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Structure and chemistry of the (111)Sc_2O_3/(0001) GaN epitaxial interface

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The structure and chemistry of the (111)Sc_2O_3/(0001) GaN epitaxial interface grown by molecular-beam epitaxy have been investigated. High-resolution transmission electron microscopy reveals an abrupt Sc_2O_3/GaN interface with a hexagonal misfit dislocation network. These dislocations have Burgers vectors of $(a/3)\langle 11\bar{2}0\rangle_{GaN}$ and line directions parallel to $\langle 1\bar{1}00\rangle_{GaN}$, with an average spacing of ~3.8 nm. Scanning transmission electron microscopy and electron energy loss spectrometry reveal the intermixing of Sc, O, and N over a region with a width of ~1.5 nm at the interface. © *2010 American Institute of Physics*. [doi:10.1063/1.3454924]

Due to its high dielectric constant (~14) and large band gap (~6.3 eV), Sc_2O_3 is promising for gate dielectric applications in GaN-based metal-oxide-semiconductor devices.[1] The Sc_2O_3/GaN interface structure and chemistry are crucial for the performance of such devices. For instance, the lattice mismatch induced misfit dislocations (MDs) at the Sc_2O_3/GaN interface may act as Coulomb potential scattering centers and reduce the carrier mobility in the underlying channel.[2] Furthermore, interdiffusion or chemical reactions at the Sc_2O_3/GaN interface may cause property degradation of Sc_2O_3 and/or GaN. Recently, epitaxial growth of (111)-oriented Sc_2O_3 films on (0001) GaN by molecular-beam epitaxy (MBE) and pulsed-laser deposition (PLD) was reported.[3,4] High-resolution transmission electron microscopy (HRTEM) was employed to study the thermal stability of the PLD-grown Sc_2O_3/GaN interface.[4] Extra care, however, must be taken for the direct interpretation of the interface chemistry based on HRTEM images, considering that the contrast in HRTEM images depends on the specimen thickness and microscope imaging parameters, as well as the structure and chemical composition of the specimen.[5] Moreover, there is to-date a lack of a detailed investigation of the Sc_2O_3/GaN interface structure, such as the characteristics (Burgers vectors, origin, density, etc.) of the MDs. In this letter, we investigate the interface of an MBE-grown Sc_2O_3/GaN heterostructure. The characteristics of the interface MDs were determined using HRTEM, and the interface chemistry was studied using a combination of scanning transmission electron microscopy (STEM) and electron energy loss spectrometry (EELS).

The Sc_2O_3 film was grown on a commercially available (0001) GaN-on-sapphire substrate[6] by reactive MBE. The MBE setup is described in detail elsewhere.[7] Prior to the growth of the oxide layer, the GaN-on-sapphire substrate was etched using a HCl:H_2O=1:1 solution for 2 min.[8] A 30-nm-thick Sc_2O_3 film was grown at a substrate temperature of 400 °C in a scandium flux of $\sim 2\times 10^{13}$ atoms/cm^2 s and an oxygen background of $\sim 2\times 10^{-7}$ Torr. Cross-sectional TEM specimens were prepared using conventional mechanical thinning followed by argon ion milling. The interface structure characterization and chemical analysis were carried out on a JEOL 2010F field emission TEM/STEM facilitated with a Gatan Enfina™ 1000 EELS system. All EEL spectra were collected under STEM mode with a dispersion of 0.2 eV/channel and a resolution of ~1.4 eV. The nominal size of the electron probe used for STEM and EELS was 0.5 nm. By imaging the probe using a charge coupled device camera and measuring the intensity distribution, the full-width at half-maximum of the probe and the probe size that encompassed 90% of the beam current were determined to be ~0.26 nm and 0.72 nm, respectively. We will use the more conservative value of 0.72 nm as the probe size in the following EELS data analysis. The semiconvergence angle was 7.25 mrad and the collection angle was 6.92 mrad for the EELS acquisition. High-angle annular dark-field (HAADF) STEM images were collected with an inner detector radius of 63.5 mrad. The microscope was operated at 200 kV for all studies.

Four-circle x-ray diffraction (XRD) was used to establish the epitaxial orientation relationship between the Sc_2O_3 film and the underlying GaN (Ref. 9). θ-2θ and ϕ scans indicate that this relationship is $(111)\times[1\bar{1}0]_{Sc_2O_3}\parallel(0001)[11\bar{2}0]_{GaN}$ plus a twin variant related by a 180° in-plane rotation. The 222 and 440 *d*-spacings of the Sc_2O_3 film are 2.86 ± 0.01 Å and 1.74 ± 0.01 Å, respectively, close to those of bulk Sc_2O_3 (2.842 Å for 222 and 1.740 Å for 440). Thus, the epitaxial Sc_2O_3 film is nearly fully relaxed. Figure 1 is a low-magnification TEM image of the Sc_2O_3/GaN heterostructure, in which a columnar microstructure is observed for the Sc_2O_3 film. Selected area diffraction (inset in Fig. 1) confirms the crystallographic relationship between Sc_2O_3 and GaN determined by XRD.

The atomic structure of the Sc_2O_3/GaN interface was examined using HRTEM. A typical HRTEM image is shown in Fig. 2, in which an abrupt Sc_2O_3/GaN interface without secondary phases is observed. Due to the −9.1% lattice mismatch between the epitaxial Sc_2O_3 film and the GaN sub-

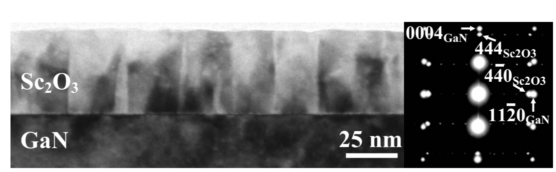

FIG. 1. A low-magnification TEM image of the Sc_2O_3/GaN heterostructure. The inset shows a SAD pattern collected from an area containing both Sc_2O_3 and GaN.

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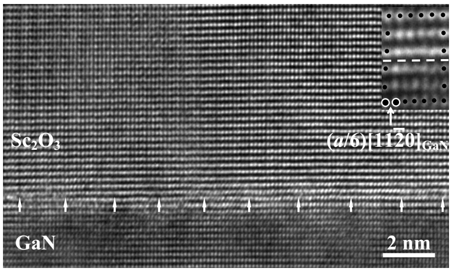

FIG. 2. Cross-sectional HRTEM image of the Sc_2O_3/GaN interface. The zone axis is $[11\bar{2}]_{Sc_2O_3}/[1\bar{1}00]_{GaN}$. The inset shows a Burgers circuit drawn around a MD.

strate, an array of MDs with line directions $\boldsymbol{l}$ parallel to $[1\bar{1}00]_{GaN}/[11\bar{2}]_{Sc_2O_3}$ formed at the interface. The arrows in Fig. 2 indicate a few such MDs. HRTEM was also carried out in the $[11\bar{2}0]_{GaN}/[1\bar{1}0]_{Sc_2O_3}$ direction, where interface MDs were not observed. Considering the symmetry of the $(0001)_{GaN}$ and $(111)_{Sc_2O_3}$ planes, three sets of MDs are expected to exist at the GaN/Sc_2O_3 interface with dislocation lines parallel to $[1\bar{1}00]_{GaN}/[11\bar{2}]_{Sc_2O_3}$, $[01\bar{1}0]_{GaN}/[1\bar{2}1]_{Sc_2O_3}$, and $[\bar{1}010]_{GaN}/[\bar{2}11]_{Sc_2O_3}$. These results are similar to those of an MBE-grown Sc_2O_3 film on a (111) Si substrate, in which MDs with line directions parallel to $[11\bar{2}]_{Si/Sc_2O_3}$, $[1\bar{2}1]_{Si/Sc_2O_3}$, and $[\bar{2}11]_{Si/Sc_2O_3}$ were observed to form a hexagonal network at the Sc_2O_3/Si interface.[10]

By drawing Burgers circuits as exemplified in the inset in Fig. 2, the Burgers vector of these MDs was determined to be $(a/6)[11\bar{2}0]_{GaN}$ [or $(a/8)[1\bar{1}0]_{Sc_2O_3}$]. It is interesting to note that this is a half of $(a/3)[11\bar{2}0]$, the Burgers vector of a common perfect-dislocation lying on the (0001) basal planes of hexagonal close-packed (hcp) crystals.[11] In the Sc_2O_3/Si heterostructure, the Burgers vector of the interfacial MDs determined by HRTEM was $(a/4)[1\bar{1}0]_{Si}$ [or $(a/8)[1\bar{1}0]_{Sc_2O_3}$], which was also a half of that of a perfect dislocation in Si, $(a/2)[1\bar{1}0]_{Si}$.[10] It was argued that the Burgers vector of the MDs at the Sc_2O_3/Si interface was, in fact, $(a/2)[1\bar{1}0]_{Si}$, and $(a/4)[1\bar{1}0]_{Si}$ was an artifact probably related to the HRTEM image contrast caused by the overlapping of two offset MD arrays in a hexagonal network[10] Considering that the $(a/6)[11\bar{2}0]$ partial dislocations are not likely to form in hcp crystals given the fact that the stacking faults with such partial dislocations are not energetically favorable,[11] we believe that the observed MDs at the Sc_2O_3/GaN interface have a Burgers vector of $(a/3)\times[11\bar{2}0]_{GaN}$. The $(a/6)[11\bar{2}0]_{GaN}$ Burgers vector displayed in the HRTEM image could be an artifact related to the image contrast, similar to the case in the Sc_2O_3/Si heterostructure.[10]

To determine the density of the interface MDs, the number of MDs was counted from several HRTEM images collected from different regions. A total of 43 MDs were observed over a range of ~81.5 nm along the $[1\bar{1}0]_{Sc_2O_3}/[11\bar{2}0]_{GaN}$ direction in the $(11\bar{2})_{Sc_2O_3}/(1\bar{1}00)_{GaN}$ cross-section, which leads to an average dislocation spacing of ~1.9 nm. As discussed in Ref. 10, since the MDs form a hexagonal network, the observed dislocation spacing is a half of the spacing between the parallel dislocations. Therefore,

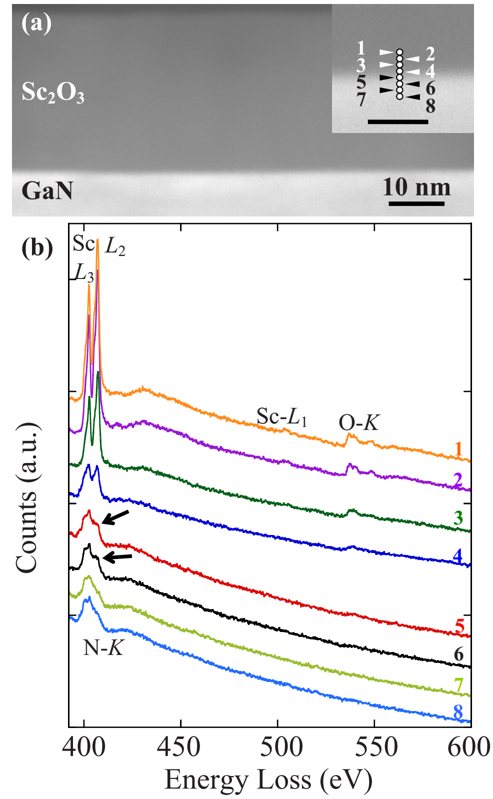

FIG. 3. (Color online) (a) HAADF STEM image of the Sc_2O_3/GaN heterostructure. The inset in (a) shows schematically the positions of the electron probes used in the EELS profile across the interface. The scale bar in the inset is 5 nm. The EEL spectra with the edges of Sc, O, and N are shown in (b). The arrows in (b) indicate the shoulders of the N K edges created by the overlapping of the Sc L_2 edge.

the hexagonal dislocation network at the Sc_2O_3/GaN interface consists of MDs with an average spacing $d\approx 3.8$ nm. The mismatch strain relaxed by the interface MDs is thus estimated to be $\varepsilon=b/d\approx 8.8\%$, with b the average of $(a/3)\times[11\bar{2}0]_{GaN}$ and $(a/4)[1\bar{1}0]_{Sc_2O_3}$. This is consistent with the XRD results that the -9.1% lattice mismatch between the Sc_2O_3 film and the GaN substrate is nearly fully relaxed. We note that the relaxed mismatch strain would only be ~4.4% if $b=(a/6)[11\bar{2}0]_{GaN}$. This further supports our assertion that the MDs at the Sc_2O_3/GaN interface have a Burgers vector of $(a/3)[11\bar{2}0]_{GaN}$.

In order to determine the thermal stability of the heterostructure, HAADF STEM and EELS were used to examine the chemical abruptness of the Sc_2O_3/GaN interface. Figure 3(a) shows a Z-contrast HAADF STEM image collected from the Sc_2O_3/GaN interface region, in which the intensity is proportional to approximately the square of the average atomic number Z of the projected atomic column.[12] Due to the lower average atomic number, the Sc_2O_3 epilayer appears darker than the GaN substrate. As illustrated in the inset in Fig. 3(a), EEL spectra were collected point-by-point using an electron probe across the Sc_2O_3/GaN interface in 0.51 nm steps. The specimen was tilted carefully to the $[11\bar{2}]_{Sc_2O_3}$ (and $[1\bar{1}00]_{GaN}$) zone axis so that the incident electron beam was parallel to the interface during EEL spectra collection. Typical spectra consisting of Sc L, N K, and O K edges are shown in Fig. 3(b).

It is evident in Fig. 3(b) that the Sc L and O K edges appear in spectra collected from positions 1 to 3, while the

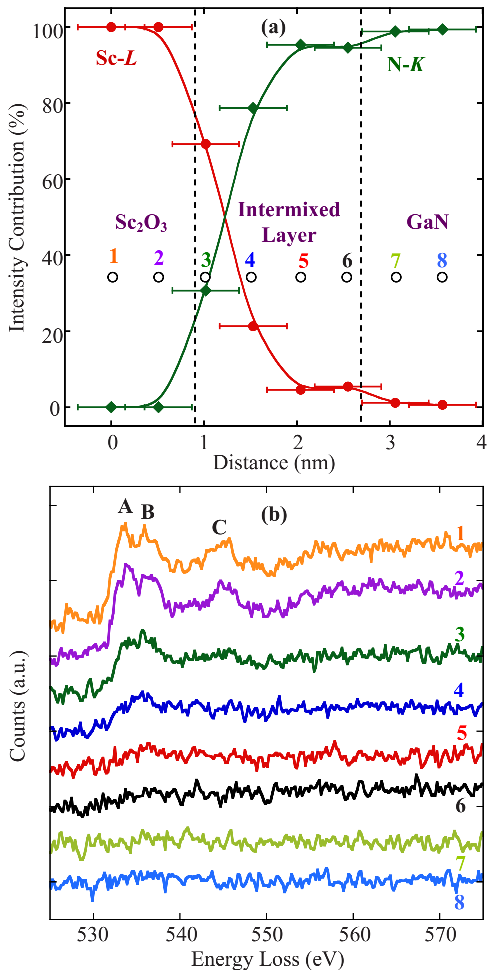

FIG. 4. (Color online) (a) Intensity contributions of Sc and N at the interface region. The error bars of the contributions are smaller than the size of the data points and the lines are intended as a guide to the eye. The two vertical dashed lines indicate the approximate interface positions of different layers. (b) Background-subtracted O *K* edges from the spectra shown in Fig. 3(b).

N *K* edge is present in spectra collected from positions 5 to 8. All of the above three edges are observed in the spectrum collected from position 4, in which the peaks near 400 eV result from the overlapping of the Sc *L* and N *K* edges. A shoulder in the N *K* edge caused by the Sc L_2 edge is also observed in spectra collected from positions 5 and 6. In order to determine the contributions from Sc and N to the overlapped Sc *L* and N *K* edges near 400 eV in the spectra, multiple least-squares fitting[13] was applied using the DIGITALMICROGRAPH software.[14] The N *K* edge collected from the GaN substrate and the Sc *L* edge collected from the Sc_2O_3 film far away from the interface were used as references in the fitting. Figure 4(a) shows the intensity contribution of Sc *L* and N *K* to the overlapped peaks near 400 eV in the spectra shown in Fig. 3(b). We find that the N *K* edge does not contribute to spectra 1 and 2, while spectra 3 to 6 evidently consist of Sc *L* and N *K* edges. The intensity contribution of the Sc *L* is ~1% at positions 7 and 8. Such a low contribution is most likely a result of the interaction between the tail of the electron beam and Sc at position 6, considering that the Sc *L* edge possesses a much higher intensity than the N *K* edge. The existence of a very small amount of Sc at these two positions cannot, however, be completely ruled out.

The evolution of the O *K* edge is shown in Fig. 4(b). The O *K* edge is invisible in spectra collected from positions 7 and 8, suggesting the O concentration is negligible beyond position 6. We also notice that the energy loss near edge structure (ELNES) of the O *K* edge in the spectra recorded from positions 1 and 2 is similar to that of the spectrum collected from the Sc_2O_3 film far away from the interface (not shown), which further confirms the chemical purity of Sc_2O_3 at these two positions. Moreover, the ELNES of the O *K* edge from positions 1 and 2 are different than those from positions 3 to 6. For example, the initial peak splitting (A,B) and the second peak (C) evident in spectra 1 and 2 gradually vanish as the electron probe moves toward the GaN. Such a change in the ELNES suggests the occurrence of Sc_2O_3 and GaN intermixing during deposition, which resulted in a different bonding of the O atoms in the interface region than in the Sc_2O_3 film away from interface.

The above EELS analyses indicate the possible presence of an intermixed layer between positions 2 and 7 (point-to-point distance is ~2.55 nm), even though HRTEM revealed an apparently abrupt Sc_2O_3/GaN interface. Taking into account the ~0.72 nm electron probe size and beam spreading up to ~0.69 nm under the EELS acquisition conditions,[15] the spatial resolution of the EELS analyses is ~1.00 nm as calculated by adding the electron probe size and the beam spreading in quadrature. Thus, the intermixed layer thickness is ~1.5 nm.

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