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MOCVD growth of ZnO films on Si(1 1 1) substrate using a thin AlN buffer layer

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Abstract

High-quality ZnO films were grown on Si(1 1 1) substrate by MOCVD using a thin AlN buffer layer. A low-temperature ZnO buffer layer was further introduced to accommodate the lattice mismatch and thermal expansion coefficient mismatch between the ZnO epitaxial layer and the AlN buffer layer. In situ laser reflectance measurements show that two-dimensional growth has been obtained, and a smooth surface morphology is demonstrated by atomic force microscopy (AFM) measurements. X-ray diffraction (XRD) results show that the ZnO film is a single crystal. The FWHMs of (0 0 2) and (1 0 2) ω-scans for the 2.1 μm thick layer are 410 and 1321 arcsec, respectively. Free excitonic emission can be observed at low temperature and becomes dominant in the photoluminescence spectra above 120 K.
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1. Introduction

ZnO is a promising material for light emitters in the UV region. Compared with other wide band-gap semiconductors, ZnO has a larger exciton binding energy (59 meV) [1], which provides more efficient excitonic emissions at room temperature [2]. ZnO has also been employed in a vast range of devices including surface acoustic-wave devices and varistors [3]. The substrate selection is a crucial issue of ZnO growth. Although high-quality bulk ZnO substrates are now under development, their high cost and limited availability currently preclude their use in mass production environments. Heteroepitaxially grown ZnO to date has predominantly been grown on sapphire. However, sapphire is expensive,

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insulating and limited in size. Silicon, on the other hand, is an attractive substrate because of its low cost, good thermal conductivity, high crystalline quality, and availability of large size substrates and all types of conductivity. Unfortunately, the mismatch of lattice constants (15%) and thermal expansion coefficients (56%) between ZnO and Si(1 1 1) are quite large. Hence, growth of high-quality ZnO films on Si(1 1 1) will be a great challenge. In previous work, single crystal ZnO films have been grown using a Zn initial layer [4] or a thick GaN template [5,6]. By depositing an initial Al layer, we also obtained single crystal ZnO films on Si(1 1 1) [7]. However, these films have a FWHM of the (0 0 2) ω-scan of around 0.2°–0.3°, which are far inferior to ZnO films grown on sapphire [8,9]. In the present work, we use a thin AlN buffer layer to grow ZnO film on Si(1 1 1) substrate. AlN has the same wurtzite structure and a relatively small lattice mismatch (5%) to ZnO. The thermal expansion coefficient of AlN ($4.2 \times 10^{-6}\,K^{-1}$) [10] is in the middle between ZnO ($4.75 \times 10^{-6}\,K^{-1}$) [4] and Si ($2.6 \times 10^{-6}\,K^{-1}$) [4]. More importantly, single crystal AlN buffer layers can been grown directly on Si(1 1 1) [11]. All these properties suggest that AlN will be an appropriate buffer for ZnO films grown on Si(1 1 1) substrates.

2. Experiment

The AlN buffer layer was grown on a 2 in Si(1 1 1) substrate by a low-pressure MOCVD system (Thomas Swan Couple-Shower-Head). Prior to the AlN deposition, the Si(1 1 1) substrate was annealed at 1100 °C for 5 min in a H_2 ambient. Next, the 200 Å AlN buffer layer was deposited. The ZnO film was grown on the AlN/Si(1 1 1) template in a home made atmospheric pressure MOCVD. At first, a 400 Å ZnO buffer layer was grown at 160 °C. Then the buffer layer was annealed at 850 °C for 15 min. After that, the temperature was lowered to 680 °C, and the ZnO epitaxial layer was deposited. For the ZnO growth, DEZn and H_2O were used as the Zn and O precursors, respectively. During the ZnO growth, the morphology evolution of the film surface was investigated by an in situ reflectance monitor system that comprises a modulated 635 nm laser diode beam. After growth, the surface morphology of the ZnO film was studied by interference microscopy (OLYMPUS, BX51) and AFM (Benyuan Nano Instrument, China). ω-rocking curves of the film were measured using a double crystal X-ray diffractometer (QC200, BEDE Instruments, UK), in which Cu K_α line was used as the source and Ge (0 0 4) was used as the monochromator. Photoluminescence of the film was measured at a temperature range from 10 to 120 K. The 325 nm line of a He–Cd laser was used as the excitation source.

3. Results and discussion

Fig. 1 shows the trace of the reflectance intensity of the ZnO film at different times during growth. As an evidence of quasi-two-dimensional growth, regular oscillations can be seen in the reflectance. The growth time for each oscillation period is calculated to be 135 s from the reflectance trace. The thickness for one period can be calculated using the formula

$$2nd = \lambda,$$

where λ is the wavelength of the incident laser, n is the refractive index of ZnO, and d is the thickness

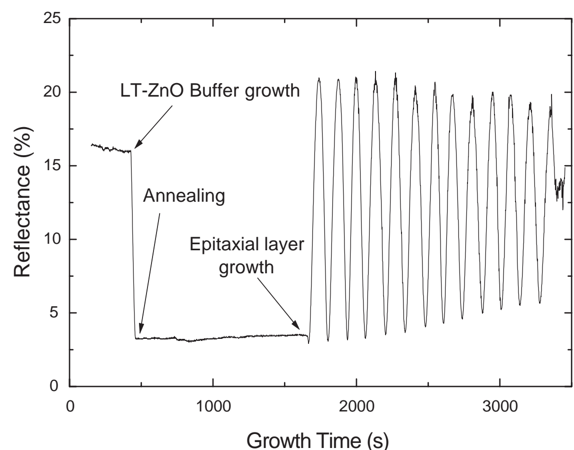

Fig. 1. Reflectance trace of the ZnO sample grown on AlN/Si(1 1 1) template.

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of a period. If $n = 2.0$ [1] is used, d can be calculated to be 158.8 nm. So that a growth rate $R = 1.2\,\mathrm{nm/s}$ is obtained, the total film thickness for 30 min growth is calculated to be 2.1 μm. Our growth rate (4.2 μm/h) is markedly faster than other reported values [4,5], indicating a greater potential for mass production using our growth method.

Fig. 2 (a) shows the microscopic image of the sample. The image shows a very flat surface, but several cracks can be seen clearly. The cracks are possibly formed during the cooling down process, due to the large mismatch of thermal expansion coefficients between ZnO and Si. The distance between the cracks is around 400 μm, and the crack density is estimated to be $25\,\mathrm{cm}^{-1}$. Nahhas et al. [6] reported a crack-free ZnO film on a GaN/Si(1 1 1) template, but the thickness of their ZnO sample is only 0.5 μm. It is well known that thicker strain films are more likely to crack than thinner ones due to stress. Kawamoto et al. [4] reported a crack density of $1.6 \times 10^2\,\mathrm{cm}^{-1}$ for a 1.0 μm thick ZnO film grown on Si(1 1 1) substrate. Our value is nearly an order of magnitude lower than this value. The AFM images of the film surface are shown in Fig. 2(b). For a scan area of 10 μm × 10 μm, the RMS roughness is 2.7 nm. The inset at the left top of Fig. 2(b) is an image for a scan area of 2 μm × 2 μm. In this region the RMS roughness is 1.7 nm.

The (0 0 2) and the (1 0 2) ω-rocking curves of the film are shown in Fig. 3. The FWHM of the (0 0 2) reflection is 410 arcsec. This value is significantly smaller than our previously obtained result by using only an Al initial layer [7]. It is also smaller than reported FWHMs for ZnO films grown on Si (1 1 1) using a Zn initial layer [4] or a thick GaN template [5,6]. This means that the AlN buffer layer is very effective to reduce the structural defects caused by the large lattice and thermal mismatch between ZnO and Si. To investigate the in-plane crystallinity of the ZnO film, an ω-scan for the (1 0 2) plane was performed. The rocking curve is shown in Fig. 3, and the FWHM is 1321 arcsec. The (1 0 2) ω-rocking curve has been suggested to be a more reliable indicator of total dislocation density than the (0 0 2) reflection [12]. To the best of our knowledge, no (1 0 2) rocking curves have been reported for ZnO films grown on Si(1 1 1) substrates until now. Comparing with GaN, it is shown that our FWHM values are comparable to high-quality GaN films grown on a Si(1 1 1) substrate [13,14].

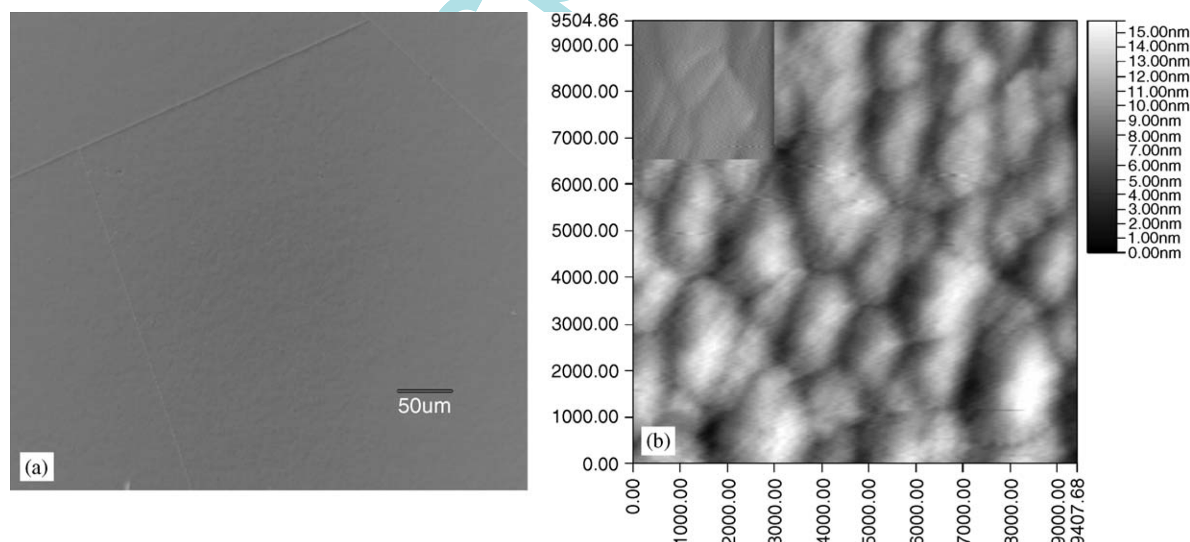

Fig. 2. (a) Microscopic image and (b) AFM images for the ZnO film grown on AlN/Si(1 1 1) template. The inset of (b) is a detailed scan for a small area (2 μm × 2 μm).

Fig. 4 gives the result of a temperature-dependent PL measurement of our ZnO/AlN/Si(1 1 1) sample. At 10 K, the spectrum is dominated by a peak at 3.353 eV. On the higher energy side, a shoulder appears at 3.366 eV. When the temperature increases, the intensity of the peak at 3.353 eV decreases, while the peak at 3.366 eV increases gradually and becomes dominant at 120 K. The temperature dependence of the intensity of the two peaks shows a typical nature of dissociation of bound excitons to free excitons.

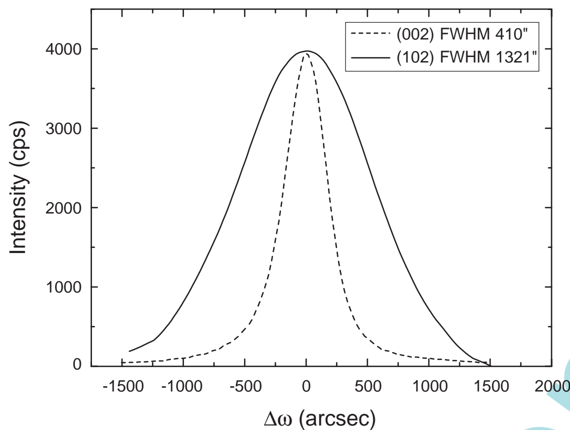

Fig. 3. Normalized (0 0 2) and (1 0 2) ω-rocking curves of the ZnO film grown on AlN/Si(1 1 1).

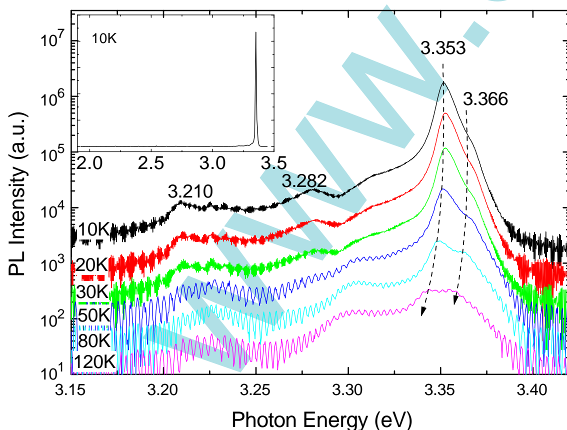

Fig. 4. Temperature-dependent PL spectra of the ZnO film measured from 10to 120 K. Inset at the left top shows the wide range spectrum measured at 10 K.

Thus, we attribute the peaks at 3.366 and 3.353 eV to emission from bound excitons and free excitons, respectively. It should be noted that the energy position of the free excitonic emission has a large red shift (10 meV) compared to that of bulk ZnO [1] and ZnO films grown on sapphire [15], indicating a large tensile strain in the film. This is caused by the large mismatch of the lattice constants and thermal expansion coefficients between ZnO and Si. The peaks at 3.282 eV and 3.210 eV are the 1LO and 2LO phonon replicas of the bound exciton peak, judged from their energy distances from the bound exciton peak (1×72 and 2×72 meV, respectively) [16]. The inset of Fig. 4(a) shows a wide range spectrum measured at 10 K. Only the exciton peak is seen, and the commonly observed green luminescence is absolutely absent, indicating the high optical quality of the film.

4. Summary

High-quality ZnO film has been grown on Si(1 1 1) substrate by using a thin AlN buffer layer. The film shows good crystallinity as demonstrated by XRD measurements. The film shows a flat surface and a low crack density. Strong excitonic emission is observed in low-temperature PL, and no deep-level emission is observed.

Acknowledgements

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