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Effect of MgO in ZnO films grown on nitrided sapphires

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Abstract

An improved MBE-grown ZnO film on nitrided sapphire was obtained by introducing an MgO buffer layer before the ZnO growth. The effect of MgO layer was systematically studied by transmission electron microscopy investigations. It was found that the island feature of MgO buffer promoted the strain relaxation of the nitrided layer, which, in turn, improved the quality of the ZnO film.
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1. Introduction

As a wide-band-gap (3.37 eV) semiconductor with unique promising electronic and optoelectronic properties, ZnO has been investigated extensively in the last decade [1–6]. The current challenge is to fabricate device-quality ZnO films for their practical use [3]. Like GaN films, wurtzite ZnO films have been generally grown on (0 0 0 1) sapphire substrates, although there is a significant lattice mismatch (18.3%) between them. In order to decrease various defects caused by the lattice mismatch, many efforts have been made to secure high-quality ZnO films with a low density of defects (mainly dislocations) [2,3], such as low-temperature (LT)-ZnO buffer layer and post-annealing has been used to reduce dislocations in subsequent layers grown at high temperatures (HT) [7,8]. Among different strategies, nitridation of sapphire has been verified as an effective way to decrease the defects and to improve the quality of ZnO films [3,9]. Since the crystal structure and quality of the nitrided layer (AlN) is very sensitive to the nitridation conditions (such as the substrate temperature, nature of the nitrogen source, gas flowrate) [10,11], significant efforts have been devoted to develop high-quality ZnO films through tuning the nitridation conditions [3,9]. However, very few studies have been carried out to investigate microstructures of the AlN-nitrided layer and its effect on the quality of ZnO films. As a consequence, the growth mechanism of ZnO films remains unclear, although it is vitally important for design and manufacture of device-quality ZnO films with desired properties.

In our previous studies [3,12], nitridation of (0 0 0 1) sapphire surfaces has been successfully employed to control the polarity of epitaxially grown ZnO films. However, the dislocation densities in those studies remain high due to the unrelaxed AlN-nitrided layer by its underlying sapphire substrate. For this reason, the subsequently grown ZnO films experienced a high strain, which, in turn, resulted in a high density of dislocations in the ZnO films.

In this study, by introducing an MgO buffer layer between the AlN-nitrided layer and the ZnO film, we aimed

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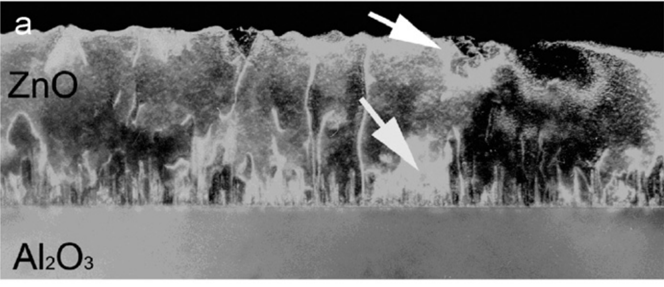
to grow an improved ZnO film with a relatively low density of dislocations and a smooth surface. The fundamental reason for this achievement was determined by detailed characterizations using transmission electron microscopy (TEM).

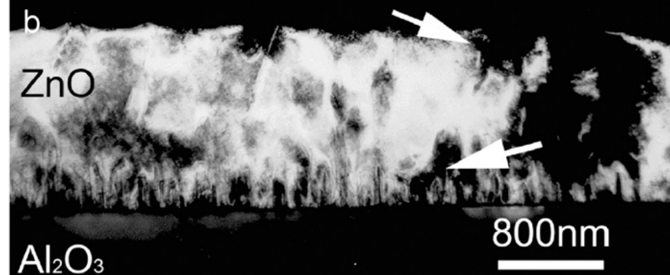
2. Experimental procedure

Two ZnO thin films were epitaxially grown on (0 0 0 1) sapphire substrates in a radio frequency (RF) plasma-assisted molecular beam epitaxy (MBE) system (OmniVac) using an elemental Zn source and two RF-plasma sources. The fluxes of nitrogen and oxygen gases were controlled by two mass-flow controllers. For sample A, the sapphire substrate was thermally cleaned at 800 °C and nitrided at 350 °C. After nitridation, a conventional two-step growth of ZnO, i.e., LT-ZnO buffer at 450 °C (10 min) and HT-ZnO epilayer at 650 °C (180 min), was performed. For sample B, an additional MgO layer was grown between the nitrided AlN layer and the ZnO film at 450 °C, followed by thermal annealing at 750 °C for 20 min. Then, the LT-ZnO buffer layer and HT epilayer were deposited at 450 °C (10 min) and 650 °C (180 min), respectively. Both these samples were finally subjected to a 30 min annealing at 750 °C after the growth of the HT-ZnO epilayer. The in-plane epitaxial relationship, surface morphology and crystallinity of grown ZnO films were monitored *in situ* by the reflection high-energy electron diffraction (RHEED) attached with the MBE system and were investigated by cross-sectional TEM (XTEM) in a Philips CM200 field emission gun TEM equipped with a Gatan image filtering (GIF) system (operating at 200 kV). TEM specimens were prepared by the conventional mechanical grinding and polishing, followed by ion beam thinning in a Gatan precision ion polisher system.

3. Results and discussion

Figs. 1(a) and (b) are a pair of typical dark-field XTEM images with $g = \pm 0002^*$ taken from sample A. By comparing the two XTEM images, one can clearly see inversed white/black contrasts when imaged with opposite g, indicating the existence of inversion domains (IDs)—marked by arrows [13,14]. In addition, a high density of dislocations (about $10^{10}\,\text{cm}^{-2}$) can also be estimated using a method proposed in Ref. [13]. In order to understand the detailed atomic structures at the interfacial region, high-resolution TEM (HRTEM) was carried out. Fig. 1(c) shows an example in which the AlN-nitrided layer sandwiched between the ZnO film and the sapphire substrate can be clearly seen. It is of interest to note that (1) IDs [the left part AlN(Al) being Al-polarity and the right part AlN(N) being N-polarity] can be seen in the nitrided layer, which extended to the ZnO films; (2) the IDs in the ZnO film are also observed [marked by arrows in Figs. 1(a) and (b)]; and (3) a significant misfit strain was found in the nitrided layer evidenced by its distorted





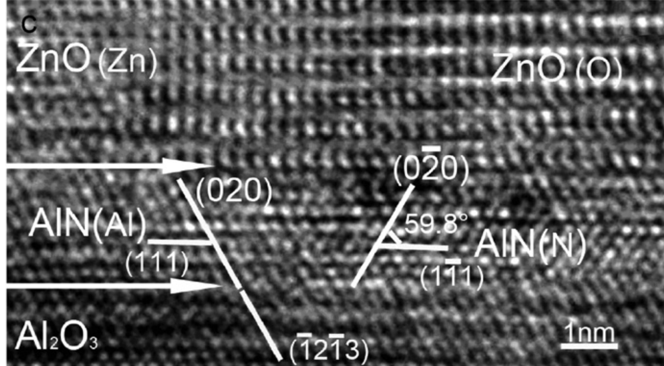


Fig. 1. Typical dark field XTEM image of sample A with $g = 0002^*$ and (a) $g = 000\bar{2}$ (b). (c) An HRTEM image showing interfaces of ZnO/AlN/sapphire substrate.

atomic planes (the angles between {0 2 0} and {1 1 1} being measured as 59.8° as opposed to the relaxed system of 54.7°) [12], which has been transferred into the ZnO film with a high density of dislocations, i.e., the nitrided layer did not act as a buffer layer in terms of the strain relaxation between the ZnO film and the sapphire substrate.

In comparison, HRTEM was carried out for sample B, as given in Fig. 2. Fig. 2(a) shows clearly the interfacial region containing interfaces among ZnO/MgO/AlN/sapphire layers and the substrate. Extensive TEM investigations, coupled with the RHEED observations (not shown here), confirmed the orientation relationships between ZnO, MgO, AlN and sapphire as $ZnO_{[11\bar{2}0]}\|MgO_{[10\bar{1}]}\|AlN_{[10\bar{1}]}\|sapphire_{[10\bar{1}0]}$ and $ZnO_{[0001]}\|MgO_{[111]}\|AlN_{[111]}$ (or $AlN_{[1\bar{1}1]}$)$\|sapphire_{[0001]}$ The magnified image of the interface between AlN and sapphire (Fig. 2(b)) shows clearly, like in the case of sample A, IDs existing in the nitrided layer as Al-polarity is in the left and N-polarity is in the right. Nevertheless, the AlN-nitrided layer in sample B has been relaxed to the zinc-blended structure (54.7° between {0 2 0} and {1 1 1} atomic planes and misfit dislocations found in the AlN/sapphire interface—inset in Fig. 2(b), a

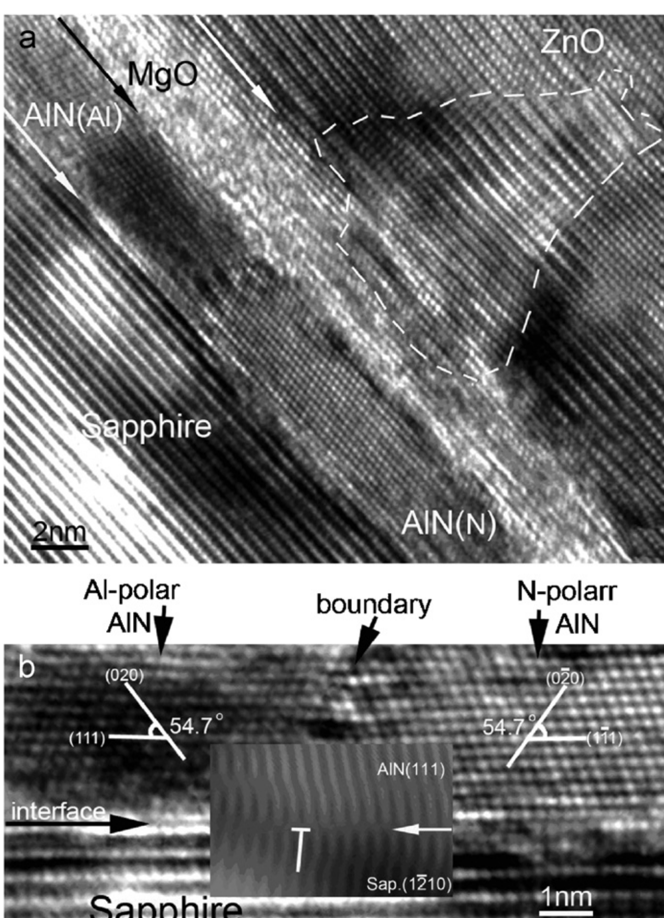


Fig. 2. (a) A typical HRTEM image of sample B showing interfacial region of ZnO/MgO/AlN/sapphire. (b) The magnified image showing the AlN/sapphire interface with a misfit dislocation seen in the inset (a Fourier-filtered image showing atomic planes of AlN {1 1 1} and sapphire {1 $\bar{2}$ 1 0}.

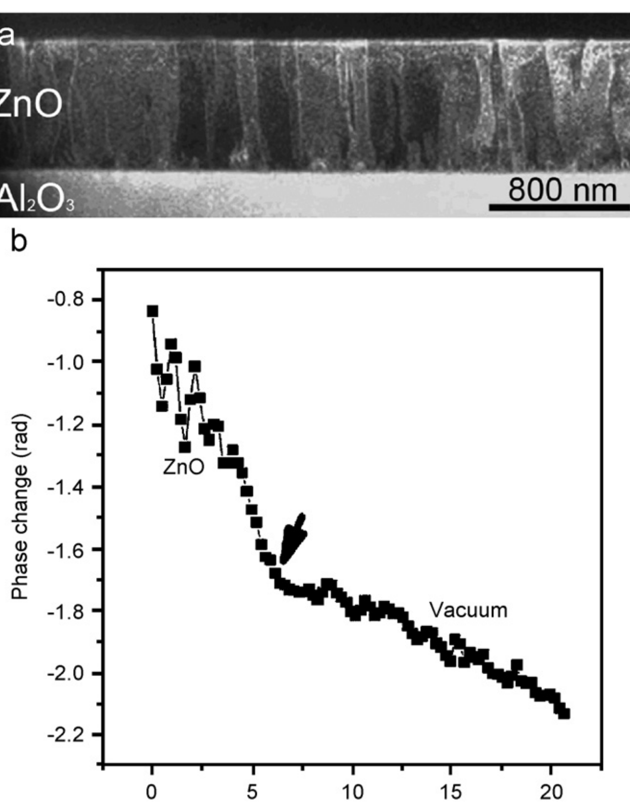


Fig. 3. (a) A typical dark-field TEM image of sample B with $g = 0002^*$, showing no IDs. (b) The phase (electrical potential) change profile extracted by electron holography, from which the O-polarity of the ZnO film was determined.

Fourier-filtered image [15] to clearly show a misfit dislocation) with a sharp interface with its underlying sapphire substrate and is very uniform with a thickness of ~3.5 nm.

The question now is how the misfit strain in the AlN layer is released. To answer this question, it is noticed that (1) the adjacent MgO layer has an island feature; (2) misfit dislocations were found in the AlN/sapphire interface as shown in the inset of Fig. 2(b) and (3) as outlined earlier, a post-growth annealing process was carried out at 750 °C. It is well known that the dislocation loops/sections might be presented in the grain boundaries and/or highly strained interfaces, such as MgO/AlN. It is more likely that some dislocations are the right dislocations for relieving the misfit strain in the AlN layer. During the annealing process, these dislocations prefer to move to the AlN/sapphire interface (the strain relaxation starts once dislocations move into the AlN layer, and the deeper they go, the more the misfit strain relaxed) [16]. Eventually, these dislocations elongate at the AlN/sapphire interface to form misfit dislocations and, in turn, to ultimately relieve the misfit strain in the AlN layer. In contrast, for sample A, the misfit strain in the AlN layer was not relaxed even after annealing after the final HT-ZnO growth. Similar results have been reported previously [3,12]. This indicates that the relaxation of the AlN layer is closely associated with the introduction of the MgO (cubic) buffer layer.

For the ZnO film to be practically useful, it is necessary to produce high-quality ZnO films with unipolarity. For this reason, it is necessary to evaluate the polarity of the grown ZnO film and their dislocation density. Fig. 3(a) is a dark-field XTEM image with $g = 0002^*$ taken from sample B, showing the uniform polarity as no white/black contrast was observed. Electron holography was employed to further determine the polarity of the ZnO film. Fig. 3(b) is a phase-change profile extracted from the hologram of the ZnO film by a reference hologram in vacuum [12,17]. Since the phase change is proportional to the electrical potential [17], the phase-change profile shows the electrical potential distribution near the surface region of the ZnO film and its characteristic suggests an O-polarity [12,17], confirming that the ZnO film has the [0 0 0 $\bar{1}$] orientation. It is of interest to note that the dislocation density reduced significantly in sample B and was estimated to be $10^9\,cm^{-2}$. This raises a question of how the MgO layer affects the quality of the ZnO film. To answer this question, we

noticed again that the adjacent MgO layer has an island characteristic at the MgO/ZnO interface as shown in Fig. 2(a), similar to the observation by Chen et al. [18], who suggested that the nucleation of ZnO would favourably take place in the island regions. These islands increase the wetting of ZnO and promote the 2D growth of the ZnO epilayer, resulting in an improved ZnO film. As can be noticed, the introduction of the MgO buffer resulted in the relaxation of the nitrided layer, which would make the ZnO film less stressed when compared with the case of the unrelaxed nitrided layer. Moreover, the MgO buffer layer decreases the lattice mismatch between ZnO and sapphire, when compared with the case in sample A where only LT-ZnO buffer layer is employed on the unrelaxed nitrided sapphire substrate. As a consequence, a reduced dislocation density is anticipated in the ZnO film.

4. Conclusion

In conclusion, detailed atomic structures, the polarity and the quality of the ZnO films on nitrided sapphire substrates with/without the MgO buffer layer have been investigated by TEM. It has been found that direct growth of the ZnO film on nitrided sapphire results in an unrelaxed AlN layer with IDs, which further causes IDs and a high density of dislocations in the ZnO films. However, the situation can be significantly improved after introducing a strain relaxation and ID ceasing MgO layer between the AlN-nitrided layer and the ZnO film. This work suggests that the introduction of the MgO layer is a feasible pathway to ultimately fabricate device quality and unipolar ZnO films.

Acknowledgements

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