Thermal pretreatment of sapphire substrates prior to ZnO buffer layer growth

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(Received 2 April 2013; accepted 25 July 2013; published 12 August 2013)

The properties of ZnO buffer layers grown via metal-organic chemical vapor deposition (MOCVD) on sapphire substrates after various thermal pretreatments are systematically investigated. High-temperature pretreatments lead to significant modifications of the sapphire surface, which result in enhanced growth nucleation and a consequent improvement of the surface morphology and quality of the ZnO layers. The evolution of the surface morphology as seen by atomic force microscopy indicates an obvious growth mode transition from three-dimensional to quasi-two-dimensional as the pretreatment temperature increases. A minimum surface roughness is obtained when the pretreatment temperature reaches 1150 °C, implying that a high-temperature pretreatment at 1150 °C or above may lead to a conversion of the surface polarity from O-face to Zn-face, similar to processes in GaN material growth via MOCVD. By analyzing the evolution of the film properties as a function of pretreatment temperature, the optimal condition has been determined to be at 1150 °C. This study indicates that a high-temperature pretreatment is crucial to grow high-quality ZnO on sapphire substrates by MOCVD. © 2013 American Vacuum Society.

[http://dx.doi.org/10.1116/1.4817825]

I. INTRODUCTION

ZnO has attracted considerable interest as a wide and direct band gap semiconductor material and can be used in solar cells, ultraviolet photodetectors, and short-wavelength light emitting devices. Many achievements have been made due to the fact that high-quality ZnO epitaxial layers can be grown using various methods, such as molecular beam epitaxy, pulsed laser deposition, and metal-organic chemical vapor deposition (MOCVD). The MOCVD technique has been a proven method to grow high-quality III–V semiconductor materials and is also believed to be suitable for ZnO growth.

Up to now, systematic and optimized high-quality ZnO MOCVD growth techniques have not been attained due to the diverse selection of Zn and O precursors and a lack of well-developed commercial MOCVD systems. Comparable to GaN epitaxy, (0001) sapphire is believed to be a good substrate choice for ZnO growth due to the similar hexagonal structures. However, the crystal quality of ZnO films directly grown on a sapphire substrate is usually poor due to a large lattice mismatch and the formation of rotation domains. Various buffer layers have been employed to improve the ZnO MOCVD growth.

In addition to the low-temperature buffer layer technique mentioned above, which has been confirmed to successfully improve the GaN-based heteroepitaxy on a lattice mismatched sapphire substrate, a critical step in this approach is high-temperature pretreatment of the sapphire substrate prior to the buffer layer growth. It is well established that nitridation of the sapphire surface before GaN growth can improve the material properties. This nitridation plays a critical role in the growth mode of the buffer layers and the crystal quality of the overlaying GaN epilayers. For ZnO growth, however, few results have been reported upon the effect of sapphire substrate thermal pretreatments.

In this work, the effects of the sapphire thermal pretreatment and post-in situ annealing upon the ZnO buffer layer growth have been systematically studied. The post-in situ annealing shows an obvious effect on the structure and properties of the ZnO buffer layers, and thermal pretreatment at different temperatures is found to cause pronounced changes in the surface morphology and the crystallinity. By observing the thermal pretreatment-induced modification of the sapphire surface, we have inferred the mechanism of the surface nitridation, which is believed to be beneficial to the initial nucleation of ZnO and the subsequent growth of ZnO epilayers.

II. EXPERIMENT

The ZnO buffer layers were grown on (0001) sapphire substrates at low pressure in a home-built vertical MOCVD reactor. The geometry of the reactor was similar to the Thomas Swan Closed Couple Showerhead (TS-CCS) but with smaller dimensions. The cylindrical vertical reactor was made of stainless steel, with the water-cooled showerhead (Ø = 8 cm) and susceptor located in the center of the reactor. The showerhead nozzles (Ø = 0.3 mm) were uniformly distributed on the underside of the showerhead spaced at a distance of 4 mm from each other. Adjacent nozzles were used to input different kinds of reaction precursors to prevent parasitic gas phase reactions. The standard process used for the samples studied in the work is described as follows: First, the sapphire substrates were individually treated in a nitrogen and hydrogen mixed environment at four different temperatures for 5 min. Second, ZnO buffer layers were grown on the pretreated...
sapphire substrates for 30 min at 470 °C using high-purity DMZn as the Zn precursor and t-BuOH as the O precursor. Finally, an in situ annealing process at 1000 °C was carried out in a nitrogen and nitrous oxide mixed environment for 5 min to improve the surface morphology and structural quality of the as-grown ZnO buffer layers. The obtained ZnO films are then marked as samples A, B, C, and D, corresponding to different pretreatment temperatures of 1050, 1100, 1150, and 1200 °C, respectively. The thicknesses of the samples A–D are 461.8, 583.4, 584.3, and 582.4 nm, respectively, which were measured by fitting the reflectance spectra recorded by a thin film measurement system (Avantes).

In order to investigate the annealing effect of the buffer layers, another two samples labeled samples E and F were grown at the same growth conditions as sample C without the postannealing process. However, sample E was grown on a pretreated substrate, while sample F was grown on an untreated substrate. In addition, two sapphire substrates were also employed for references and comparisons, including an as-received substrate labeled sample G and a thermally pretreated substrate labeled sample H.

The crystallinity of the ZnO materials was analyzed by high-resolution x-ray diffraction (HRXRD) using a Philips X’pert Pro diffractometer equipped with a Cu-ray source (λ = 0.15405 nm). The surface morphology was investigated by atomic force microscopy (AFM, Nanoscope IIIa, Digital Instruments, Inc.). The photoluminescence (PL) spectra were recorded at room temperature, using an He-Cd laser (λ = 325 nm) as the excitation source. Hall measurements (Keithley Instruments, Inc.) using indium as the electrode material were performed at room temperature in a van der Pauw configuration.

III. RESULTS AND DISCUSSION

Since the buffer layer surface morphology is crucial to subsequent high-temperature growth of the ZnO epilayers on a sapphire substrate, an AFM is employed on samples A–F to investigate the surface. The images shown in Fig. 1 are obtained over a scanning area of 5 × 5 μm². We find that the average domain size increases with pretreatment temperature and reaches its maximum value at 1150 °C. In addition, the surface roughness (z-range root mean square), as shown in Fig. 3(a), decreases with the pretreatment temperature, reaching its minimum value at 1150 °C. The evolution of the surface roughness indicates that the growth mode likely changes from three-dimensional to quasi-two-dimensional as the pretreatment temperature increases from 1050 to 1150 °C.

Figure 2(a) shows the XRD patterns of samples A–D. All samples exhibit a ZnO (0002) preferential orientation parallel to the c-axis of a sapphire substrate. The diffraction peak becomes stronger when the pretreatment temperature is increased from 1050 to 1150 °C and reaches its maximum peak height at 1150 °C. Figure 3(b) shows the coherence lengths of the sample series calculated from the XRD patterns. The Scherrer’s equation we employed to calculate the coherence length and the inhomogeneous strain of the films is described as follows:

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\begin{align*}
\delta \theta_{002} &= \frac{\lambda}{2D \cos \theta_{002}} + \varepsilon_{in} \tan \theta_{002} \\
\delta \theta_{004} &= \frac{\lambda}{2D \cos \theta_{004}} + \varepsilon_{in} \tan \theta_{004}
\end{align*}
\]

where \( \lambda \) is the wavelength of the Cu Kα line, \( \delta \theta \) and \( \theta \) denote the full width at half maximum (FWHM) and the center of the diffraction peak, respectively, and \( D \) and \( \varepsilon_{in} \) are the calculated values of the coherence length and inhomogeneous strain along the z axis, respectively. The coherence length increases from 140 to 210 nm when the pretreatment temperature is increased from 1100 to 1150 °C. However, when the pretreatment temperature exceeds 1150 °C, the coherence length decreases. The maximum value of the coherence length can be attributed to improvement of the crystallization of the ZnO buffer layer when the substrate is pretreated at 1150 °C. The surface domain sizes of the sample series as seen in the AFM images are plotted in Fig. 3(b) for comparison with the coherence length values. The FWHM values of the ZnO (0002) ω-scan rocking curve show a similar temperature-dependence trend as the surface roughness and are plotted in Fig. 3(a) for comparison.

The optical properties of the ZnO buffer layers are investigated using room-temperature (RT) PL, as shown in Fig. 2(b). The FWHM of the near band edge emission (NBE),
shown in Fig. 3(c), displays a similar temperature dependence as surface roughness. However, a strong deep level emission (DLE) in the band gap can be observed in sample C. The DLE peak near 522 nm can be ascribed to radiative recombination via deep levels of native defects, such as zinc vacancies ($V_{Zn}$)\textsuperscript{11} or oxygen vacancies ($V_{O}$)\textsuperscript{12–14}. Figure 3(c) shows the normalized intensity ratio of the NBE peak to the DLE peak around 522 nm at RT. The ratio of NBE to DLE decreases when the pretreatment temperature increases, reaches a minimum value at 1150°C, and further optimization needs to be employed to improve the optical quality. In fact, our recent experiments have shown the observed visible emission can be greatly suppressed by further optimization of the growth temperature and the II/VI ratio used for the ZnO buffer layer growth.

Hall measurements are applied on samples A–D, and Fig. 3(d) shows the carrier concentration and Hall mobility of the sample series. The carrier concentration increases with increasing pretreatment temperature and reaches its maximum value of $7.5 \times 10^{18}$ cm$^{-3}$ at the temperature of 1150°C.

In situ annealing of the buffer layers is an important factor influencing their structure and properties. Therefore, we also study the effect of postgrowth annealing by comparing

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**Fig. 2.** (Color online) (a) XRD $\alpha$-2$\theta$ scan patterns and (b) RT PL spectra of ZnO buffer layers as a function of the pretreatment temperature.

**Fig. 3.** (Color online) (a) RMS surface roughness (black stars) and FWHM of the x-ray rocking curve (blue squares) as a function of the pretreatment temperature. (b) Coherence length (black stars) and domain size (blue squares) of the samples as a function of the pretreatment temperature. The coherence length is derived from HRXRD measurements and the domain size from AFM images. (c) Intensity ratio of NBE to DLE (black stars) and FWHM of the NBE (blue squares) as a function of the pretreatment temperature. (d) Variation of mobility (black stars) and carrier concentration (blue squares) as a function of the pretreatment temperature.
two samples with and without the in situ annealing process. In Fig. 1, the surface morphologies of samples E and C are examined, where we can see that sample E shows a flat surface with some hexagonal pits, but sample C shows a flat surface with some hexagonal pits. The in situ high-temperature annealing causes crystallization of sample C due to temperature-induced Ostwald ripening and the FWHM of the (0002) ω-scan rocking curve decreases from 0.44° to 0.30° between samples E and C. Moreover, as shown in Fig. 4(a), a stronger NBE is observed from sample C due to the Ostwald ripening, which results in improvement of the optical properties. Room temperature Hall measurements on samples E and C also show that the carrier mobility increases from 16.5 to 37.0 cm² V⁻¹ s⁻¹, respectively, along with an increase in carrier concentration from 8.1 × 10¹⁷ to 7.5 × 10¹⁸ cm⁻³, respectively.

The above study shows that the in situ annealing contributes to the improvement of the ZnO buffer layers but cannot be completely responsible for all of the significant changes in the structure and properties observed in samples A–D. This suggests that the pretreatment temperature also plays an important role in producing high-quality ZnO buffer layer growth. We next make a direct comparison of the effect of the thermal pretreatment, and Fig. 1 shows the surface morphologies of samples E and F with sample thickness of 577.2 and 472.6 nm, respectively. In contrast to the sample F surface, a much smoother surface is attained on sample E with a significantly lower density of pyramids. Meanwhile, the coherence length calculated using Scherrer’s equation increases from 145 nm for sample F to 185 nm for sample E. Figure 4(a) plots the RT PL spectra of samples F and E. Both of the samples show similar NBE spectra, indicating that thermal pretreatment has little influence on the optical property improvement of the buffer layers. However, the crystal quality is greatly improved, as seen from the changes in the XRD (0002) ω-scan rocking curves. The FWHM of the XRD (0002) ω-scan rocking curves decreases from 0.73° in sample F to 0.44° in sample E, as shown in Fig. 4(b), which is consistent with the coherence length increase obtained earlier. Furthermore, RT Hall measurements for samples F and E show an increased value of carrier mobility from 7.1 to 16.5 cm² V⁻¹ s⁻¹, respectively, which further certify the role that high-temperature pretreatment play in the improvement of buffer layer quality.

Many studies on the high-temperature pretreatment of sapphire for GaN growth by MOCVD and hydride vapor phase epitaxy have been reported previously. Masu et al. reported the formation of a one nanometer-thick AlN single crystal on the surface of sapphire substrates at 1050 °C. Dwikusuma et al. confirmed that the nitrogen incorporated in the sapphire surface is caused by reactions between NH₃ and sapphire, and a previous study reported that the reaction between sapphire and N₂ only occurs at temperatures greater than 1200 °C. As shown from the thicknesses of samples A–F (A/461.8 nm, B/583.4 nm, C/584.3 nm, D/582.4 nm, E/577.2 nm, and F/472.6 nm), the pretreatment process with a temperature of at least 1100 °C causes significant surface modification of the sapphire substrate, resulting in an enhanced nucleation of ZnO with an enhanced growth rate. It has also been suggested that thermal pretreatment may cause a change in the polarity of the GaN surface, from N-terminated to Ga-terminated, as the temperature of the pretreatment is increased. This would cause a much smoother surface on the samples pretreated at high temperatures. The thermal annealing of a sapphire substrate in an ambient oxygen atmosphere has also been previously reported to improve the ZnO growth and film quality by Wang et al. However, the surface morphology in that work is vastly different from ours due to a different ambient annealing atmosphere. The ambient oxygen should cause an oxygen-terminated sapphire surface, which may be responsible for the rough surface covered with grains that was observed in that work.

In order to understand the reason that the thermal pretreatment of the sapphire substrate has an effect on the ZnO buffer layer growth, we investigate the surface morphology changes of the sapphire substrate induced by thermal pretreatment. As shown for GaN growth on sapphire, high-temperature thermal pretreatment in mixed ambient N₂ and H₂ may cause a surface reaction of the ambient gases with the sapphire, resulting in intermediate phases, such as AlN or Al₂O₃ layers, forming on the sapphire surface. This reaction and the resulting intermediate layer may cause roughening of the sapphire surface, which may also provide nucleation sites for
the ZnO buffer layer growth. Moreover, this intermediate layer is believed to play a critical role in relieving the large mismatch of the lattice constants and the thermal expansion coefficients between the ZnO epilayer and the sapphire substrate. The surface morphology changes can be easily observed by AFM as shown in Fig. 5, whose images are obtained at an arbitrary surface region of $1 \times 1 \mu m^2$ size of the sapphire substrate before (sample G) and after (sample H) the high-temperature pretreatment process. The thermal pretreatment induces distinct changes in the sapphire surface morphology, as discussed above. The surface root mean square roughness (RMS) of samples G and H is 0.220 and 0.105 nm, respectively. The slightly higher RMS of sample G is due to scratches on the sapphire surface. The XRD measurements do not show any second phases that may have been formed by the thermal pretreatment process, but the detection limits are such that a very thin intermediate layer may be indetectable.

The effect of thermal pretreatment on GaN growth has been previously explained using the approach of an enhanced Ga atom migration rate on the growing surface, where it is suggested that the Ga adatoms possess greater mobility on the pretreated sapphire, thereby enhancing the lateral growth of the buffer layer. This may also be an effective explanation for ZnO buffer layer growth by MOCVD, where the migration rate of zinc atoms may increase with the pretreatment temperature, resulting in the smooth surface morphology observed on the buffer layer. The surface polarity changes induced by thermal pretreatment observed during GaN growth may also occur in this work. The surface thermal pretreatment may cause a change of the grown ZnO surface polarity from O-face to Zn-face as the temperature increases, with the result of a much smoother surface morphology and a higher crystal quality achieved on sample C grown with a pretreatment temperature of 1150°C. However, further experiments to determine the surface polarity of the ZnO buffer layers, such as chemical etching, should be employed to obtain more knowledge about the underlying mechanism governing the effect of the thermal pretreatment on the ZnO growth.

IV. SUMMARY AND CONCLUSIONS

The mechanism to grow high quality ZnO buffer layers on sapphire substrates via MOCVD is investigated in this work. A high-temperature pretreatment leads to significant modification of the sapphire surface, which results in enhanced growth nucleation and the consequent improvement of the surface morphology and quality of ZnO layers. The evolution of the surface morphology as investigated by AFM indicates an obvious growth mode transition from three-dimensional to quasi-two-dimensional as the pretreatment temperature increases. A minimum surface roughness is obtained as the pretreatment temperature reaches 1150°C, implying that this temperature or higher for a pretreatment may lead to a conversion of the surface polarity from O-face to Zn-face, similar to the process undergone during GaN material growth via MOCVD. The optimal pretreatment temperature is determined to be 1150°C by analyzing the evolution of the film properties with changing pretreatment temperature. This study indicates that a high-temperature pretreatment is crucial to grow high-quality ZnO buffer layers on sapphire substrates via MOCVD.

ACKNOWLEDGMENTS

This research was supported by the State Key Program for Basic Research of China under Grant No. 2011CB302003, National Natural Science Foundation of China (Nos. 61025020, 60990312, and 61274058), Basic Research Program of Jiangsu Province (BK2011437), and the Priority Academic Program Development of Jiangsu Higher Education Institutions.


