Influence of TMAI preflow on AlN epitaxy on sapphire

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The trimethylaluminum (TMAI) preflow process has been widely applied on sapphire substrates prior to growing Al-polar AlN films by metalorganic chemical vapor deposition. However, it has been unclear how the TMAI preflow process really works. In this letter, we reported on carbon's significance in the polarity and growth mode of AlN films due to the TMAI preflow. Without the preflow, no trace of carbon was found at the AlN/sapphire interface and the films possessed mixed Al- and N-polarity. With the 5 s preflow, carbon started to precipitate due to the decomposition of TMAI, forming scattered carbon-rich clusters which were graphitic carbon. It was discovered that the carbon attracted surrounding oxygen impurity atoms and consequently suppressed the formation of $\text{Al}_x\text{O}_y\text{N}_z$ and thus N-polarity. With the 40 s preflow, the significant presence of carbon clusters at the AlN/sapphire interface was observed. While still attracting oxygen and preventing the N-polarity, the carbon clusters served as randomly distributed masks to further induce a 3D growth mode for the AlN growth. The corresponding epitaxial growth mode change is discussed.

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AlN and its alloys $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($0 < x < 1$) have large and direct bandgaps, which are suitable for ultraviolet (UV) devices.^{1,2} However, due to the limited availability and high cost of bulk AlN substrates, most of the UV devices have been developed and produced on AlN templates grown on sapphire substrates by metalorganic chemical vapor deposition (MOCVD). Achieving desirable AlN films depends primarily on the initial growth stage conditions including the substrate pretreatment by NH_3 preflow (i.e., nitridation)^{3–6} and trimethylaluminum (TMAI) preflow (i.e., TMAI preflow)⁷ in particular.

The N-polarity growth of AlN films was often observed after the nitridation.^{3,7} Also, the decomposition of sapphire amid the hydrogen ambient causes the creation of the N-polarity of the film.⁸ Oxygen (O) released from the sapphire decomposition was found to play a significant role in the formation of N-polar AlN films. Studies have confirmed that it was the $\text{Al}_x\text{O}_y\text{N}_z$ intermediate layer formed on the sapphire surface that led to the subsequent growth of N-polar AlN films.^{6,9} As the N-polar AlN films generally have rough surfaces, the suppression of the $\text{Al}_x\text{O}_y\text{N}_z$ formation is crucial for the MOCVD growth of UV devices.^{7,9}

A few approaches have been reported to suppress the N-polarity and to promote the Al-polarity amid the nitridation. Mohn *et al.* showed that a well-designed annealing process of the nucleation layer (NL) was necessary to suppress the N-polarity.⁶ Several groups have investigated the impact of the temperature dependence of the nucleation processes on the polarity and crystal quality.^{3,9} In addition, a thin medium-temperature AlN-NL can reportedly transform N-polarity into Al-polarity and eventually impact the growth mode of the high-temperature AlN layers.^{10,11}

Moreover, the TMAI preflow was found to be beneficial for achieving metal-polar GaN or AlN films on sapphire. A “two-metallic-atomic-monolayers” model was proposed to explain the Al-polarity formation, where two monolayers of Al were introduced due to the TMAI preflow, and thus, the N-polarity was inverted to the Al-polarity.^{12–16} However, there has been no direct experimental evidence reported supporting this model. Hence, it is still unclear how the TMAI preflow process can lead to the Al-polarity and how different doses of the TMAI preflow can result in different growth modes of AlN films.

In this work, a series of AlN templates with different doses of the TMAI preflow were grown by MOCVD on (0001) sapphire substrates. We conducted a detailed analysis of the carbon (C) existence, in particular, at the AlN/sapphire interface where the AlN-NL was grown. We found that the C played a primary role in determining the polarity and growth mode of the subsequent AlN film. A correlation between the C clustering and the polarity and growth mode is presented.

The AlN layers were grown on *c*-plane sapphire substrates using in an AIXTRON close-coupled showerhead (CCS) reactor. TMAI and NH_3 were used as precursors with H_2 as the carrier gas. The growth processes comprised four steps: (1) prior to each growth, the sapphire substrates were baked at 1110 °C for 5 min in a H_2 ambient; (2) then, a flow of TMAI was introduced with preflow times of 0, 5, and 40 s (hereafter, sample 1, sample 2, and sample 3, respectively) at a fixed flow rate of 1.72×10^{-5} mol/min at a substrate temperature of 940 °C; (3) subsequently, the AlN growth started with a 15 nm AlN-NL at 940 °C; (4) finally, a 3 μm AlN layer was grown at 1100 °C. Except for the TMAI preflow time, the other growth parameters were the same for the three samples.

The reactor pressure was kept constant at 85 mbar. Besides samples 1–3, we also prepared two samples with 5 and 40 s TMAI preflow (hereafter, TMAI-only samples) under the identical MOCVD condition, without the subsequent AlN growth.

Figures 1(a)–1(c) show the scanning electron microscopy (SEM) images of samples 1–3, respectively. The results exhibited significant differences in the surface morphology. Without the TMAI preflow, sample 1 exhibits an incomplete coalescence surface covered with irregular rod-shape features, indicating a columnar growth mode. With the 5 s preflow, the surface of sample 2 is smooth, hinting the Al-polarity. With the 40 s preflow, the surface of sample 3 has developed sharp multi-facets, with a mixture of rod and wall-shape nanostructures. Then, the polarity of samples 1–3 was determined by immersing the samples in a 44% wt aqueous potassium hydroxide (KOH) solution at 80 °C for 2 mins, which removed the N-polar AlN completely.⁸ The etching results are shown in Figs. 1(d)–1(f). Figure 1(d) shows that the surface of sample 1 includes both hexagonal pyramids and bare sapphire surfaces (marked by the black arrow). Because the KOH etching rate of the N-polar AlN film is much higher than that of the Al-polar film,^{3,9} the polarity of the remained AlN film in the form of porous pyramids was predominantly Al-polar and that of the AlN film on the bare sapphire surface was predominantly N-polar, which were completely removed during the etching. Figure 1(e) shows a smooth surface, indicating that sample 2 remained intact, and thus, the film is Al-polar. In Fig. 1(f), although the highly tilted facets of sample 3 were etched away during the KOH etching process, the majority of films remained on sapphire, which suggests that sample 3 is Al-polar. Here, we observed a distinct surface morphology between Samples 1 and 3 before the etching although both were Al polar, indicating different growth modes that will be addressed in detail later.

Microstructures were revealed via high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). We also studied the compositional variation of Al $L_{2,3}$ as well as nitrogen (N) K -edge, carbon (C) K -edge, and oxygen (O) K -edge distributions by using electron energy-loss spectroscopy spectrum imaging (EELS-SI) in the STEM mode. For sample 1 without the preflow, Fig. 2(a) shows a HAADF-STEM image of the first 300 nm. Alternating stripes with different contrast were observed where the stripes were vertically aligned along the growth direction. Figure 2(b)

presents a zoomed-in image of the AlN-NL (15 nm) and high-temperature AlN (HT-AlN) film. The uniformly distributed atomic layers with less contrast above the NL indicate an improved crystal quality as the subsequent AlN film was grown at a higher temperature. Figure 2(c) shows the elemental mapping of Al, N, O, and C from the AlN/sapphire interface. The EELS maps indicate uniformly distributed Al and N elements without the presence of C or O in the NL.

For sample 2 with the 5 s preflow, Fig. 3(a) shows a high density of small voids and Fig. 3(b) shows nanoscale voids also existing in the AlN-NL. This could be a result of the incomplete coalescence of these small nucleation islands/grains. Figure 3(c) presents the elemental mapping of the Al, N, O, and C. Similar to sample 1, a relatively uniform distribution of O and N elements was observed. But a slight accumulation of C (yellow clusters within the white dashed box of the C map) at the AlN/sapphire interface consistent with a slight reduction in Al concentration (dark clusters within the white dashed box of the Al map) can be noticed. These maps suggest the presence of scattered C-rich clusters near the NL/sapphire interface.

For sample 3 with the 40 s preflow, Fig. 4(a) shows larger voids compared to sample 3 and Fig. 4(b) shows that the NL contained nanoscopic features which were in darker contrast. Figure 4(c) exhibits the elemental mapping of Al, N, O, and C in the NL. Interestingly, in the areas with reduced Al or N, we observed the significant presence of C and O, in correspondence with the rod-like features. This indicates that C-rich clusters were formed during the preflow process. The C atoms formed C-rich crystallites in the shapes of irregular nanostructures and thus mask prior to the AlN-NL growth. The masking effect is more prominent in sample 3 due to the larger C cluster size, leading to larger voids, as shown in Fig. 4(a).

C is one of the most common impurities in nitride films grown by MOCVD,^{17–19} originating mostly from the dissociation of metalorganic (MO) molecules including TMAI.²⁰ At the preflow temperature of 900 °C, the TMAI molecules dissociated into dimethylaluminum (DMAI), monomethylaluminum (MMAI), and methyl radicals during the preflow.^{21,22} The substrate temperature was sufficiently high to break the C–H bonds and produce graphitic C on the sapphire surface prior to the AlN-NL growth.²¹

As a result, after 5 s of preflow, a slight accumulation of C was noticed, as shown in the C-map in Fig. 3(c). Thus, we

FIG. 1. SEM plan-view images of morphological changes of Samples 1, 2, and 3, including (a)–(c) before and (d)–(f) after KOH etching, respectively.

FIG. 2. (a) A HAADF-STEM image of the lower boundary of sample 1. (b) The selected region (green dashed area) in (a), indicating the high-resolution image of AIN-NL and HT-AIN (above the white dashed line). (c) The elemental map of the Al $L_{2,3}$ (green color) and N (blue color), O (red color), and C (yellow color) K -edges from the red dashed area in (a).

believe that the 40 s preflow has caused excessive accumulation of C atoms at the sapphire surface, forming C-rich 3D islands. Some brighter yellow features might be C-rich with a small fraction of Al atoms, as shown in the C map in Fig. 4(c). It is worth pointing out that the spatial O concentration in the O map was proportional to that of C. This indicates

that C can strongly attract O released from surroundings. The primary source of O is the sapphire substrate which reportedly led to $Al_xO_yN_z$ and thus N-polarity in the absence of the TMAI preflow,⁹ such as sample 1.

Figures 5(a) and 5(b) show the EELS spectra of C and O K -edges extracted from the C and O maps shown in Figs. 2–4(c). For sample 3, the spectral intensities of C and O increased significantly compared to those of Samples 1 and 2.

FIG. 3. (a) A HAADF-STEM image of the lower boundary of sample 2 (white arrow indicates the small voids). (b) The selected region (green dashed area) in (a), indicating the high-resolution image of AIN-NL and HT-AIN (above the white dashed line). (c) The elemental map of the Al $L_{2,3}$ (green color) and N (blue color), O (red color), and C (yellow color) K -edges from the red dashed area in (a). The white dashed rectangular area in the C and Al map indicates the AIN-NL/sapphire interface.

FIG. 4. (a) A HAADF-STEM image of the lower boundary of sample 3 (white arrow indicates the voids). (b) The selected region (green dashed area) in (a), indicating the high-resolution image of AIN-NL and HT-AIN (above the white dashed line). (c) The elemental map of the Al $L_{2,3}$ (green color) and N (blue color), O (red color), and C (yellow color) K -edges from the red dashed area in (a).

FIG. 5. EELS spectra showing (a) C and (b) O *K*-edge from the AlN/sapphire interface. (c) Raman spectra of TMAI-only samples with 0, 5, and 40 s of preflow.

Furthermore, the longer the preflow time was the stronger the intensities were for both C and O. This confirms that C captured O on the sapphire surface, preventing the formation of $\text{Al}_x\text{O}_y\text{N}_z$ and thus N-polar AlN. The capture was due to the low formation energy of the $\text{C}_\text{N}-\text{O}_\text{N}$ (Ref. 23) or a kind of complex, such as the Al-C-O complex.^{24,25}

To further verify the existence of graphitic C on the sapphire surface after the preflow process, Raman measurements were carried out on the TMAI-only samples. Raman measurements were carried out on the TMAI-only samples in a Horiba Jobin Yvon confocal Micro-Raman HR 800 system, using a 473 nm laser excitation source. Figure 5(c) shows the Raman spectra of TMAI-only samples. Clearly, we observe two prominent peaks at 1354 and 1600 cm^{-1} , which were attributed to the D and G band of graphitic C in the sample that was subjected the 40 s preflow.²⁶ Furthermore, the two peaks are both broadened and the ratio of the D peak intensity to that of the G peak is close to 1. This confirms a distribution of C clusters with different orders and dimensions.²⁷ The two peaks are barely noticeable in the sample which was pre-treated for only 5 s as the duration was too short. As expected, the Raman spectral intensity of graphitic C is consistent with the EELS signal intensity of the C element with different preflow durations. Also, we notice that the Raman peaks from the sapphire substrates are identical among the three TMAI-only samples.

Additionally, the surface morphology of the TMAI-only samples was examined by SEM, as shown in Fig. 6. After the 5 s preflow, we clearly observed spotty graphitic C on the sapphire surface. The size of C clusters varied approximately from 5 to 20 nm from the atomic force microscopy (AFM) scan (not shown here). With 40 s of preflow, “islands” with 50–100 nm diameter of graphitic C were formed on sapphire substrates. These results imply that a long-time TMAI flow caused the “islands” to grow both vertically and horizontally. Also, the formation of such “C islands” could occur if other organometallic sources, such as trimethylgallium (TMGa) or trimethylindium (TMIn), are used. Epitaxial growth of graphitic C on sapphire²⁸ or direct deposition of nanocarbon materials²⁹ using propane or methane as a C source by CVD has been reported earlier, and the growth or deposition of the

graphitic film highly depends on the pressure, flow, growth temperature, and substrates. The van der Waals epitaxy is the likely growth mechanism of graphene and graphitic films by CVD on sapphire due to the extreme large lattice mismatch.³⁰

Because of the absence of the preflow process in sample 1, no C was introduced on the sapphire surface prior to the AlN epitaxy. Thus, the diffused O from sapphire formed the $\text{Al}_x\text{O}_y\text{N}_z$ intermediate layer, which led to the mix polar AlN film, as shown in Fig. 7(a).^{5,6,31} However, with the 5 s TMAI preflow, small C-rich clusters which captured the O impurity formed on the sapphire surface in sample 2, as illustrated in Fig. 7(b). Thus, no $\text{Al}_x\text{O}_y\text{N}_z$ intermediate layer was formed at the initial stages of the AlN epitaxy, leading to a uniform Al-polar film growth. Meanwhile, a quasi-3D growth mode was introduced due to the formation of C-rich clusters. As the growth continued, these small islands/grains coalesced and the surface became smooth, which means that a 2D-growth (layer by layer) was established in the end. This process is similar to the growth of a high-quality and smooth GaN film with a combination of quasi-3 and 2D growth modes.^{32,33} Eventually, a uniform and smooth surface of the AlN template was obtained as shown in the AFM image. Once the sapphire substrate was over-treated, like sample 3, a thicker layer with large C-rich clusters was formed [as shown in Fig. 6(c)], which attracted surrounding O simultaneously, as shown in Fig. 4(c).³⁴ Furthermore, the C-rich clusters at the NL acted as a mask, thus leading to a 3D growth mode throughout the subsequent template growth. Finally, the AlN nanocolumns were formed, as shown in the AFM image in Fig. 7(c).

In summary, a detailed study of the influences of TMAI preflow on the graphitic C generation at the AlN/sapphire interface was presented. The evolution behavior of polarity and growth mode changing of the AlN films caused by the C was carried out. Due to the absence of TMAI preflow, the AlN film had a mixed polarity. C-rich clusters were introduced due to the decomposition of TMAI. A slight introduction of C was found to be beneficial for creating Al-polar AlN films due to C capturing surrounding O atoms, and thus, the polarity of the AlN film was preserved as Al-polarity. Meanwhile, a quasi-3D growth mode of AlN was formed at

FIG. 6. (a)–(c) SEM plan-view images of the surface morphology of TMAI-only samples with 0, 5, and 40 s of preflow, respectively.

FIG. 7. (a)–(c) Schematics of the film polarity and growth mechanism with corresponding 3D AFM images of samples 1–3, respectively. The figures show how the C clusters impact the polarity and growth mode.

the beginning of the growth via the small C-rich islands. As the film grew thicker, the small islands coalesced and a smooth surface was obtained. However, excessive preflow resulted in the complete 3D growth of an Al-polar film. In other words, a shift of the growth mode from quasi-3D to 3D was identified due to the formation of large C-rich 3D clusters, leading to a nanocolumn growth mode. These results indicated the importance of the precise control of the C presence on the surface prior to the AlN epitaxy and proved that the TMAI preflow process could be a practical way for controlling the crystallographic polarity and the growth mode of AlN films via the intentional formation of graphitic C on the sapphire's surface.

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