Structural characterization of Zn-polar ZnO films grown on Mg-modified α-Al₂O₃ (0001) surface

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Abstract: The structure of the ZnO films grown on (0001) sapphire using surface modification of magnesium pre-exposure has been investigated by high resolution transmission electron microscopy, electron holography and X-ray energy dispersive spectroscopy. It is found that pre-deposition of an ultrathin magnesium film on the sapphire substrate plays a key role in zinc polarity selection and rotation domains elimination of ZnO films. In the resulting sharp interfaces of ZnO/MgO/sapphire, an ordered MgO layer ([3 atomic layers) was observed, which serves as a uniform template for nucleation and growth of a single-domain ZnO film.

Keywords: ZnO; TEM; polarity; electron holography; X-ray

1 Introduction

With the fast development of wurtzite ZnO and related alloys, increased attention has been paid to the polarity of ZnO films because the polarity of the films have a strong influence on their growth process, surface morphology and electronic properties. ZnO films can directly grown on (0001) sapphire, however, it usually contains a large number of defects due to the big lattice mismatch (18.4%) between ZnO film and sapphire, and inversion domains and rotation domains were also observed in the ZnO epilayers. Although extensive study has been done on defects in epitaxial ZnO films, the characteristics of the two different polarities of ZnO films and their polarity controls have not been well understood. Hong et al. have systematically studied the polarity control and characterization of ZnO films grown on Gr-polar GaN, from which they controlled the growth of Zr and Gr-polary ZnO films by Zn pre-exposing and Gr-plasma pre-exposing on GaN. Kato et al. controlled the polarity of ZnO by varying the MgO buffer layer thickness on the sapphire substrate. However, no further information about the structure of the ZnO films was given. In this study, we’ll report the Zr-polar ZnO films grown on sapphire by the interface engineering and characterized by high resolution transmission electron microscopy (HRTEM), electron holography (EH), and X-ray energy dispersive spectroscopy (EDS).

2 Experimental procedure

Two ZnO samples under investigation in this study were prepared on sapphire (0001) substrates using a radio frequency plasma-assisted molecular beam epitaxy system (OmniVac). The base pressure in the growth chamber was about 1.33 × 10⁻⁸ Pa. After sapphire...
substrates were introduced into the growth chamber, thermal cleaning (TC) was carried out at 800 °C for 1 hour under an ultra-high vacuum condition. The substrate temperature was then decreased for preparation of ZnO films. For sample A, ZnO film was directly grown on substrate by using the conventional two-step growth method (i.e. a low temperature (LT) buffer layer growth at 260 °C followed with a high temperature epilayer growth at 650 °C). Rotation domains were observed in this sample. Whereas, an additional surface modification process was adopted for sample B before the same two-step growth process as that of sample A. First, the substrate temperature was further decreased to 100 °C for the deposition of a thin Mg film with a thickness of 5 nm. Then, the substrate temperature was increased to 260 °C for growth of ZnO buffer layer. The in-plane epitaxial relationship, surface morphology evolution and crystallinity were monitored in situ by reflection high energy electron diffraction (RHEED). The cross-sectional TEM specimens were prepared by the conventional method including cutting, mechanical polishing, dimpling, and finalised by Ar+ ion-beam thinning. Before TEM observations, a plasma cleaner was used to remove any contaminations on the surfaces of TEM specimens. TEM investigations were carried out in a CM12 TEM, a FEI Tecnai F20 equipped with EDS, and a CM200 TEM. Off-axis holograms were performed by applying a positive bias of 100 V on the electrostatic biprism installed at the selective aperture.

3 Experimental results

Figure 1 shows the dark-field TEM micrographs of sample B. As delineated in the figures, Figs. 1 (a) and 1 (b) were taken with \( g = 0002 \) and \( g = 000 \overline{2} \) under the two-beam condition, respectively. The black/white contrasts can be seen from Fig. 1. This contrast could be attributed to the tilted crystal grains and/or the inversion domains. It is of interest to note that both Figs. 1 (a) and 1 (b) were taken by two opposite \( g \), both under the two-beam conditions.

There is no contrast inversion in these two dark-field TEM images, suggesting that there are no inversion domains in the ZnO thin film. Therefore, the thin film has a single polarity. In fact, the contrast is due to the mosaic structure (not rotation domain) within the film, similar to those reported previously. In addition, our X-ray diffraction measurements also show no rotation domains (not shown here). Here, we determined the polarity using the EH technique developed by Xu et al. The HRTEM image (Fig. 2 (a)) of the ZnO film shows a clear crystalline structure without amorphous layer at the rim. The electron hologram of the ZnO film (Fig. 2...
The hologram of ZnO film (Bar = 5 nm) was acquired in the case that the specimen was tilted away from any zone axis and the magnification is comparatively (to HRTEM) low. A reference hologram was also collected without the presence of the specimen in the field of view for the purpose of eliminating distortions due to the incoherent illumination and spherical aberration during the reconstruction of the hologram. Fig. 2 (c) is the phase image reconstructed from Fig. 2 (b) together with the reference hologram. In order to reveal the phase shift in the vacuum region clearly, one-dimensional profile was extracted by the line scans perpendicular to the ZnO film and is shown in Fig. 2 (d). This profile was averaged over 40 line scans along the direction normal to the scanning direction for the improvement of the signal-to-noise ratio. From Fig. 2 (d), one can clearly see that phase change in the vacuum region increases with increasing distance to the edge of the sample. Based on the conclusion by Xu et al.\textsuperscript{[14]}, we can determine that the characteristic of the measured phase profile coincides to the Zr-polarity, i.e., the film normal is parallel to the [0001] orientation.

In addition, EDS and HRTEM technique have been used to study the interface of sample B. Fig. 3 shows an EDS profile within the interface, in which Mg peak can be clearly identified, even though Mg concentration is relatively low. This suggests the existence of Mg in the interface, which was further confirmed with the HRTEM investigations in the interface. An example is shown in Fig. 4, where the HRTEM image was taken along the [10 10] sapphire direction. From Fig. 4, a sharp and ordered interface with 3 atomic layers of MgO between ZnO film and sapphire substrate can be clearly identified.
4 Discussion

Our above experiments of the ZnO films with Zn polarity demonstrate that the surface structure of the sapphire substrate plays a key role in the polarity selection of subsequent ZnO films. It is well known that α-Al2O3 (0001) surface has a very complex atomic arrangement and there are three possible surface termination layers, i.e., an Al monolayer, an Al bilayer and an O layer depending on surface treatment conditions[15]. In these configurations, the first surface structure is non-polar and therefore the most stable, whereas, the other two are cation-polar and anion-polar, respectively[16]. An Al monolayer terminated surface is disadvantageous for the single domain formation of polar films, such as AlN, GaN and ZnO. For example, inversion domains were observed in ZnO films directly grown on the Al monolayer terminated surface. In order to control the polarity of ZnO epitaxial films, the sapphire surface must be pretreated to form a polar structure, either cation-polar or anion-polar, before the ZnO growth. For our samples, the long time TC at 800 °C in ultra-high vacuum was used to obtain cation-polar sapphire (0001) surface. Our experiments show that this cation polarity can be extended into subsequent ZnO films. In this way, the Zr-polar ZnO film was formed as demonstrated in sample B. Especially, an ultra thin Mg film was deposited on the thermally cleaned sapphire (0001) surface so as to protect the polar surface from degradation when it was exposed to oxygen plasma. In situ observations of RHEED patterns of this sample revealed that a MgO film was formed due to the rapid oxidation of Mg film when the ZnO film growth initiates, which is attributed to the much stronger bonding between Mg and O than that between Zn and O. In this case, the cation polarity was extended from sapphire
(0001) surface to MgO and finally to the ZnO (0001) films. Some research groups have reported that, by exposure of Mg during the growth of GaN film, a G-polar GaN was changed to a N-polar GaN layer[17] or by inserting a MgO interlayer during the growth of ZnO film, a Zr-polar ZnO was inverted to a O-polar ZnO[18], however, they deposited Mg in a N-rich or O-rich condition. In our case, a Mg film was deposited at 100 °C under ultra-high vacuum condition on TC pretreated α-Al2O3 (0001) before the growth of ZnO. The formation of this ultra-thin MgO layer is under Mg-rich condition when the growth of ZnO is started, which is favorable for formation of a Mg-polar wurtzite MgO on Al terminated substrate. Therefore, a Zr-polar film was obtained. This result is just opposite to the growth of O-polar wurtzite MgO buffer layer reported in Ref. 13, where oxygen rich condition was used.

For sample A, the direct growth of ZnO buffer on Al-terminated sapphire substrate results in formation of rotation domains and inversion domains[19]. Due to the much stronger bonding of Al-O than that of Zr-O, the topmost Al will be oxidized again when the ZnO film growth initiates, resulting in the change of the surface structure of substrate. This result indicates that the Mg protection of substrate surface in sample B plays a key role in the polarity control of ZnO films grown on the sapphire (0001) surface.

5 Summary

By pre-exposing magnesium on the (0001) sapphire substrate, we successfully acquired the Zr-polar ZnO films. The detailed structural and polarity characteristics of as-grown ZnO thin film have been comprehensively determined by HRTEM, EH, and EDS. The Mg-protection of TC pretreated sapphire (0001) substrate results in a sharp ZnO/MgO/sapphire interfaces. The ultra thin MgO layer (3 atomic layers) was revealed to play a key role in the polarity selection of ZnO films grown on sapphire (0001) surface.

Reference:

预处理蓝宝石衬底法制备的ZnO极性外延薄膜的结构研究

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摘要: 通过分子束外延法在经Mg预处理的蓝宝石衬底上制备了ZnO单晶薄膜, 利用高分辨透射电镜、电子全息和X射线能谱对该薄膜的结构进行了细致的研究。结果表明, 在蓝宝石衬底上预沉积一层很薄的Mg层, 可以生长均匀Zn极性的ZnO外延薄膜。ZnOΠMgOΠ蓝宝石的界面非常清晰锐利, 同时在界面处可以观察到大约3个原子层的MgO。预沉积的Mg薄层对随后ZnO的极性选择起了关键性作用。

关键词: ZnO薄膜; 透射电子显微术; 电子全息术; 极性; X射线能谱