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Growth orientations of semipolar ZnO on GaN$(1\,1\,\bar{2}\,2)$

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On semipolar GaN$(1\,1\,\bar{2}\,2)$, epitaxial ZnO grown by chemical vapor deposition can form in two different semipolar orientations as evidenced by transmission electron microscopy and X-ray diffraction. One orientation relationship is shown to be ZnO$(1\,1\,\bar{2}\,2)$//GaN$(1\,1\,\bar{2}\,2)$ and $[\bar{1}\,1\,0\,0]_{ZnO}//[\bar{1}\,1\,0\,0]_{GaN}$ which is expected for ZnO growth on GaN$(1\,1\,\bar{2}\,2)$, while the other is a newly found relationship of ZnO$(\bar{1}\,0\,1\,\bar{1})$//GaN$(0\,0\,0\,2)$ and $[5\,\bar{7}\,2\,\bar{3}]_{ZnO}//[\bar{1}\,1\,0\,0]_{GaN}$.

1. Introduction

Wurtzite semiconductors are of great interest in optoelectronic applications, in particular, GaN and ZnO of wide bandgap. Due to the asymmetry of wurtzite structure the presence of spontaneous polarization field in the *c*-axis results in attenuation of electron–hole recombination rate which is known as quantum-confined Stark effect. The effect crucially lowers the luminous efficiency and the performance of light-emitting devices [1]. Though most of the wurtzite semiconductors are grown in *c*-orientation, nonpolar and semipolar orientations can provide better performance by reducing the Stark effect. It has been shown that semipolar GaN growth may have some advantages over nonpolar GaN such as a larger growth window and better surface morphologies [2].

ZnO (a=3.249 Å, c=5.206 Å) has a band gap of 3.37 eV with large free exciton binding energy which is expected to exhibit outstanding optical properties. Similar to GaN, nonpolar and semipolar ZnO can enhance the quantum efficiency [1,3,4]. Compared with intensive studies on semipolar GaN, semipolar ZnO has received less attention so far. Though growth of semipolar $(1\,1\,\bar{2}\,\bar{2})$, $(1\,0\,\bar{1}\,2)$ and $(1\,0\,\bar{1}\,\bar{1})$ ZnO have been recently demonstrated [5–7], it still lacks of good understanding. As ZnO and GaN have similar lattice parameters (GaN: a=3.189 Å, c=5.185 Å), the GaN substrate provides an excellent template for growth of epitaxial ZnO [8]. In this study $(1\,1\,\bar{2}\,2)$ semipolar GaN is used for the growth of semipolar ZnO. Structural characterization by X-ray diffraction (XRD) and transmission electron microscopy (TEM) shows that semipolar ZnO grown on GaN exhibits two different orientations.

2. Experimental

GaN$(1\,1\,\bar{2}\,2)$ was obtained from a faceted *a*-plane GaN template grown on 2 inches *r*-plane sapphire by metal–organic chemical vapor deposition, as shown in Fig. 1a. The GaN$(1\,1\,\bar{2}\,2)$ facets on the surface were identified with using scanning electron microscopy (SEM) and XRD.

ZnO was grown by chemical vapor deposition in a vertical tube furnace at 500 °C using zinc acetylacetonate as the precursor with N_2 carrier gas. Also, O_2 gas was separately flowed into the furnace. The flow rates of N_2 and O_2 were respectively 30 and 120 sccm. The N_2/O_2 ratio was maintained at 0.25. The crystallinity of thin films was examined with high-resolution XRD. The surface morphologies were observed by using SEM. The orientation relationships of ZnO on the faceted GaN template were also investigated by using cross-sectional TEM (XTEM). A dual-beam focused ion beam system was used to prepare cross-sectional specimens for SEM and TEM observations.

3. Results and discussion

All the crystallographic directions in SEM were verified with XRD using sapphire and GaN reflections based on sapphire wafer flat (//sapphire *a*-plane and GaN *m*-plane). On the GaN template, the top flat surface is of *a*-plane with other faceted planes on the inclined sides (Fig. 1a). Here we only focus on GaN$(1\,1\,\bar{2}\,2)$ facets which are inclined 31.5° with *a*-plane and have an average area about $2\times4\ \mu m^2$. Fig. 1b is the top-view SEM image of ZnO grown on *a*-plane and GaN$(1\,1\,\bar{2}\,2)$, showing the island-like surface morphology for ZnO on the $(1\,1\,\bar{2}\,2)$ faceted GaN. Fig. 1c shows the cross-sectional view of the sample after cutting by focused ion beam to reveal ZnO on the inclined $(1\,1\,\bar{2}\,2)$ and flat *a*-plane GaN surfaces. Fig. 2a shows a XRD $\omega/2\theta$ pattern of ZnO on GaN/sapphire in which ZnO exhibits only the $(1\,1\,\bar{2}\,0)$ peak, implying that it

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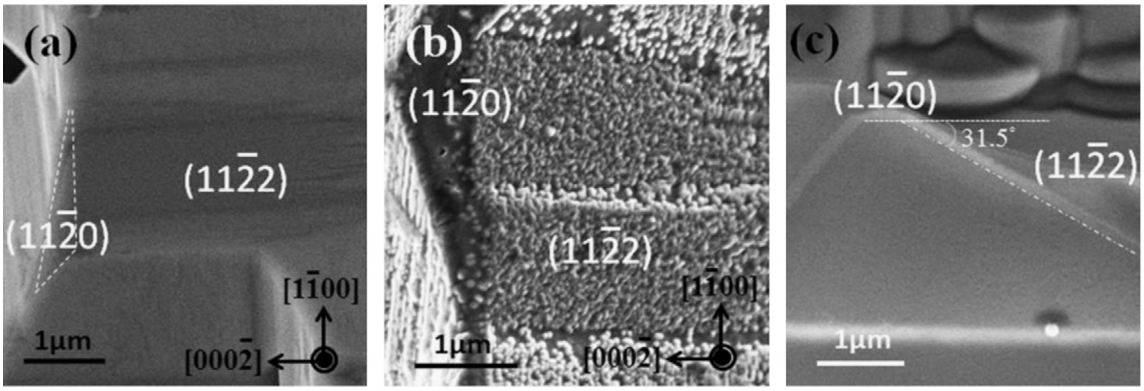

Fig. 1. SEM images showing (a) the top-view surface morphology of GaN, (b) the surface morphologies of ZnO on the GaN facets in top-view, and (c) the ZnO/GaN cross-section after focused ion beam milling.

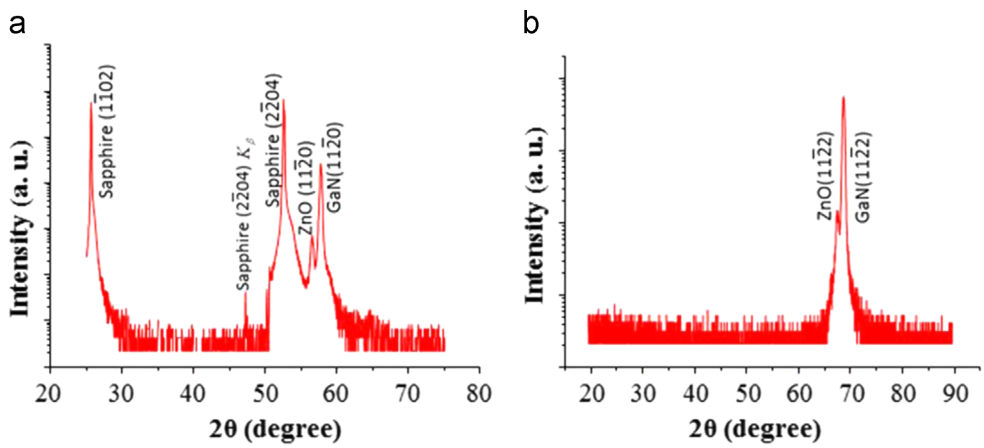

Fig. 2. (a) XRD $\omega/2\theta$ pattern of ZnO on GaN/sapphire, and (b) χ-compensated (30°) $\omega/2\theta$ XRD scan pattern to show both GaN and ZnO(1 1 $\bar{2}$ 2) reflections.

may be in epitaxy with nonpolar and semipolar GaN facets. Fig. 2b shows a χ-compensated $\omega/2\theta$ scan pattern (χ-tilt about 30° with GaN *c*-axis) in which only (1 1 $\bar{2}$ 2) peaks of both ZnO and GaN can be seen, suggesting that ZnO(1 1 $\bar{2}$ 2) epitaxially grows on the GaN(1 1 $\bar{2}$ 2) facets with the same orientation. To ensure that the ZnO(1 1 $\bar{2}$ 2) reflection in the XRD pattern is only generated from the ZnO thin film formed on GaN(1 1 $\bar{2}$ 2) facet, we used XTEM to examine the orientation of the ZnO film with GaN. A typical bright field XTEM image in Fig. 3a (beam//$[\bar{1}\ 1\ 0\ 0]_{GaN}$) shows that the ZnO film thickness is about 160 nm, and the ZnO film exhibits bright and dark diffraction contrast which may arise from the difference in orientations. Fig. 3b shows the corresponding selected-area diffraction (SAD) pattern in which two coexisted patterns are clearly revealed. One of the patterns can be identified with the $[\bar{1}\ 1\ 0\ 0]_{GaN}$ zone axis pattern, whereas the other one is $[5\ \bar{7}\ 2\ \bar{3}]_{ZnO}$, indicating $[\bar{1}\ 1\ 0\ 0]_{GaN}//[5\ \bar{7}\ 2\ \bar{3}]_{ZnO}$. Surprisingly, no ZnO *a*-plane diffraction spots can be seen in this zone-axis pattern with GaN *a*-plane diffraction spots. Instead, it can be found that ZnO($\bar{1}$ 0 1 $\bar{1}$) is almost parallel to GaN(0 0 0 2) and ZnO($\bar{1}$ 1 0 $\bar{4}$) is slightly tilted about 7° away from GaN(1 1 $\bar{2}$ 2). From the SAD pattern and high-resolution TEM (HRTEM) shown later, it can be shown that the ZnO grains in bright contrast in Fig. 3a are oriented along $[5\ \bar{7}\ 2\ \bar{3}]_{ZnO}$-axis, while those in dark contrast are actually oriented with $[\bar{1}\ 1\ 0\ 0]_{GaN}$ in the cross-section view. Thus, it is reasonable that the ZnO(1 1 $\bar{2}$ 2) reflection in the XRD pattern is resulted from the ZnO in dark contrast. For the ZnO in bright contrast, it can be designated as ($\bar{1}$ 1 0 $\bar{4}$)-oriented ZnO with respect to the ZnO/GaN interface. To further verify the orientation relationships, we have prepared another thin TEM specimen for HRTEM observations from the same ZnO/GaN sample. The HRTEM images in Fig. 3c–e taken from GaN and different ZnO grains with bright and dark contrast around the same ZnO/GaN interface region (*i.e.* on the same GaN facet) with the beam along the same $[\bar{1}\ 1\ 0\ 0]_{GaN}$ direction show the lattice fringes of GaN and ZnO in [$\bar{1}$ 1 0 0] zone (Fig. 3c and e), and a distinctly different lattice fringes of ZnO in Fig. 3d, ensuring that two orientation types of ZnO grains form on GaN(1 1 $\bar{2}$ 2). Also the fast Fourier transform (FFT) patterns of the GaN and ZnO lattice images in the insets of Fig. 3c–e clearly confirm that the ZnO grains are aligned with $[\bar{1}\ 1\ 0\ 0]_{ZnO}$ and $[5\ \bar{7}\ 2\ \bar{3}]_{ZnO}$ directions. Consequently, the orientation relationships between ZnO and GaN can be deduced as ZnO(1 1 $\bar{2}$ 2)//GaN(1 1 $\bar{2}$ 2) and $[\bar{1}\ 1\ 0\ 0]_{ZnO}//[\bar{1}\ 1\ 0\ 0]_{GaN}$, and ZnO($\bar{1}$ 0 1 $\bar{1}$)//GaN(0 0 0 2) and $[5\ \bar{7}\ 2\ \bar{3}]_{ZnO}//[\bar{1}\ 1\ 0\ 0]_{GaN}$. As a result, the interpretation of the SAD pattern in Fig. 3b should be taken into consideration that the ZnO reflections in [$\bar{1}$ 1 0 0] zone axis pattern actually coincide nearly with GaN ones as they have a small mismatch. To verify the formation of the ($\bar{1}$ 1 0 $\bar{4}$)-oriented ZnO on the GaN facets of the template is a general case, we used the asymmetrical grazing exit method to obtain the reciprocal space map of ZnO($\bar{1}$ 1 0 $\bar{4}$) shown in Fig. 4 as it is absent in $\omega/2\theta$ scans because of the its scattering angle.

For these two orientation relationships of ZnO with GaN, ZnO(1 1 $\bar{2}$ 2) grown on GaN(1 1 $\bar{2}$ 2) is as expected to follow

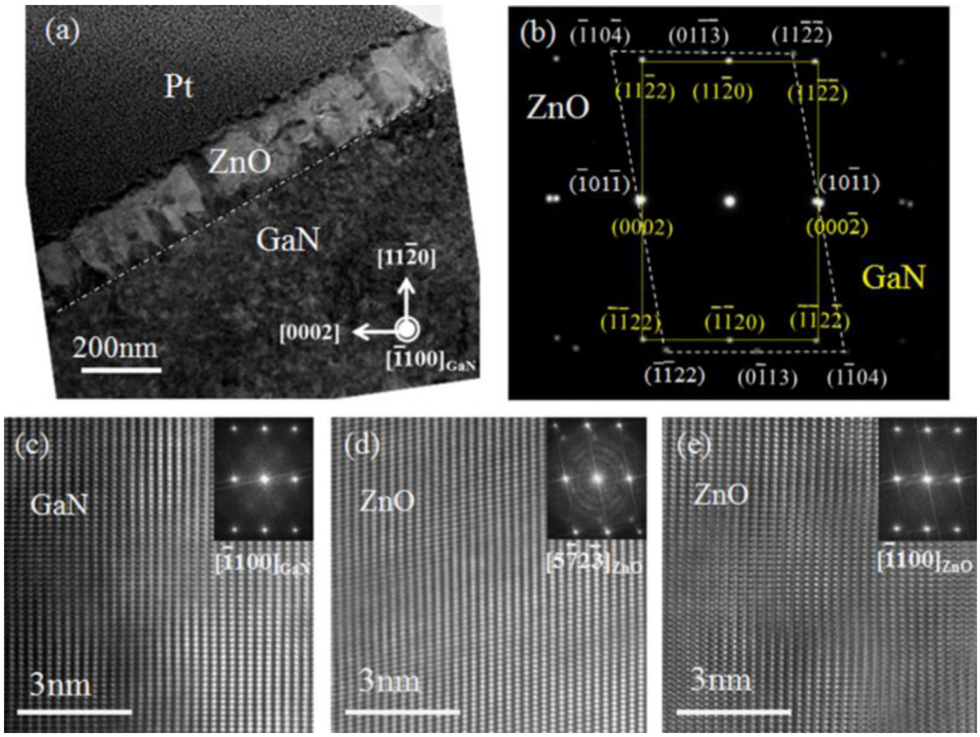

Fig. 3. (a) Bright field XTEM micrograph and (b) SAD pattern. (c)–(e) HRTEM images along GaN[$\bar{1}$ 1 0 0] showing lattice fringes of (c) GaN in [$\bar{1}$ 1 0 0]$_{GaN}$, (d) ZnO in [$\bar{5}$ 7 $\bar{2}$ $\bar{3}$]$_{ZnO}$, and (e) ZnO in [$\bar{1}$ 1 0 0]$_{ZnO}$ with FFT patterns in the insets.

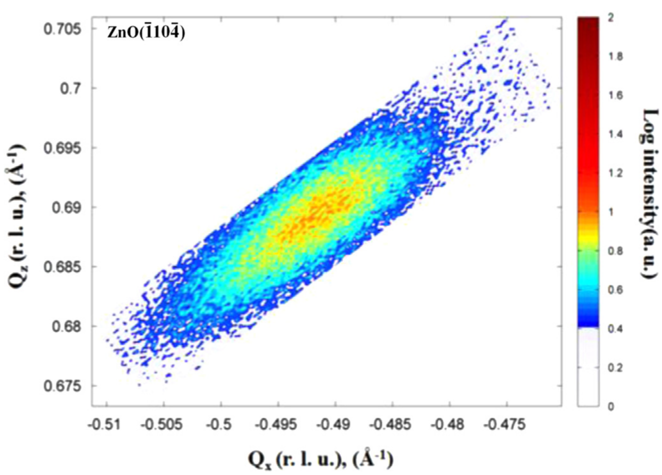

Fig. 4. RSM of ZnO ($\bar{1}$ 1 0 $\bar{4}$).

the GaN lattice because they have a lattice mismatch of 2.9% in [$\bar{1}$ 1 0 0]$_{GaN}$ direction and 1.6% in [1 1 $\bar{2}$ $\bar{3}$]$_{GaN}$direction. However, it is unexpected for the other orientation relationship of ZnO with GaN(1 1 $\bar{2}$ 2) from which it can be deduced that ZnO also has a small lattice mismatch of 0.4% with GaN in [$\bar{1}$ 1 0 0]$_{GaN}$ (//[5 $\bar{7}$ 2 $\bar{3}$]$_{ZnO}$) direction, and -4.5% in [0 0 0 2]$_{GaN}$ (3.57° deviated from [2 0 $\bar{2}$ 1]$_{ZnO}$).

4. Conclusions

Semipolar ZnO can epitaxially grow in two different orientation types on GaN(1 1 $\bar{2}$ 2). XRD, SAD, and HRTEM results provide clear evidence that one of the orientation relationships between ZnO and GaN is ZnO(1 1 $\bar{2}$ 0)//GaN(1 1 $\bar{2}$ 0) and [$\bar{1}$ 1 0 0]$_{ZnO}$//[$\bar{1}$ 1 0 0]$_{GaN}$, and the other one is ZnO($\bar{1}$ 0 1 $\bar{1}$)//GaN(0 0 0 2) and [5 $\bar{7}$ 2 $\bar{3}$]$_{ZnO}$//[$\bar{1}$ 1 0 0]$_{GaN}$.

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