

Growth of the Single-Crystalline ZnO Films on Si (111) Substrates by Plasma-Assisted Molecular-Beam Epitaxy

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ABSTRACT

This report describes the growth of single-crystalline ZnO films on Si (111) substrates by plasma-assisted molecular-beam epitaxy. X-ray diffraction measurement shows that c-axis oriented ZnO films are easily grown on Si (111) substrates. However, in-plane random rotational domains are included in the ZnO films due to the inevitable oxidation of substrate surface at the initial stage of ZnO growth. By employing a thin CaF₂ buffer layer between the ZnO films and Si substrates, we have succeeded in suppressing the generation of rotational domains and in obtaining an intense ultraviolet photoluminescence even at room temperature. These results indicate that the use of CaF₂ buffer layer is promising for the growth of device-quality ZnO films on Si (111) substrates.

INTRODUCTION

Wide and direct band-gap semiconductor ZnO has attracted much attention to the room-temperature operating ultraviolet lasers and sensors because of its large exciton binding energy of about 60 meV [1]. To integrate these optoelectronic devices with Si-base electrical circuitry, however, high-quality ZnO growth on Si substrates is a key issue although the direct growth is apt to yield in-plane rotational domains by the oxidation of substrate surface at the initial stage of ZnO growth [2]. Recently, Iwata *et al.* demonstrated that the plasma-assisted nitridation of Si substrate prior to ZnO growth was effective to suppress the oxidation of Si surface although in-plane 30° rotational domains still remained in the ZnO films [2]. We notice the use of CaF₂ buffer layer as an alternative way to suppress the oxidation of Si surface. This idea is promoted by the recent work of Ko *et al.* that reports the growth of single-crystalline ZnO (0001) films on bulk CaF₂ (111) substrates using plasma-assisted molecular-beam epitaxy (MBE) [3]. In this heterosystem, the epitaxial relationship is reported to be $[2\bar{1}\bar{1}0]$ ZnO (0001) // $[\bar{1}10]$ CaF₂ (111) [3]. Due to the close lattice matching of about 0.6 % between CaF₂ (111) and Si (111), we can expect single crystalline MBE growth for the CaF₂ buffer layer [4,5]. In this paper, we report the effect of CaF₂ buffer layer on the ZnO films grown on Si (111) substrates.

EXPERIMENTAL PROCEDURE

The growth in this experiment was carried out using an Epiquest-MBE system equipped with effusion K-cells for Zn and CaF₂ sources and an rf-plasma cell for oxygen radical source.

The growth process was *in-situ* monitored by a reflection high-energy electron diffraction (RHEED) system operated at 15 KV. Compound CaF_2 with a purity of 4 N was used for the CaF_2 growth, and elemental Zn with a purity of 7 N and oxygen gas with a purity of 6 N were used for the ZnO growth. (111)-oriented p-type ($\sim 0.01 \Omega\text{-cm}$) Si was used as the substrates. The substrates were degreased in toluene, acetone, and ethylalcohol, and then boiled in HNO_3 bath at 130°C for 5 minutes. Subsequently, we dipped the substrates in a solution of 50 % HF for 20 minutes to remove the native oxide on the surface, and then thoroughly rinsed them in de-ionized water after dipping in a solution of NH_4F for 2 minutes. This chemical process is known to be effective to prepare a hydrogen-terminated surface with the flatness in an atomic scale [6]. By an immediate mounting on a substrate holder and loading in the MBE growth chamber, the clean surface of Si with 7×7 reconstruction was obtained in the growth chamber after elevating the substrate temperature up to 800°C . During ZnO growth, oxygen flow rate and rf power were kept at 0.30 ccm and 350 W, respectively. The base pressure was $\sim 5\times 10^{-8}$ Pa and the working pressure during ZnO growth was $\sim 1\times 10^{-4}$ Pa in the growth chamber.

In Fig. 1, (a) and (b) show the schematics of the sample structures with and without a CaF_2 buffer layer, respectively. We compare these two different samples on structural and optical properties. The ZnO film of sample (b) is directly grown on the Si clean surface without the insertion of CaF_2 buffer layer. The ZnO film of sample (a), on the other hand, is grown on a 30-nm-thick CaF_2 buffer layer. This CaF_2 buffer layer was grown at 650°C on the Si clean surface at a rate of 60 nm/h. The orientation of the resulted CaF_2 layer was (111) in agreement with that of Si substrate. Then the CaF_2 buffer layer was exposed to a defocused electron beam (15 KV, $\sim 25 \mu\text{A}$) from the RHEED gun. This exposure to electron beam was performed to remove the uppermost fluorine atoms and to generate fluorine vacancies on the CaF_2 surface [4,5]. Since fluorine-deficient CaF_2 surface is more energetically active [4,5,7], we expected the electron-beam exposure to enhance the wettability for ZnO growth.

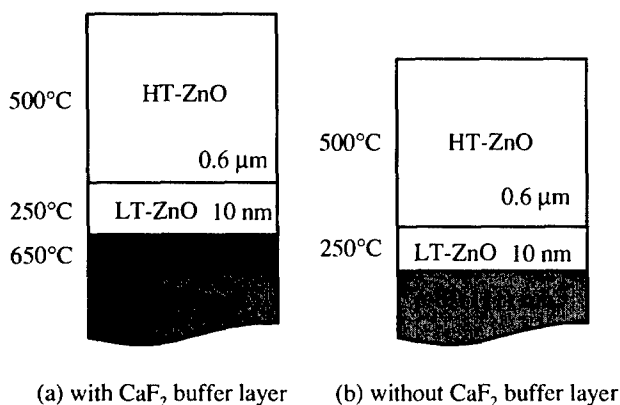


Figure 1. Schematics of two different ZnO/Si (111) heterostructures. (a) and (b) are the ZnO films with and without a CaF_2 buffer layer, respectively.

For both samples, the ZnO films of initial 10-nm-thick were deposited at 250°C using a growth rate of 200 nm/h to promote the nucleation of epitaxial growth [3]. After this low-temperature (LT) ZnO growth, the substrate temperature was elevated once up to 750°C under a Zn-beam irradiation to experience the LT-ZnO films an *in-situ* thermal annealing. Then we cooled down the substrate temperature to 500°C, and grew a high-temperature (HT) ZnO layer of 600 nm using a growth rate of 400 nm/h. We expected the combination of LT-ZnO growth and *in-situ* thermal annealing to improve both the crystalline quality and surface morphology of the ZnO films.

After the growth, these samples were characterized by atomic force microscopy (AFM) in air, x-ray diffraction (XRD) using Cu-K α radiation, and photoluminescence (PL) using the 325 nm line of a 20 mW He-Cd laser as the excitation source.

RESULTS AND DISCUSSION

In Figure 2, (a) and (b) show the RHEED patterns during growth. As seen from the pattern (1) of Figs. 2 (b), 7 $\times$ 7 streaks were observed from the surface before growth, indicating the clean and flat surface of the Si (111) substrate [6]. When the LT-ZnO was directly grown on the Si clean surface, the streak 7 $\times$ 7 pattern immediately changed into a ring pattern of which dependence on the direction of incident electron beam was not observed. This ring pattern essentially continued till the end of HT-ZnO growth as shown by the patterns (2) to (4) of Figs. 2 (b), although a little change to a spotty pattern was observed for the surface after HT-ZnO growth. These results indicate that polycrystalline or in-plane rotational domains are easily included in the ZnO layer due to the formation of amorphous Si-oxide on the Si surface.

On the contrary, a six-fold-symmetry pattern was observed when the LT-ZnO was grown on the CaF₂ buffer layer. At the very beginning of the LT-ZnO growth, a diffused spotty pattern like

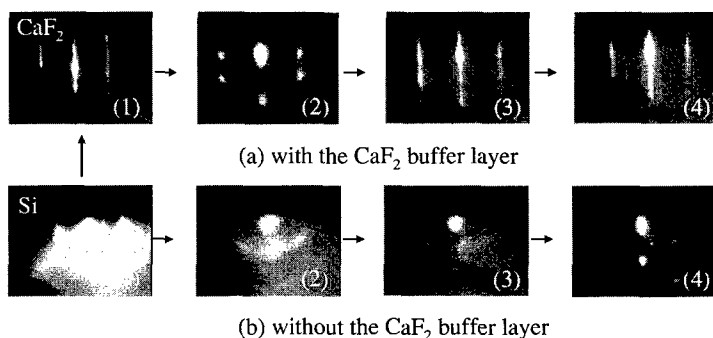


Figure 2. RHEED patterns observed from the samples with and without the CaF₂ buffer layer. In both series (a) and (b), for the samples with and without the CaF₂ buffer layer, (1) to (4) correspond to the surfaces before the LT-ZnO growth, after the LT-ZnO growth, after the annealing, and after the HT-ZnO growth, respectively.

(2) in Figs. 2 (a) appeared. The rod-spacing of the LT-ZnO is $\sim 16\%$ wider than that of the CaF_2 buffer layer, which is in good agreement with the difference in lattice constants between these two bulk materials, suggesting the strain-free growth of the ZnO epilayer. By the *in-situ* annealing at 750°C , this diffused spotty pattern was changed to a streaky one. The sharp streaks in the pattern (4) of Figs. 2 (a), from the surface after the HT-ZnO growth, indicate that both crystalline quality and surface morphology are dramatically improved by the use of the CaF_2 buffer layer.

It was revealed by AFM measurement that a typical root-mean-square (rms) roughness of the CaF_2 surface was $\sim 0.48\text{ nm}$ in $10 \times 10\ \mu\text{m}^2$ area. In agreement with the RHEED observation, the surface morphology became rough (rms roughness $\sim 4.0\text{ nm}$) after the LT-ZnO growth on the CaF_2 buffer layer. However, it was improved to be $\sim 2.5\text{ nm}$ after the HT-ZnO growth. Although similar improvement was also experienced by the sample without the CaF_2 buffer layer, the resulted morphology of the HT-ZnO surface was inferior (rms roughness $\sim 3.3\text{ nm}$) to that of the sample with the CaF_2 buffer layer.

In order to study their structural quality, we measured XRD of these two different samples. In Fig. 3 of θ - 2θ scan, (a) and (b) of which correspond to those in Fig. 1, two intense peaks located at 34.5° and 72.5° in both spectra closely agree with the (0002) and (0004) reflections from bulk ZnO, respectively. Since other peaks related to ZnO are not observed, both ZnO films with and without the CaF_2 buffer layer are considered to be highly c-axis oriented on the Si substrates. However, we found a large difference between these two samples in the in-plane crystalline quality by using the pole-figure measurement of XRD in the $\{10\bar{1}0\}$ diffraction. Note that θ - 2θ diffraction only reflects in-depth crystalline quality. In Fig. 4 of pole-figures, (a) and (b)

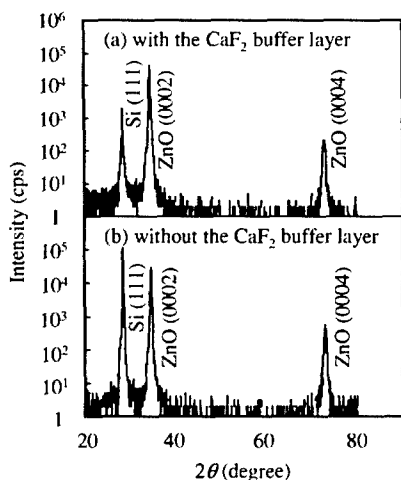


Figure 3. X-ray diffraction spectra in the θ - 2θ configuration from the ZnO films (a) with and (b) without the CaF_2 buffer layer.

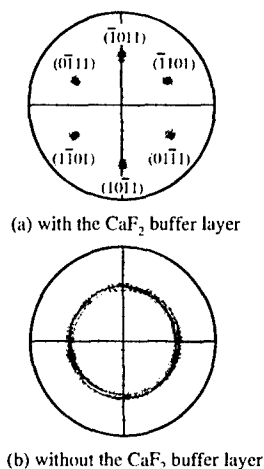


Figure 4. Pole-figures in the $\{10\bar{1}0\}$ configuration of x-ray diffraction from the ZnO films (a) with and (b) without the CaF_2 buffer layer.

are observed from the samples with and without the CaF_2 buffer layer, respectively. It is indicated that the ZnO film grown on the CaF_2 buffer layer is free from rotational domains and twins, since clear six-fold-symmetry is seen for the ZnO $\{10\bar{1}0\}$ reflection. On the contrary, the ring pattern of Fig. 4 (b) indicates that random rotational in-plane domains are included in the ZnO (0001) films when directly grown on Si substrates. Considering the RHEED pattern change in Fig.2 (b), these random rotational domains may be predominantly included in the bottom ZnO layer.

In order to compare these two samples on their optical properties, we measured PL spectra at 20 K although the spectra are not shown here. From the sample with the CaF_2 buffer layer, only narrow and intense peaks at 3.33 eV and 3.36 eV were observed. These peaks are attributed to the excitons localized at neutral acceptors and donors, respectively [8,9]. Since the full-width at half-maximum (FWHM) of these peaks was relatively small (~ 7 meV) and there was no sign from defect-related transitions, we can conclude that high-quality ZnO growth was achieved on the CaF_2 buffer layer. On the contrary, the sample without the CaF_2 buffer layer was found to contain many defects in the ZnO film, since broad peaks from defect-related transitions appeared at around 1.8 eV and 2.2 eV. These defect-related transitions are probably associated with non-stoichiometric recombination centers such as single-ionized oxygen vacancies and/or single-negatively-charged oxygen interstitials [10].

Figure 5 shows the PL spectrum measured at 300 K from the sample with the CaF_2 buffer layer. An intense peak from the excitons in ZnO is observed at 3.29 eV. The observed energy for the peak closely agrees the previously reported value for the free excitons in the ZnO films grown on sapphire substrates [8]. As shown by the inset of Fig. 5, the intensity of defect-related emission band is quite small (less than 1/400 of the intensity of excitonic emission) even at room temperature. Note that such a stable existence of free excitons is due to the large binding energy, and is promising for short-wavelength excitonic lasers operating at room temperature.

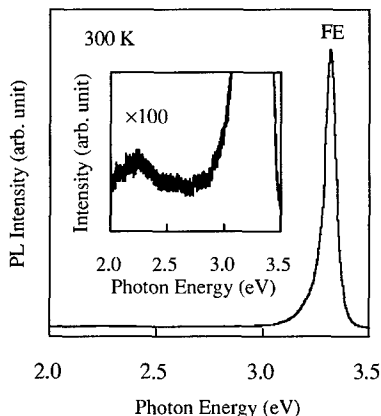


Figure 5. Room-temperature PL spectrum from the ZnO film with the CaF_2 buffer layer. An intense peak from free excitons is observed at 3.29 eV. Inset shows the vertically magnified spectrum.

This strong excitonic emission with a small FWHM of about 70 meV is a direct evidence for the high-quality of the ZnO films grown on the CaF₂ buffer layer.

CONCLUSION

We have succeeded in the MBE growth of the single-crystalline ZnO (0001) films on Si (111) substrates by using a thin CaF₂ (111) buffer layer. RHEED and XRD measurements show the growth of single-crystalline ZnO films without any rotational domains and twins. PL measurement reveals that an intense excitonic emission is dominant for the ZnO films even at room temperature. These results demonstrate that high-quality ZnO growth is achieved by using the CaF₂ buffer layer to suppress the oxidation of Si surface at the initial stage of ZnO growth.

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