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Improvement of the crystalline quality of the ZnO epitaxial layer on a low-temperature grown ZnO buffer layer

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Abstract

In this paper, a high-quality ZnO thin film was first grown on a Si(1 1 1) substrate by plasma-assisted molecular beam epitaxy. A ZnO thin film grown at 300°C was used as an intermediate layer for the growth. The dependence of the ZnO thin-film quality on the substrate temperature was studied by using X-ray diffraction and photoluminescence (PL). Only poly crystal ZnO could be obtained from direct growth on the Si substrate, because of the large differences in lattice constant between the Si substrate and ZnO thin film and the existence of an oxide layer on the Si surface. The best ZnO was obtained at a substrate temperature of 550°C. A low-temperature ZnO buffer layer is induced between the substrate and ZnO film to reduce the effects of the oxide layer and the mismatch. Next, a high-temperature ZnO layer is deposited on this buffer layer to obtain a high-quality thin film. The effects of the buffer layer on the structure and PL of ZnO thin films are studied. For the ZnO films employing the buffer layer, only one peak from the ZnO (0 0 2) orientation is obtained in the X-ray diffraction measurement, and the full-width at half-maximum (FWHM) of the (0 0 2) ZnO peak is less than 0.180°. The ZnO thin film exhibits a smooth surface as measured by atomic force microscopy, and the PL spectra show a strong ultraviolet band emissions with little or no deep-level emission related to defects. The FWHMs of the PL spectra are narrower compared to the ZnO film without a buffer layer. These measurements indicate that high-quality ZnO films can be obtained by employing a low-temperature grown ZnO buffer layer.

Keywords: A1.Atomic force microscopy; A1. Photoluminescence; A1. X-ray diffraction; A3. Plasma-assisted molecular beam epitaxy; B1. ZnO; B2. Semiconducting II–VI materials

1. Introduction

In recent years, much attention has been paid to wide band gap semiconductor materials for their use in blue light emitting and short-wavelength laser diodes [1]. As a well-known wide band gap semiconductor, ZnO is gaining importance for these possible applications, because of its ultraviolet emission at room temperature. It has a wide band gap of 3.3 eV at room temperature and a high exciton binding energy of 60 meV, which

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allow for efficient ultraviolet emission from recombination of the exciton and make it suitable for ultraviolet laser-emitting devices [2–4]. There are two problems limiting the commercialization of ZnO. One is the need to obtain pure crystalline materials; the other is to produce p-type ZnO films on n-type ZnO material. Ultraviolet ZnO devices will require pure crystalline materials and the ability to fabricate p-type ZnO.

Sapphire substrates have been widely used to grow ZnO thin films and high-quality ZnO has been obtained [5]. Silicon (Si) is another promising substrate, because it is not only of interest for the integration of optoelectronic devices but also cheaper and easier to cleave in comparison to sapphire. However, one serious problem is the effect of the large mismatch and thermal expansion coefficients between the Si and ZnO associated with the oxide layer on the Si surface, which causes the direct growth of ZnO thin films on Si substrates to be a difficult task. There are few papers dealing with the direct growth of ZnO thin films on Si substrates [6], and only poly crystal ZnO thin films have thus fare been obtained, because of the large mismatch and the oxidation of the Si surface. Attempts were made to utilize a thin Zn buffer [7], nitrification of the Si surface by NH_3 [8,9], and employing epitaxial ZnS thin films [10] as a buffer layer; however, little progress was made. There is no report about the improvement of the ZnO quality by employing a low-temperature grown ZnO buffer layer on a Si substrate by plasma-assisted molecular beam epitaxy (P-MBE), though Bang et al. [11] have recently studied the effects of the ZnO buffer layer thickness on the properties of ZnO thin films deposited on *c*-plan sapphire substrates by radio-frequency magnetron sputtering.

In this paper, the influence of a low-temperature grown ZnO buffer layer on the structure and photoluminescence properties of ZnO films grown on Si(1 1 1) substrates by P-MBE is reported for the first time.

2. Experiment

ZnO thin films were deposited on Si(1 1 1) substrates by P-MBE. The Si(1 1 1) substrates were cleaned with ethanol for 5 min, acetone for 10 min, followed by ethanol for an additional 5 min. Next, the surface oxidized layer was etched with H_2SO_4:H_2O_2(3:1) for 10 min, HF:H_2O(1:20) for about 1 min, HCl:HNO_3(3:1) for 10 min, and then with HF:H_2O(1:20) for about 1 min. Finally, the surface was washed with de-ionized water and blow dried in dry nitrogen. Elemental Zn with a purity of 6 N and O_2 gas with 5 N purity were used as groups II and VI sources, respectively. After chemical cleaning and etching, the substrate was then heated for 5 min at 300°C to remove contamination and then thermally cleaned at about 650°C for 30 min. Then the substrate was inserted into the growth chamber.

In order to investigate the effects of the substrate temperature on the quality of ZnO thin films, a series of samples were grown directly on Si substrates with different substrate temperatures in the range of 350–700°C. The O_2 flow rate was controlled by a gas flowmeter. The zinc pressure was measured using an ionization gauge. The background pressure was less than 1×10^{-9} mbar. In order to investigate the effects of the low-temperature grown ZnO buffer layer on the quality of the ZnO thin film, a low-temperature ZnO buffer layer was deposited at 300°C for about 200 s just before the ZnO thin film growth at 550°C. The growth rate was about 1 Å s^{-1} with the O_2 flow rate at 1 sccm and the Zn flux at 1×10^{-6} mbar. The thickness of the ZnO buffer layer was about 20 nm. Then the ZnO thin film was grown on the buffer layer at 550°C for 2 h with the same flow rate of the O_2 and zinc. The detailed growth conditions are listed in Table 1.

To characterize the crystal structure of these films, X-ray diffraction (XRD) experiments were performed using a D/maxrA X-ray diffraction spectrometer (Rigaku) with a CuK_α line of 1.54 Å. Atomic force microscopy (AFM) measurements were also conducted. For the optical characterization, photoluminescence (PL) spectra were measured in the wavelength range of 350–625 nm. The 325-nm line of a He–Cd laser operated at a power of 50 mW was used as the excitation source.

Table 1
Deposition conditions of ZnO thin films with different substrate temperatures

Sample	Substrate temperature (°C)	Zinc pressure ($\times 10^{-6}$ mbar)	Oxygen flow rate (sccm)	RF power (W)	Buffer layer
a	350	1	1	300	Without
b	450	1	1	300	Without
c	550	1	1	300	Without
d	600	1	1	300	Without
e	700	1	1	300	Without
f	550	1	1	300	With

3. Results and discussion

3.1. Dependence of ZnO thin films on the substrate temperature

Figs. 1(a)–(e) show the XRD spectra of ZnO thin films prepared by P-MBE on the Si substrates at different temperatures. All the ZnO thin films were polycrystalline with the preferred orientations of (0 0 2) ZnO as shown in Fig. 1. Moreover, the full-width at half-maximum (FWHM) of the (0 0 2) ZnO peak at 34.42° decreases significantly with increasing substrate temperature for temperature ranging from 350°C to 550°C, and then increases with increasing substrate temperature from 550°C to 700°C. The FWHMs of samples a, b, c, d and e are 0.34°, 0.32°, 0.22°, 0.25° and 0.31°, respectively. According to the Scherrer formula [12], the mean grain sizes of samples a, b, c, d and e are 25.5, 27.1, 39.5, 33.8 and 27.3 nm, respectively. The temperature dependence of the grain size can be explained by the migration and diffusion of the reactants. At low temperature, the zinc and oxygen atoms can be absorbed easily on the substrate surface, and they diffuse into the nucleation sites to form ZnO film. However, the lower migration and diffusion rates lead to the formation of ZnO crystal grains with different orientations, which have smaller sizes and cause a rough surface. With increasing substrate temperature, the grain size becomes larger and the film has a smoother surface due to the enhancement of the atomic migration ability. At higher temperatures, the decreasing of the grain size is due to the increasing of the re-evaporation process. Therefore, the quality of the ZnO thin films is improved by heating the substrate, and 550°C is the best substrate temperature for the deposition of ZnO thin films on Si(1 1 1).

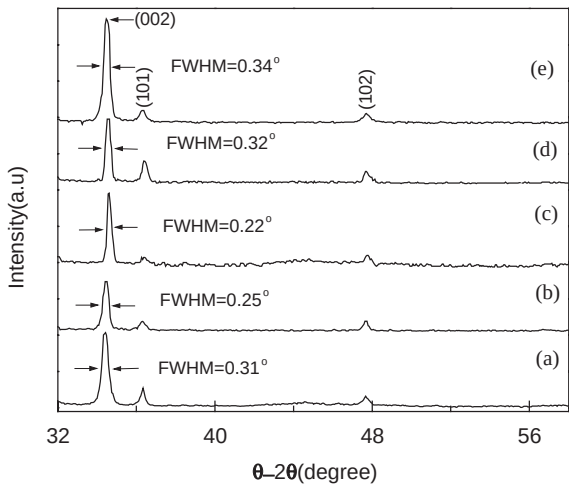

Fig. 1. X-ray diffraction patterns of ZnO thin films grown on Si(1 1 1) substrates prepared at different substrate temperatures: (a) 350°C; (b) 450°C; (c) 550°C; (d) 600°C; and (e) 700°C.

Figs. 2(a)–(e) shows the PL spectra of the above samples. The FWHM of the ultraviolet (UV) band becomes narrower with increasing substrate temperature from 350°C to 550°C, and then becomes wider with increasing substrate temperature ranging from 550°C to 700°C. The FWHMs of the PL spectra (UV) of samples a, b, c, d and e are 92, 91, 89, 110 and 124 meV, respectively. The PL emission related to a deep level is decreased with increasing substrate temperature up to 550°C. The shift of the UV emission peak is probably caused by the quantum confinement effect [13] due to the different ZnO grain sizes. At low deposition

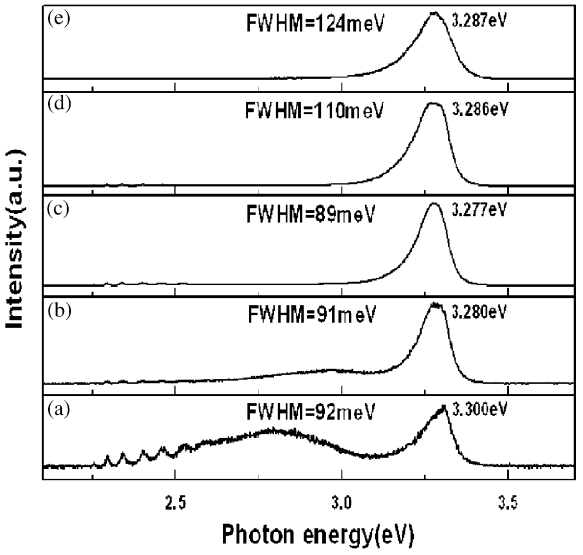

Fig. 2. PL spectra of ZnO thin films grown on Si(1 1 1) substrates prepared at different substrate temperatures: (a) 350°C; (b) 450°C; (c) 550°C; (d) 600°C; and (e) 700°C.

temperature, the size of the ZnO grains and the structural defects cause the blueshift and the broadening of UV peak in the PL spectra. With the increasing temperatures, the grain size becomes larger and more homogeneous, so the UV peak shifts toward the low-energy side, and the FWHM becomes narrower. The result indicates that 550°C is the optimal deposition temperature for growth of ZnO thin films on Si(1 1 1) substrates by P-MBE.

3.2. The effect of the low-temperature grown ZnO buffer layer on the quality of ZnO thin films

The results described above show us that only polycrystalline ZnO thin films were obtained from direct growth on the Si substrate. Previous research on the growth of ZnO films on Si has revealed the importance of the substrate surface during the initial stages of the growth, particularly the lattice mismatch and oxidation of the Si surface. In this paper, we first obtained high-quality ZnO thin film deposited on a Si substrate via employing a low-temperature grown ZnO buffer layer, onto which a high-temperature ZnO thin film was deposited. In order to investigate the effect of the low-temperature grown ZnO buffer layer on the quality of the ZnO thin film, epitaxial ZnO thin films were grown on Si(1 1 1) with (sample f) and without (sample c) the low-temperature grown buffer layer at the optimal substrate temperature of 550°C. The detailed grown conditions are listed in Table 1.

Fig. 3 shows the XRD spectra for samples c and f. For the ZnO thin film (c) without the buffer layer, the XRD result exhibits a strong (0 0 2) diffraction peak and some other weak oriented peaks, indicating that the ZnO thin film is a poly crystal structure with a preferred orientation of (0 0 2). The FWHM of the (0 0 2) peak is 0.224°. For the ZnO epitaxial layer (f) employing the buffer layer, only one peak from the ZnO(0 0 2) orientation is observed in the XRD measurement, and the FWHM of the (0 0 2) ZnO peak becomes narrower and has a value of 0.18°. It is clearly seen that the crystal quality of the ZnO thin film is improved by employing the low-temperature grown ZnO buffer layer. The existence of the low-temperature buffer layer may reduce the effects of the oxide layer and the lattice mismatch on the quality of the ZnO films. The nucleation of the ZnO buffer layer grown at low-temperature is relatively easy to form on the Si surface, because the sticking coefficient is large and the growth mode is amorphous. This amorphous ZnO buffer

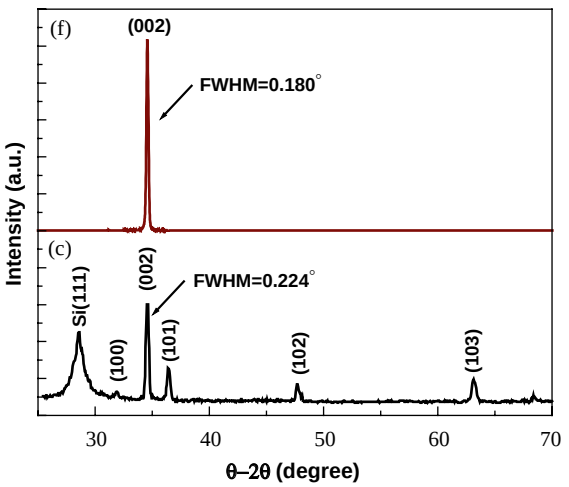

Fig. 3. X-ray diffraction patterns of ZnO thin films with (f) and without (c) the low-temperature grown ZnO buffer layer.

layer confines most of the dislocations generated at the interface between the substrate and ZnO thin film into the buffer layer. The interfacial ZnO buffer layer is expected to reduce and relax the effects of the abrupt change of lattice constant between the Si substrate and the ZnO thin film, as well as the effects of the oxide layer at the Si surface, both resulting in the formation of a homogeneous and crystalline ZnO thin film grown on the buffer layer. Thus, the crystal structure of the ZnO thin film grown at high-temperature could be transformed from an amorphous structure to a crystalline one after employing an appropriate low-temperature ZnO buffer layer.

Fig. 4 shows the difference between the AFM images of samples c and f. In this experiment, we find that the surface roughness and the grain shape of ZnO thin films were dramatically improved by employing the low-temperature grown ZnO buffer layer, compared to the ZnO thin films without the buffer layer. The root-mean-square (RMS) roughness of samples f and c are 2.550 and 16.109 nm, respectively. The mean grain sizes of samples f and c are 48.2 and 38.8 nm, respectively. For the ZnO thin film employing the low-temperature grown buffer layer, the AFM pattern exhibits a smoother surface, compared to the ZnO thin films without the buffer layer.

Fig. 5 shows the difference between the PL spectra of samples c and f. For the ZnO thin film without the buffer layer (c), the PL spectrum shows an ultraviolet band emission located at 3.277 eV related to the bound exciton and a weak emission related to deep level defects. The FWHM of the ultraviolet band is 89 meV. For the ZnO films employing the buffer layer (f), a strong ultraviolet band emission is observed in PL spectra. There are two peaks in the UV emission band located at 3.310 and 3.270 eV. The origins are considered to be emissions of the free excitons and bound excitons, respectively. The FWHM of the ultraviolet band is 72 meV, and the emission related to the free-exciton recombination is observed only after employing the ZnO buffer layer. The above results demonstrate that the existence

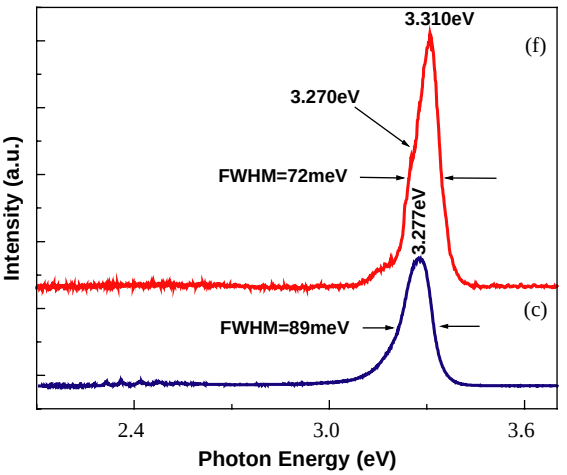

Fig. 5. PL spectra of ZnO thin films grown on Si(1 1 1) substrates with (f) and without (c) the low-temperature grown ZnO buffer layer.

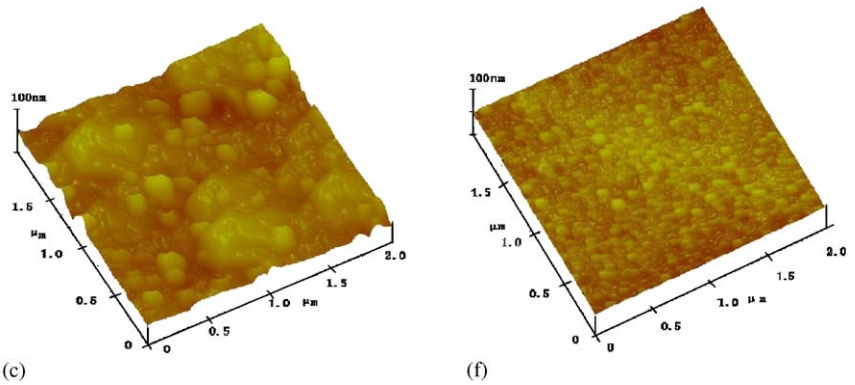

Fig. 4. AFM images of ZnO thin films grown on Si(1 1 1) substrates with (f) and without (c) the low-temperature grown ZnO buffer layer.

of the ZnO low-temperature buffer layer enhances the quality of the ZnO thin film.

4. Conclusion

ZnO films were deposited on Si(1 1 1) substrates by P-MBE. For the ZnO thin films grown directly on the Si substrate, only poly crystal ZnO could be obtained, because of the large differences in lattice constants between the Si substrate and ZnO thin film and the existence of an oxide layer on the Si surface. Through use of a low-temperature grown ZnO buffer layer, one can confine the misfit dislocation and the defects into the buffer layer and reduce the detrimental effects of the oxidation and the mismatch, thus allowing the crystal structure of the ZnO thin films to be transformed from a polycrystalline structure to a crystalline one. The AFM images and the photoluminescence spectra show that the quality of the ZnO thin film is improved by the ZnO buffer layer. The results demonstrate that high-quality ZnO thin films can be obtained on Si substrate by growing on top of a low-temperature grown ZnO buffer layer.

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