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Effect of growth temperature on a-plane ZnO formation on r-plane sapphire

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The effect of growth temperature on a-plane ZnO formation on r-plane sapphire has been systematically investigated by employing *in situ* high pressure reflection high-energy electron diffraction, atomic force microscopy, and high-resolution x-ray diffraction. For film growth above and below 600 °C, it is shown that there is a significant difference in growth rate and surface morphology due to the differences in the growth mode. Stripelike morphologies were observed on the surface of a-plane ZnO grown at low temperature (LT) because of differences in the growth rate along the c-axis and the growth rate normal to the c-axis. Furthermore, annealing of films grown at low temperature results in more pronounced stripe morphology and in improvement of crystallinity. © *2011 American Vacuum Society.* [DOI: 10.1116/1.3549141]

I. INTRODUCTION

Zinc oxide, a semiconductor with a hexagonal wurtzite structure ($P6_3mc$, a=3.213 Å, and c=5.213 Å),[1] has received much attention in the past decade because of its remarkable optical properties, which include a wide direct band gap and large excitonic binding energy. These properties make ZnO attractive for applications in optoelectronic devices such as light emitting diodes and laser diodes. Though the growth of high quality c-plane (0001) crystalline ZnO has already been successfully achieved,[2–4] it is well established that the built-in electrostatic field caused by piezoelectric polarization in wurtzite structure lowers the carrier recombination efficiency and degrades the optical emission properties. In order to avoid the so-called quantum confined Stark effect, nonpolar films without polarity along the growth direction are required. Hence, nonpolar a-plane and m-plane ZnO film growth has been intensively studied in recent years.

Sapphire is a commonly used substrate for growth of epitaxial optoelectronic thin films such as GaN, AlN, and ZnO. Srikant *et al.*[5] reported the epitaxial relationships of ZnO films grown on various orientation sapphire substrates including a-plane $(11\bar{2}0)$, m-plane $(1\bar{1}00)$, c-plane (0001), and r-plane $(1\bar{1}02)$ sapphire. Epitaxial orientation relationships for the growth of polar c-plane ZnO films on c-plane and on a-plane sapphire have been established. Also, nonpolar a-plane ZnO films have been successfully grown on r-plane sapphire. These films had a pure a-plane orientation, and the x-ray rocking curves exhibited a full width at half maximum (FWHM) of 0.72°–0.95° when the growth temperature was above 650 °C. However, the epitaxial orientation changed to $(0001)_{\mathrm{ZnO}} \parallel (1\bar{1}02)_{\mathrm{sapphire}}$ when the growth temperature was below 550 °C.

Though a-plane ZnO growth on r-sapphire has been studied in the past decade,[5–8] there is still much room for improvement on the crystalline quality of these films. Though high crystalline quality a-plane ZnO films can be obtained by plasma-assisted molecular-beam epitaxy (MBE),[9,10] its quality is still not comparable to that of a-plane GaN on r-sapphire even though these systems have similar lattice mismatch.[11,12]

To improve the crystallinity, it is essential to understand the growth evolution and surface morphology, which may depend on various deposition parameters. Pulsed laser deposition (PLD) is well established to grow high-quality epitaxial ZnO films on sapphire. Among experimental conditions for PLD of ZnO on sapphire, the thickness and growth temperature play important roles in determining the film quality. The advantage of using PLD for ZnO growth is that *in situ* reflection high-energy electron diffraction can be used to monitor the surface conditions during growth. Here, using reflection high-energy electron diffraction, high-resolution x-ray diffraction (HRXRD), and atomic force microscopy (AFM), we show that a-plane ZnO growth on r-sapphire by PLD at different substrate temperatures can result in a significant variation of ZnO growth rate, crystallinity, and surface morphology.

II. EXPERIMENT

ZnO films were grown on 8×8 mm^2 r-plane sapphire wafers in a Pascal laser-MBE system equipped with a KrF excimer laser and a high pressure reflection high-energy electron diffraction (RHEED) apparatus. The sapphire substrates were cleaned using acetone in the ultrasonic bath, followed by thermal cleaning in vacuum of at 850 °C and 10^{-6} torr. Thin films of ZnO were grown at temperatures ranging from 350 to 850 °C with 10 mtorr oxygen partial pressure.

The film surface was examined with *in situ* RHEED and *ex situ* AFM. Thickness and structural quality of ZnO films were evaluated using x-ray reflectivity (XRR) and x-ray rocking curve (XRC). AFM measurements were done in a Veeco Dimension 5000 scanning probe microscope system

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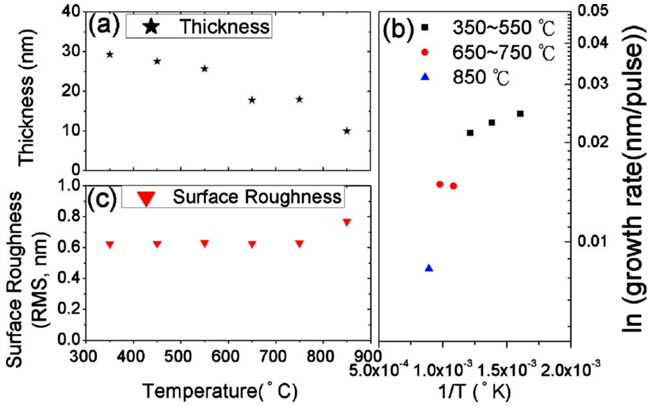

FIG. 1. (Color online) Variation of ZnO films of (a) thickness, (b) growth rates, and (c) surface roughness with growth temperature. The number of applied laser pulses for all deposition conditions was 1200.

operated in AFM tapping mode. All the X-ray experiments were performed on a Philips X'Pert Pro (MRD) diffractometer employing a graded parabolic x-ray mirror and a Ge (220) monochromator.

III. RESULTS AND DISCUSSION

The thickness and growth rates of ZnO after 1200 laser pulses at temperature ranging from 350 to 850 °C on r-plane sapphire substrates are shown in Fig. 1. Figure 1(a) clearly shows that the film thickness measured by XRR decreases with growth temperature even though these samples were grown using the same number of pulses and under otherwise the same deposition conditions. From 350 to 550 °C, the thickness slightly decreases from about 29 to 26 nm, but it significantly decreases to about 18 nm at 650 and 750 °C. The thickness of the film deposited at 850 °C is about 8 nm, which indicates a significant reduction in the growth rate with deposition temperature, as shown in Fig. 1(b). Several studies had reported that stoichiometric sublimation of ZnO takes place at an appreciable rate above 600 °C under ultrahigh vacuum conditions due to removal of lattice oxygen from the lattice.[13–15] Thus, it is likely that the lower growth rate at high temperatures might be due to the desorption and decomposition of ZnO. The corresponding surface roughness of the deposited films is shown in Fig. 1(c). All films deposited after 1200 pulses have a root-mean-square (rms) value below 0.8 nm, suggesting that all the film surfaces are very smooth.

Figure 2 shows the surface morphology of 10 nm thick ZnO films deposited at 450, 750, and 850 °C. Figure 2 shows that the surface roughness increases from 0.35 nm for the film deposited at 450 °C to 0.78 nm for the film deposited at 850 °C. The AFM images in Figs. 2(d)–2(f) show that stripelike morphology can be recognized on the surface of the films deposited at low temperature (LT), while no such characteristics can be seen on the surface of the film deposited at 850 °C. The corresponding *in situ* RHEED patterns of these 10 nm thick films are shown in Figs. 2(a)–2(c). All the patterns exhibit periodic reflections, indicating that the a-plane ZnO films deposit epitaxially on the r-plane sapphire. In the RHEED pattern of the film deposited at 450 °C, long and streaky lines can be clearly seen, indicating that the film has a smooth surface consistent with the AFM observation in Fig. 2(f). However, more spotty reflections are observed in the pattern exhibited by the film deposited at 850 °C because of its rough surface. Moriyama and Fujita[16] reported similar observations, showing that the morphology consists of three-dimensional (3D) islands when growth is at 800 °C and is stripelike at 500 °C. These results suggest that low-temperature deposition may lead to a larger flat surface, while high-temperature (HT) deposition may favor island growth in the initial stages.

To understand the surface evolution, we have done a series of *in situ* RHEED observations during growth. Figure 3 shows the RHEED patterns of ZnO taken with electron beam incident along ZnO [0001] after film growth at 450 °C (designated as LT) and after film growth at 750 °C HT. After growth of ZnO in 5 nm thickness on r-plane sapphire in the temperature range 350–850 °C, ZnO exhibits a 3D island structure as Figs. 3(a) and 3(d) show spotty reflections in the RHEED patterns. After growing 50 nm thick films, the reflections in both LT and HT RHEED patterns become streaky lines, suggesting that the surface smoothness is improved. Similar results have been reported previously and it was shown that the surface exhibits a 3D island structure at the beginning of the growth, while further growth can make the surface smoother due to the lateral growth.[16,17]

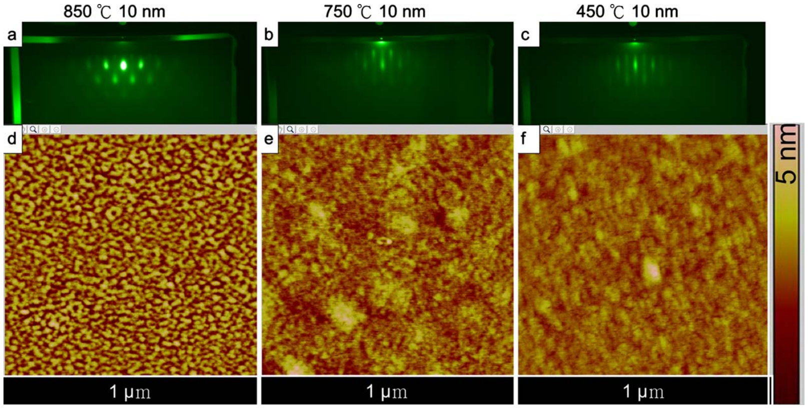

FIG. 2. (Color online) [(a)–(c)] RHEED patterns and [(d)–(f)] AFM images of 10 nm ZnO films grown at [(a) and (d)] 850, [(b) and (e)] 750, and [(c) and (f)] 450 °C.

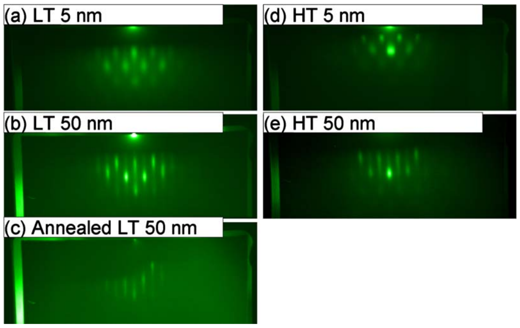

FIG. 3. (Color online) *In situ* RHEED patterns of ZnO taken with electron beam incident along ZnO [0001] after various film growth conditions. (a) After growth of 5 nm thick ZnO at 450 °C. (b) After growth of 50 nm ZnO at 450 °C and (c) after further direct annealing at 750 °C in 1×10^{-2} torr O_2. (d) After direct growth of 5 nm thick ZnO on sapphire and (e) 50 nm ZnO at 750 °C.

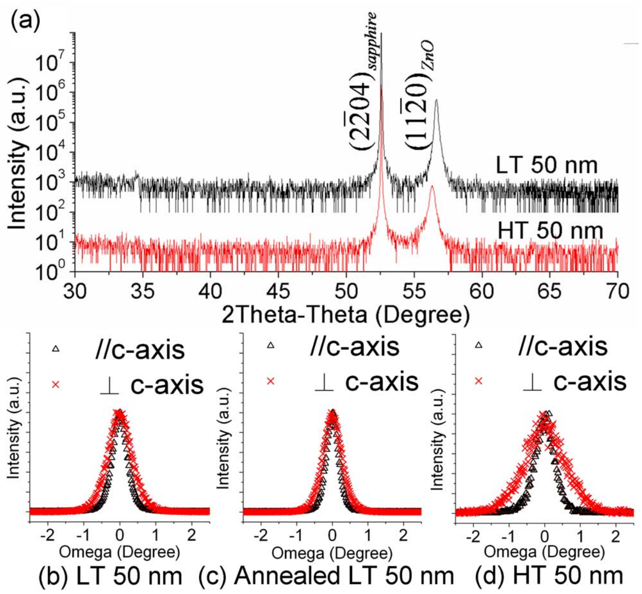

FIG. 5. (Color online) (a) X-ray $2\theta/\theta$ survey spectrum of 30°–70° taken from ZnO films growing condition with (red) 750 °C 50 nm and (black) 450 °C 50 nm. [(b)–(d)] The $(11\bar{2}0)_{ZnO}$ XRCs determined by HRXRD with 50 nm films grown at (b) 450 °C and (c) after annealing at 750 °C, and at (d) 750 °C.

The AFM images of 50 nm thick LT and HT grown ZnO films are shown in Figs. 4(a) and 4(c). These figures show that the LT ZnO exhibits stripelike morphology, whereas the HT ZnO films do not show these striped features. The fact that there is a morphology difference between LT and HT ZnO films supports the conclusion reached based on the thickness measurement shown in Fig. 1 that low temperature growth mode of a-plane ZnO is different from that at high temperature. Anisotropic diffusion rate and large strain due to anisotropic lattice mismatch between ZnO c-axis and m-axis may result in anisotropic growth of a-plane ZnO between parallel and perpendicular to the c-axis at low temperature.[18] For high temperature growth, the large anisotropic strain might be relaxed and surface diffusion might be similar at both directions, resulting in the growth rate parallel to the c-axis being not significantly different than that perpendicular to the c-axis. As a result, the surface morphology exhibits the step-terrace characteristics when the film thickness is 50 nm. The roughness measurements by AFM show that the 50 nm HT thick film has a roughness of 0.4 nm, smaller than 0.6 nm, the value for the 17 nm thick HT film [Fig. 1(c)].

Interestingly, if the 50 nm thick LT film is directly annealed at 750 °C for 10 min with oxygen pressure of 1×10^{-2} torr in the PLD chamber, the characteristics in the RHEED pattern shown in Fig. 3(c) are nearly the same as that obtained from the film that was not annealed [Fig. 3(b)], implying that the surface structure remains unchanged and the surface smoothness is similar in the direction of the electron beam. However, the AFM image in Fig. 4(b) reveals that the surface evolves into more pronounced stripe morphology as the stripe width increases to ~80–100 nm after annealing. This is in comparison to width (~50 nm) before annealing. This result suggests that increasing the deposition temperature may enhance the diffusion and lateral growth perpendicular to the c-axis.

Figure 5(a) shows x-ray $2\theta/\theta$ patterns from 50 nm thick LT and HT grown ZnO films. Clearly, only r-plane sapphire and $(11\bar{2}0)_{ZnO}$ peaks are seen at 54.5° and 56.5°, respectively, without a visible (0002) ZnO peak. The $(11\bar{2}0)_{ZnO}$ XRCs shown in Figs. 5(b)–5(d) illustrate that the FWHM of the HT film is 0.625° in the direction parallel to the c-axis and 1.314° in the direction normal to the c-axis. For the LT film, the FWHM is 0.5° in the direction parallel to the c-axis and 0.7° in the direction normal to the c-axis. Thus, low-temperature growth can result in better film crystallinity. Further annealing of the LT film at 750 °C for 10 min can improve the film crystallinity as the FWHM of the XRC decreases to 0.44° in the direction parallel to the c-axis and 0.67° in the direction normal to the c-axis.

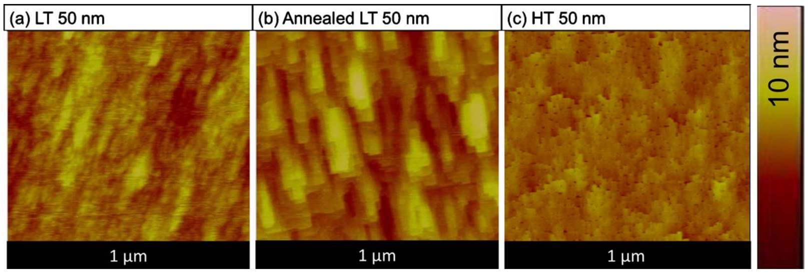

FIG. 4. (Color online) AFM images showing surface morphologies of 50 nm ZnO films grown at (a) 450 °C and (b) after annealing at 750 °C, and at (c) 750 °C.

IV. SUMMARY AND CONCLUSIONS

In conclusion, it has been shown that the growth rate of a-plane ZnO on r-plane sapphire decreases with increasing growth temperature in pulsed laser deposition. The surface morphology of a-plane ZnO grown at low temperature is stripelike, and the surface smoothness is improved with increasing film thickness. For high-temperature growth, the initial surface of the a-plane ZnO exhibits 3D island morphology that evolves to step-terrace morphology with increasing film thickness. This improves the surface smoothness. Annealing of low-temperature grown a-plane ZnO at high temperature increases the width of the stripes and the film quality.

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