I), and it was possibly due to the large density of threading dislocation in ZnO layers grown under O-rich condition [15]. Curve H, I and J in Fig. 4 shows the PL spectra for sample H, I and J, respectively. The FWHM of UV emission peak for sample H, I and J was 86, 102 and 92 meV, respectively. At the stoichiometric condition, we obtain the smallest FWHM in both XRD

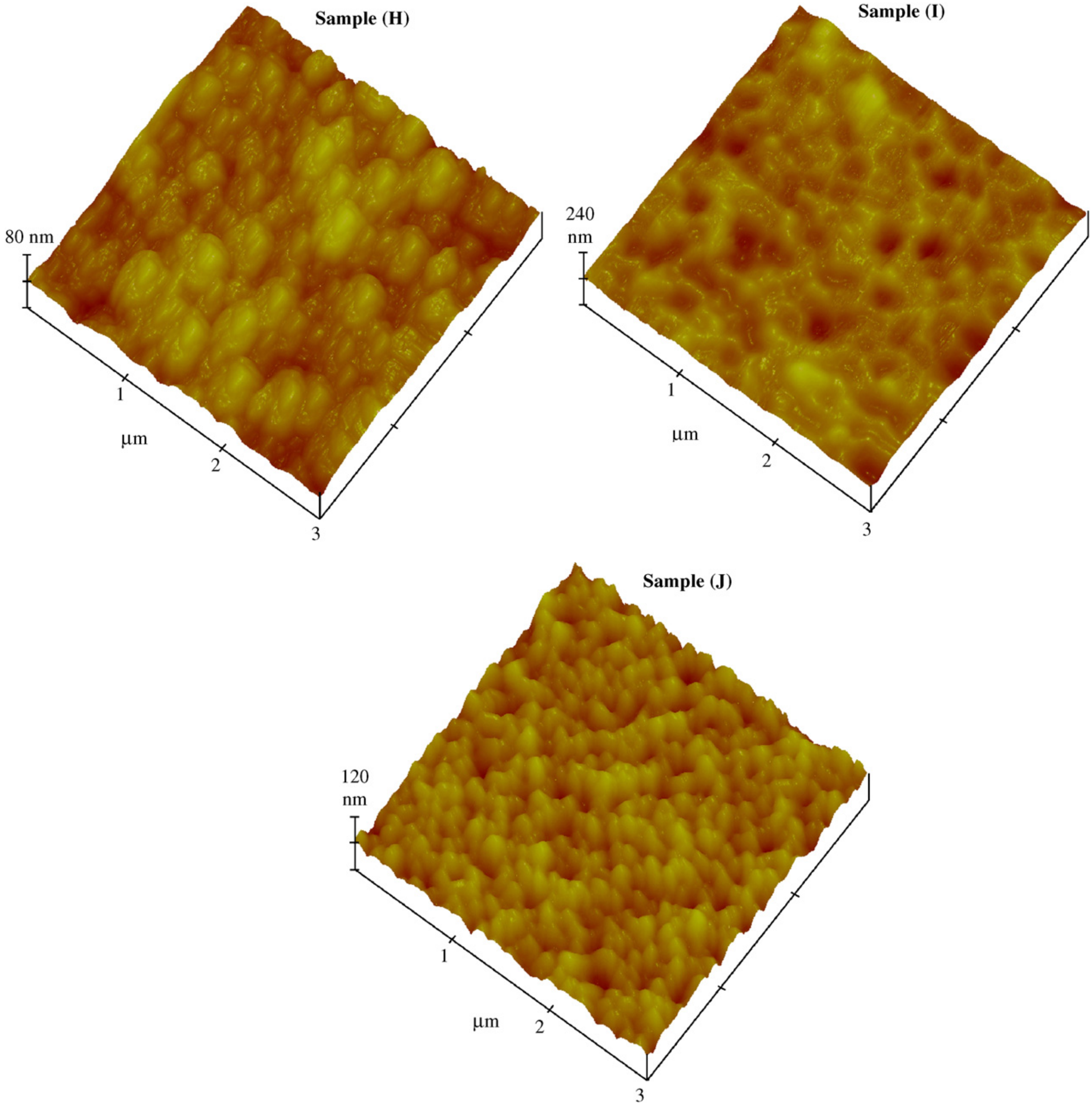

Fig. 5. AFM pattern of samples H, I and J, which was grown at stoichiometric, Zn-rich and O-rich condition, respectively.

and PL results. At the same time, it was found that ZnO layers grown under Zn-rich condition exhibited hexagonal pits morphology, while ZnO layers grown under O-rich condition exhibited island morphology according to the AFM pattern as shown in Fig. 5. Similar phenomenon was observed on ZnO sample grown on sapphire substrate and it was due to the different growth model in different Zn/O ratio. The RMS roughness for sample H, I and J was 8.95, 16.82 and 13.6 nm, respectively. So at the stoichiometric condition, we obtained satisfied results in our experiment.

4. Conclusions

Undoped ZnO samples were grown on Si substrate by P-MBE. Optical properties of ZnO thin films were improved with increasing the growth temperature. However, only poly crystal ZnO was obtained from direct growth on Si substrate By introducing a low temperature (at 350 °C) ZnO buffer layer, *c*-axis preferred orientation ZnO sample was obtained. Further adjusting the thickness of ZnO buffer layer and Zn/O ratio in the high-temperature-overgrown ZnO main layer, the best quality of ZnO thin films were obtained at 750 °C under stoichiometric growth condition on Si substrate.

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