Occurrence and elimination of in-plane misoriented crystals in AlN epilayers on sapphire via pre-treatment control*

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AlN epilayers are grown directly on sapphire (0001) substrates each of which has a low temperature AlN nucleation layer. The effects of pretreatments of sapphire substrates, including exposures to NH_3/H_2 and to H_2 only ambients at different temperatures, before the growth of AlN epilayers is investigated. In-plane misoriented crystals occur in N-polar AlN epilayers each with pretreatment in a H_2 only ambient, and are characterized by six 60°-apart peaks with splits in each peak in $(10\bar{1}2)$ phi scan and two sets of hexagonal diffraction patterns taken along the [0001] zone axis in electron diffraction. These misoriented crystals can be eliminated in AlN epilayers by the pretreatment of sapphire substrates in the NH_3/H_2 ambient. AlN epilayers by the pretreatment of sapphire substrates in the NH_3/H_2 ambient are Al-polar. Our results show the pretreatments and the nucleation layers are responsible for the polarities of the AlN epilayers. We ascribe these results to the different strain relaxation mechanisms induced by the lattice mismatch of AlN and sapphire.

Keywords: AlN, misoriented, polar, nitridation

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1. Introduction

Due to their wide band gap (6.2 eV), high thermal conductivity, and high breakdown voltage, AlN films have many potential applications in deep-ultraviolet (UV) optical devices and high power electronic devices.[1] Because of the absence of homo-substrates, nowadays AlN films are usually grown on hetero-substrates such as sapphire and SiC. However, the large lattice constant mismatch, as well as the difference in thermal expansion coefficient between AlN and these substrates makes the fabrication of high-quality AlN films a big challenge.[2] Many techniques including the two-step process, pulsed atomic layer epitaxy (PALE) and flow-modulation metal–organic chemical vapor deposition (FM-MOCVD), have been adopted to improve the crystal quality of AlN films, and great progress has been made.[3–6] Furthermore, considerable efforts have also been devoted to the study of the effects of initial treatments like nitridation in order to further enhance the quality of AlN. Unlike the GaN growth on sapphire where it is well established that nitridation is one of the key process to obtain high-quality GaN epilayers,[7–10] nitridation effects on AlN are still controversial. For AlN growth on sapphire, some studies revealed that the initial nitridation of substrates results in a relatively rough surface due to the mixed Al- and N-polarity in spite of the significantly reduced density of screw threading dislocations, while flat and Al-polarity AlN films with poor crystallinity can be obtained by growth on sapphire substrates without nitridation.[11–13] Other studies[14] showed that N-polar AlN epilayers with rough surfaces can be obtained with nitridation pretreatment at optimized FM-MOCVD growth conditions, suggesting that the pretreatment effects may be growth-scheme-dependent. Motivated by these results, in this work we study the effects of different initial pretreatments on AlN epilayers grown using our unique growth scheme, and some results different from the references are achieved.

2. Experimental procedures

The AlN epilayers under investigation were deposited on 2-inch sapphire (0001) substrates via a vertical MOCVD under a low pressure. Prior to the AlN growth, the sapphire substrates were subjected to different treatments including exposure to NH_3/H_2 and H_2 only ambients at different temperatures varying from 960 °C to 1100 °C. The flow rates of NH_3 and H_2 were 1500 sccm and 2000 sccm respectively. Then, trimethylaluminum (TMAl) and ammonia were simultaneously introduced by a H_2 carrier gas into the chamber as precursors for Al and N sources to form a thin (20 nm) nucleation layer (NL) at 870 °C. Subsequently, AlN layers each with a thickness of

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about 0.3 μm were deposited at 1050 °C via the PALE technique in the following source supply sequence: ammonia was supplied periodically, switching on for 6 s and off for another 12 s, while TMAl flow was constant, by which Al adatom mobility was enhanced. The chamber pressure was kept at 5.33×10^3 Pa during growth. The crystalline qualities are characterized by high-resolution X-ray diffraction (HR-XRD) and transmission electron microscope (TEM). Surface morphology was studied by atomic force microscopy (AFM).

3. Results and discussion

In Table 1 the respective pretreatments and the corresponding XRD results of six samples are summarized. The values of full width at half maximum (FWHM) of (0002) X-ray rocking curves (XRCs) of AlN films with exposure of sapphire substrates to a H_2 only ambient before growth reduce from 1306 arcsec to 125 arcsec as the temperature increases from 960 °C to 1100 °C. However, for the $(10\bar{1}2)$ XRCs, double peaks with about a 2.5° interval are observed for all these three samples. The typical scan is shown in Fig. 1(a). The presence of such doublet peaks in $(10\bar{1}2)$ XRCs suggests that two sets of crystal structures with an in-plane rotation may exist in the AlN films. Figure 1(a) shows XRD ϕ scans of $\{10\bar{1}2\}$ plane of a typical sample with exposure of sapphire substrate to H_2 only ambient. Six sets of equally spaced peaks with a period of 60° are observed, which are associated with the hexagonal symmetry of AlN films. A closer examination of data reveals that each set of peaks actually consists of two peaks with an interval of 3.6°, confirming the presence of two crystal phases with an in-plane rotation of about 3.6°.

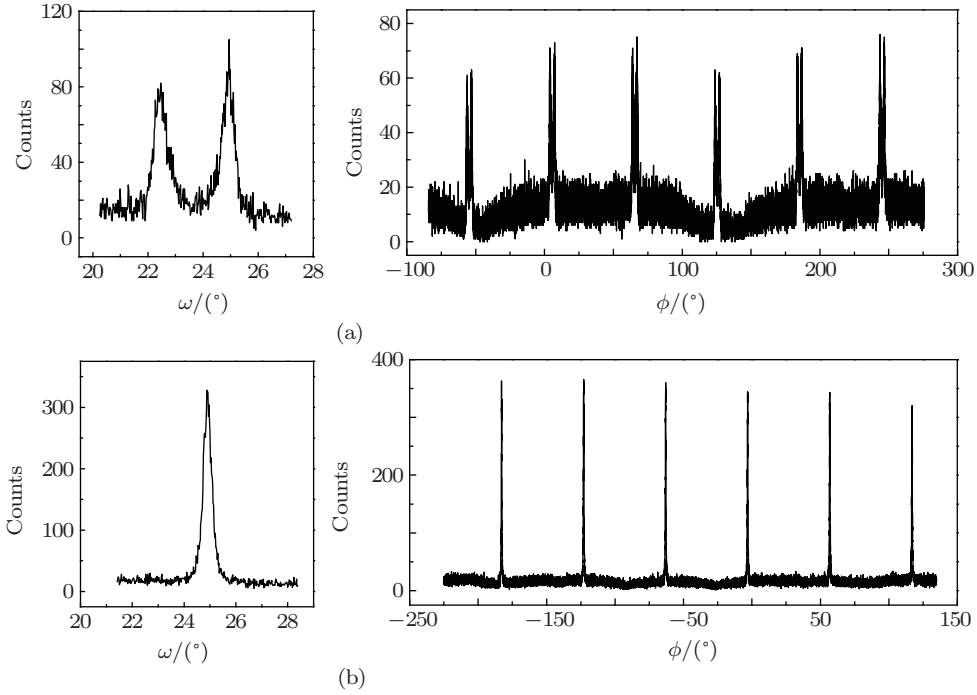


Fig. 1. $(10\bar{1}2)$ ω (left) and $(10\bar{1}2)$ ϕ (right) scan of AlN film with pretreatment in (a) H_2 only and (b) NH_3/H_2 ambient at 1050 °C.

Table 1. Summary of pretreatments and corresponding XRD results.

Sample #	Pretreatment		XRD results	
	Ambient	Temperature/°C	(0002) FWHM/arcsec	$(10\bar{1}2)$ FWHM/arcsec
A1	H_2	960	1306	doublet peaks
A2	H_2	1050	210	doublet peaks
A3	H_2	1100	125	doublet peaks
B1	H_2/NH_3	960	144	1116
B2	H_2/NH_3	1050	119	1119
B3	H_2/NH_3	1100	210	1223

In order to further clarify this issue, we measure the selected area electron diffraction (SAED) along the [0001] zone axis on the plan-view TEM samples of these AlN films by using a transmission electron microscope, and the patterns are shown in Fig. 2(a). Two sets of patterns with a rotation of about 4° are clearly observed in the diffraction pattern, which

is in good agreement with the results of XRD studies. Therefore, we conclude that these two sets of hexagonal structures are rotated around ⟨0001⟩ direction, and the relative angle with respect to each other is about 4°. To the best of our knowledge, this phenomenon has not been reported before for the AlN growth on sapphire. The possible reasons of the formation of these "twin" crystals will be discussed later. Additionally, both plan-view TEM images and AFM images (Fig. 2(a)) of these AlN films exhibit defined terrace features, suggesting the step-flow growth.

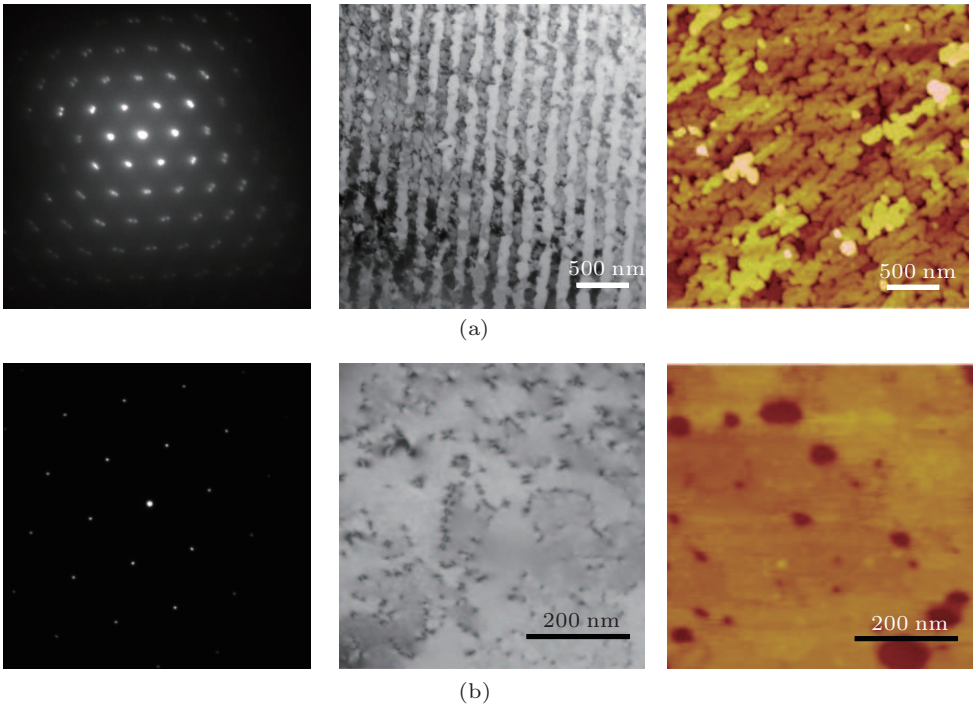


Fig. 2. (color online) TEM electron diffraction patterns (left), plan-view images (middle), and AFM surface morphologies (right) of AlN films with pretreatment of exposure to (a) H_2 only ambient at 1050 °C and (b) NH_3/H_2 ambient at 1050 °C.

On the other hand, XRD results of the AlN epilayers with pretreatment of exposure to a NH_3/H_2 ambient at temperatures from 960 °C to 1100 °C are rather different. The FWHMs of (0002) XRCs are 144, 119, and 210 arcsec, corresponding to the temperatures of 960 °C, 1050 °C, and 1100 °C, respectively. No doublet peaks are observed from $(10\bar{1}2)$ ω scan, and six 60°-apart peaks without splits in $(10\bar{1}2)$ ϕ scan are recorded, implying the existence of only one hexagonal structure. Figure 1(b) shows XRD results of AlN film with pretreatment in a NH_3/H_2 ambient at 1050 °C, which are remarkably distinct from the samples with pretreatment in a H_2 only ambient at 1050 °C. Further evidence is also provided by TEM electron diffraction pattern, in which only one set of hexagonal diffraction patterns is observed. The diffraction patterns for selected sample B2 are shown in Fig. 2(b). Besides this, the surface morphologies of these samples undergo the same trend as XRD results (Table 1), showing seemingly optimum results at a nitridation temperature of 1050 °C (Fig. 2(b)). These results are consistent with those reported in Ref. [15], in which it was claimed that nitridated substrate suffered from nitridation saturation, and the over nitridation could lead to rough surface.

Considering the fact that the crystalline properties of AlN epilayers are also highly associated with the dominant polarity of the film,[13] the polarities of the above samples with pretreatment at 1050 °C are examined by etching them in a hot (50 °C) aqueous KOH (20 wt%) solution because Al-polarity AlN crystals are more inert than the N-polarity ones in a KOH solution.[16] The surface morphologies of the etched AlN epilayers are displayed in Fig. 3. The comparison of the surface morphology of the corresponding sample between, before and after being etched shows that the surface of the AlN film with nitridation is almost intact obviously, while that of the film without nitridation becomes very rough. Besides this, the film thickness measurement by transmission spectrum confirms that the etch rate for AlN with nitridation is nearly zero and that of AlN without nitridation is very fast. These results indicate that the AlN epilayers with nitridation are of Al-polarity and those without nitridation are N-polarity dominated. These results are in disagreement with those observed in AlN films directly grown on a sapphire substrate at high temperatures without low temperature NL, where Al-polar AlN fims are usually obtained on non-nitridated sapphire substrates.[7–10]

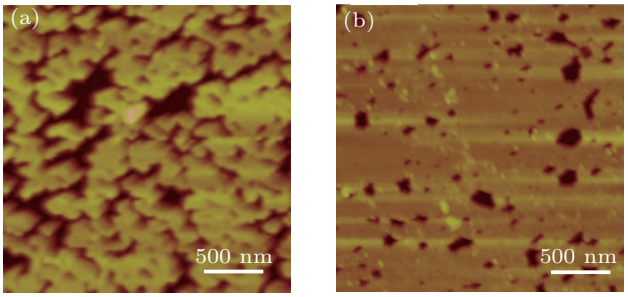


Fig. 3. (color online) Surface morphologies of AlN after being etched in hot aqueous KOH solution (a) with pretreatment in H_2 only ambient, and (b) with pretreatment in NH_3/H_2 ambient.

From the above presented results, it is evident that the pretreatments and the NL are responsible for the crystalline qualities and the polarity discrepancy between our results and the reported ones. We develop a simplified model to explain these issues based on the surface-terminating atomic species, and the schematic atomic arrangements are displayed in Fig. 4. During the growth of NL, TMAl reacts with NH_3, forming an Al–N molecule before reaching the growth front. In the case of sapphire substrate with pretreatment in a H_2 only ambient, the resulting sapphire substrate has an Al-enriching surface and these Al ions are believed to have low coordination of oxygen ions by removing the oxygen during hydrogen etching.[17] During the NL deposition, the nitrogen species of Al–N molecules lack three covalent bonds, and bond to the underlying aluminum, forming free surface toward Al-atom bonds and thus facilitating the formation of subsequently grown N-polar AlN naturally. At the same time, the compressive strain induced by the large lattice mismatch between AlN and sapphire substrates can cause the stress-enhanced migration of the Al adtoms to the energetically favorite sites, which may then form misoriented AlN (Fig. 4(a)).

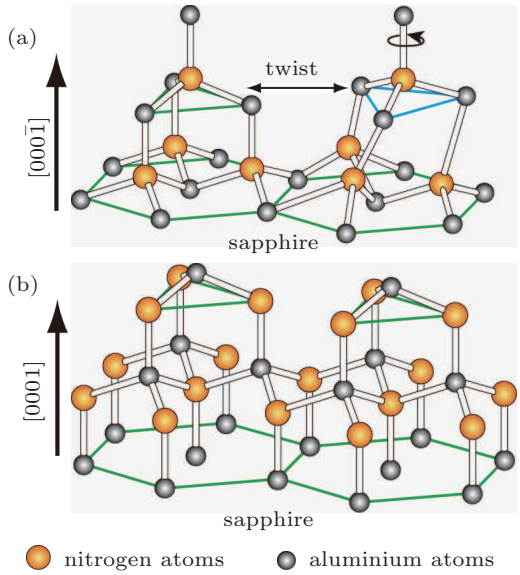


Fig. 4. (color online) Schematic atomic arrangements of AlN with pretreatment in (a) H_2 only ambient; (b) NH_3/H_2 ambient.

In contrast to the above described process, nitridation process leads to the formation of a highly defective AlN monolayer[18] and N-enriching surface. During the deposition of NL, the aluminum species of Al–N molecules lack three covalent bonds, and impact the N-enriching surface and bond to these underlying N to form three substrate-facing Al-atom bonds, leading to Al-polar AlN naturally and thus the resulting main AlN epilayer exhibits Al-polarity (Fig. 4(b)). Furthermore, the large strain induced by the lattice mismatch has already been partially relieved by the highly defective AlN monolayer, therefore, the formation of twisted crystals is avoided. In other words, the different strain relaxation mechanisms result in the occurrence and elimination of twisted crystals in the AlN films on sapphire with different pretreatments respectively. According to these pretreatment parameters, we have grown a 1.3-μm AlN using a combined growth scheme of PALE and continuous growth, and the resulting film exhibits a high crystal quality with a (0002) FWHM of 52 arcsec and (10$\bar{1}$2) FWHM of 544 arcsec.

4. Conclusions

In this paper, different pretreatments of sapphire substrates are conducted and their influences on the subsequently deposited AlN epilayers are studied by AFM, HR-XRD, and TEM. Misoriented crystals are observed in N-polar AlN epilayers with pretreatment in a H_2 only ambient. XRD (10$\bar{1}$2) Phi scans show six sets of 60°-apart doublet peaks, and electron diffraction patterns along the [0001] zone axis exhibit two sets of hexagonal diffraction patterns. The pretreatment of exposure in a NH_3/H_2 ambient eliminates these misoriented crystals and the resulting AlN is Al-face. We ascribe these results to the different strain relaxation mechanisms induced by the lattice mismatch of AlN and sapphire. A model has been developed to explain the misoriented crystal and polarity issues, suggesting that the polarity of AlN epilayer and the occurrence of misoriented phases are highly growth-scheme-dependent.

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