

# Low-temperature preparation of GaN-SiO<sub>2</sub> interfaces with low defect density. I. Two-step remote plasma-assisted oxidation-deposition process

Choelhwyl Bae and Gerald Lucovsky<sup>a)</sup>

Departments of Physics, Materials Science and Engineering, and Electrical and Computer Engineering, North Carolina State University, Raleigh, North Carolina 27695-8202

(Received 17 June 2004; accepted 23 August 2004; published 20 October 2004)

In previous studies, device-quality Si-SiO<sub>2</sub> interfaces and dielectric bulk films (SiO<sub>2</sub>) were prepared using a two-step process: (i) remote plasma-assisted oxidation (RPAO) to form a superficially interfacial oxide (~0.6 nm) and (ii) remote plasma-enhanced chemical vapor deposition (RPECVD) to deposit the oxide film. The same approach has been applied to the GaN-SiO<sub>2</sub> system. Without an RPAO step, subcutaneous oxidation of GaN takes place during RPECVD deposition of SiO<sub>2</sub>, and on-line Auger electron spectroscopy indicates a ~0.7-nm subcutaneous oxide. The quality of the interface and dielectric layer with/without RPAO process has been investigated by fabricated GaN metal-oxide-semiconductor capacitors. Compared to single-step SiO<sub>2</sub> deposition, significantly reduced defect state densities are obtained at the GaN-SiO<sub>2</sub> interface by independent control of GaN-GaO<sub>x</sub> interface formation by RPAO and SiO<sub>2</sub> deposition by RPECVD. © 2004 American Vacuum Society. [DOI: 10.1116/1.1807396]

## I. INTRODUCTION

GaN has emerged as an important material for optoelectronic and high-temperature/high-power/high-frequency device applications. As such, GaN-dielectric insulators for gate dielectrics<sup>1</sup> and surface passivation layers<sup>2</sup> have become important issues in device processing. Studies of GaN metal-insulator-semiconductor (MIS) systems have focused on reducing fixed-oxide charge and interface-trapped charge. For *n*-type GaN MIS systems, interface state density ( $D_{it}$ ) in the range of low-to-mid  $10^{11}$  cm<sup>-2</sup> eV<sup>-1</sup> has been obtained without *in situ* native oxide removal and thin intermediate layer (or sacrificial layer) preparation.<sup>1</sup> These results are remarkably different from the other compound semiconductors, where surface passivation has been an important issue to avoid thin native oxide formation between deposited oxide and substrate. Considering the deep depletion without severe Fermi-level pinning, and the low  $D_{it}$  of *n*-type GaN MIS systems, the native oxide of GaN is exempt from the critically undesirable factors such as multiple-type oxides, thermodynamic instability, metallic residue, and smaller band gap than that of the semiconductor. In the cases of GaAs metal-oxide-semiconductor (MOS) systems, improved surface passivation was initially obtained by removal of As<sub>2</sub>O<sub>3</sub> and subsequent formation of a few monolayers of Ga<sub>2</sub>O<sub>3</sub> film or (Ga<sub>2</sub>O<sub>3</sub>)<sub>1-x</sub>(Gd<sub>2</sub>O<sub>3</sub>)<sub>x</sub>.<sup>3-5</sup>

The main difference of GaN from other III-V semiconductors, such as GaAs and GaP, is the volatility of N oxide species, e.g., NO and N<sub>2</sub>O. This suggests that a thin native oxide of GaN can be used to control the semiconductor-deposited dielectric interface. The purpose of our present work is to investigate how a controlled superficially thin na-

tive oxide of GaN can improve the quality of the interface and dielectric layer of the GaN MOS system. For the oxide film deposition by a plasma-assisted process, *ex situ* wet chemical and *in situ* removal of the air-grown native oxide does not guarantee that there is no interfacial oxide because the presence of oxidant and excitation very often leads to the growth of an oxide on the substrate surface. When SiO<sub>2</sub> thin films were deposited on Si, Ge, GaAs, and CdTe using remote plasma-enhanced chemical vapor deposition (RPECVD), the substrates were slightly consumed by plasma-activated species that diffused through the deposited oxide layer and oxidized the underlying substrate.<sup>6-8</sup> These parasitic reactions, or subcutaneous oxidation, during oxide film deposition by the RPECVD process degrade the electrical characteristics of the interface. To prevent the subcutaneous oxidation of the GaAs and Ge, a thin sacrificial Si layer was deposited before the deposition of the SiO<sub>2</sub> thin film.<sup>6-8</sup> To prepare a device-quality Si-SiO<sub>2</sub> interface and dielectric bulk film (SiO<sub>2</sub>), the superficially thin oxide layer (~0.6 nm) is formed on the silicon substrate by a remote plasma-assisted oxidation (RPAO) process, and the remainder of the oxide layer is deposited by a RPECVD process.<sup>9</sup> After formation of ~0.6 nm of oxide in ~15 s, the oxidation rate slows down to ~0.3–0.4 nm/min. Therefore, during plasma-enhanced deposition at rates of ~2.5–5 nm/min, plasma-activated O species are consumed faster by deposition reactions with SiH<sub>4</sub> than by continued oxidation at the buried Si-SiO<sub>2</sub> interface.<sup>10</sup> The same RPAO-RPECVD process has been applied to SiC,<sup>11</sup> Ge,<sup>12</sup> and GaN<sup>13</sup> and has yielded a semiconductor-dielectric interface with reduced net oxide charges compared with the direct deposition of SiO<sub>2</sub> film on a semiconductor substrate.

On the other hand, the low  $D_{it}$  of GaN MIS systems also contributed to the possible underestimation of the actual  $D_{it}$ . In a wide-band-gap semiconductor, the Terman method at

<sup>a)</sup>Author to whom correspondence should be addressed; electronic mail: gerry\_lucovsky@ncsu.edu

room temperature can lead to gross underestimation of  $D_{it}$  because interface states more than  $\sim 0.6$  eV above the valence (or below the conduction) band edge cannot follow changes in dc bias at room temperature.<sup>14</sup> Therefore, high-temperature or photoassisted capacitance-voltage ( $C$ - $V$ ) measurements have been suggested to estimate  $D_{it}$  over a significant portion of the wide band gap. The present work suggests another introduced error in the estimation of  $D_{it}$  using the Terman method due to the wide band gap of GaN. The Terman method relies on a high-frequency  $C$ - $V$  measurement at a sufficiently high frequency that interface traps are assumed not to respond, but they respond to the slowly varying dc gate voltage and cause the  $C$ - $V$  curve to “stretch out” along the gate voltage axis as interface trap occupancy changes with gate bias.<sup>15,16</sup> In the estimation of  $D_{it}$  using the Terman method, it is well known that doping concentration should be known exactly to compare the difference between the measured and calculated  $C$ - $V$  curves. However, doping concentration for calculated  $C$ - $V$  curves has been selected until a close fit of  $C$ - $V$  curves was obtained over the entire voltage range because the  $C$ - $V$  characteristics of GaN MOS capacitors showed deep depletion instead of inversion. Then, the  $C$ - $V$  curve “stretch” associated with uniformly distributed  $D_{it}$  could be misinterpreted as an increased doping concentration, and can lead to the underestimation of  $D_{it}$ . The high-low frequency method or conductance method, which does not require a theoretical curve to compare with the measured curve, can be considered to reduce the uncertainty associated with doping concentration in  $C$ - $V$  characterizations of the GaN MOS system. However, due to high series resistance ( $R_s$ ) and system noise, a quasistatic or low (below 100 Hz) frequency  $C$ - $V$  curve has not been reported, and the conductance method has been used on occasion for GaN MOS analysis. In addition, there are side contact effects on the capacitance properties<sup>17</sup> for the MOS system using thin epitaxial layers grown on insulating substrates. For the GaN MOS structures, it is also difficult to properly extract the oxide-fixed charge from the flat-band voltage shift ( $\Delta V_{fb}$ ). The extraction of the fixed charge from  $\Delta V_{fb}$  has several uncertainties, such as the (i) compensated effect<sup>14</sup> among several types of charge, (ii) uncertain doping concentration of GaN MOS system, which was usually obtained from a close fit of the  $C$ - $V$  curve, and (iii) assumption of both the electron affinity of GaN and work function of the Al gate as 4.1 eV.

In this work, the occurrence of subcutaneous oxidation of GaN during plasma-enhanced deposition of SiO<sub>2</sub> films has been studied using Auger electron spectroscopy (AES) measurements. The quality of the interface and dielectric layer with/without RPAO process was investigated by fabricated GaN MOS capacitors.

## II. EXPERIMENT

The epitaxial GaN (0001) layer was grown directly on the  $c$  plane of sapphire by hydride vapor-phase epitaxy (Technologies Devices International, Inc.). Silicon was used as  $n$ -type dopant, and the thickness of the GaN epitaxial layer

was 5  $\mu\text{m}$ . The as-grown GaN layer had an electron concentration of  $5\text{--}10 \times 10^{17} \text{ cm}^{-3}$ . As-received 2-in. GaN epilayers on sapphire were degreased in organic solvents (acetone, methanol), for 20 min in each solvent. After wet-chemical treatments using 1:1:5 NH<sub>4</sub>OH:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O solution at  $\sim 80^\circ\text{C}$  and etching in 1:5 NH<sub>4</sub>OH:H<sub>2</sub>O solution at  $\sim 80^\circ\text{C}$ , the GaN samples were loaded into a multichamber system,<sup>10</sup> which provided a separate remote plasma-assisted process and on-line AES measurement.

To investigate the initial stages of oxidation of the GaN surface, AES measurements using a 3-keV electron beam were performed following each process step. The as-loaded GaN sample was exposed to reactive species from a remote N<sub>2</sub>/He discharge at 0.02 Torr to reduce residual contaminants after wet-chemical treatments.<sup>18</sup> Superficially thin GaO <sub>$x$</sub>  ( $\sim 1$  nm), with a composition close to Ga<sub>2</sub>O<sub>3</sub> or  $x \sim 1.5$ , was formed by the RPAO process at 0.3 Torr using O<sub>2</sub> source,<sup>18</sup> and a thin SiO<sub>2</sub> film was deposited by the RPECVD process at 0.3 Torr.<sup>10</sup> The substrate temperature was 300  $^\circ\text{C}$ , and plasma power was 30 W at 13.56 MHz. The experimental procedure was to alternate AES measurements with the SiO<sub>2</sub> deposition for 20 s, i.e., interrupted processing and AES analysis cycles.

For the fabrication of GaN MOS capacitors, SiO<sub>2</sub> films were deposited onto wet-chemical-treated GaN samples with/without RPAO. After gate dielectric insulator deposition, the sample was rapid-thermal annealed at  $\sim 900^\circ\text{C}$  for 30 s in Ar atmosphere. A 300-nm-thick Al layer was evaporated and defined by the conventional lithography process. For GaN MOS capacitors without RPAO, postmetallization annealing (PMA) was performed at 400  $^\circ\text{C}$  for 30 min in forming gas (N<sub>2</sub>/H<sub>2</sub>). The electrical properties of GaN MOS capacitors were investigated using an HP 4284A (precision inductance-capacitance-resistance meter). The area of the device being tested was  $4 \times 10^{-4} \text{ cm}^2$ .

## III. RESULTS AND DISCUSSION

### A. Subcutaneous oxidation of GaN during deposition of SiO<sub>2</sub>

To demonstrate subcutaneous oxidation of GaN during deposition of SiO<sub>2</sub>, two different process sequences, shown in Fig. 1, were used: (a) a direct deposition of SiO<sub>2</sub> on GaN using the RPECVD process and (b) a two-step process, i.e., RPAO process to form a superficially thin RPAO oxide layer ( $\sim 1.0$  nm), or GaO <sub>$x$</sub>  with  $x \sim 1.5$ ,<sup>18</sup> and deposition of SiO<sub>2</sub> on GaN using the RPECVD process. Figure 2 displays differential AES spectra for (i) the *in situ* N<sub>2</sub>/He-plasma-cleaned GaN sample, followed by (ii)–(vi) the SiO<sub>2</sub> deposition on the GaN sample for 20–160 s. After the N<sub>2</sub>/He plasma treatment of the GaN surface, residual C and Cl were reduced below AES detection, and the AES peak ratio of O  $KLL$  and N  $KLL$  was  $\sim 0.06$  ( $\sim 0.1$  monolayer of oxygen coverage on the GaN surface).<sup>18</sup> Increasing the deposition time of the SiO<sub>2</sub> film, the N  $KLL$  ( $\sim 378$  eV) and

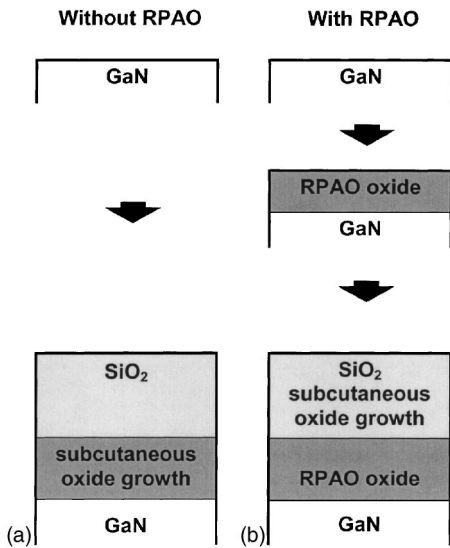


FIG. 1. Two different process sequences were used to demonstrate the presence of subcutaneous oxidation of GaN during deposition of SiO<sub>2</sub>: (a) direct deposition of SiO<sub>2</sub> on GaN using RPECVD process and (b) two-step process, i.e., RPAO process to form a superficially thin RPAO oxide layer (~1.0 nm), or GaO<sub>x</sub> with x~1.5 and deposition of SiO<sub>2</sub> on GaN using RPECVD process.

Ga (*LMM*) (~1061 eV) features mainly associated with Ga-N bonding in the GaN substrate decreased in strength, whereas the O *KLL* (~506 eV) feature mainly associated with O-Si bonding in the deposited oxide layer increased. Figure 3 displays differential AES spectra for (i) the RPAO process of the GaN sample using O<sub>2</sub> source gas, followed by (ii)-(vi) the SiO<sub>2</sub> deposition on the GaN sample for 20-160 s. Note that the N *KLL* features of both samples in

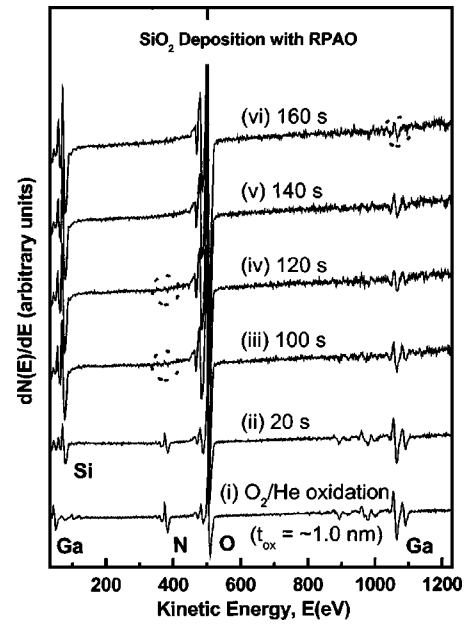


FIG. 3. Differential AES spectra for (i) RPAO process of GaN sample using O<sub>2</sub> source gas followed by (ii)-(vi) SiO<sub>2</sub> deposition on GaN sample for 20-160 s. Initial oxide thickness (*t<sub>ox</sub>*) prior to SiO<sub>2</sub> film deposition on GaN sample was ~1.0 nm.

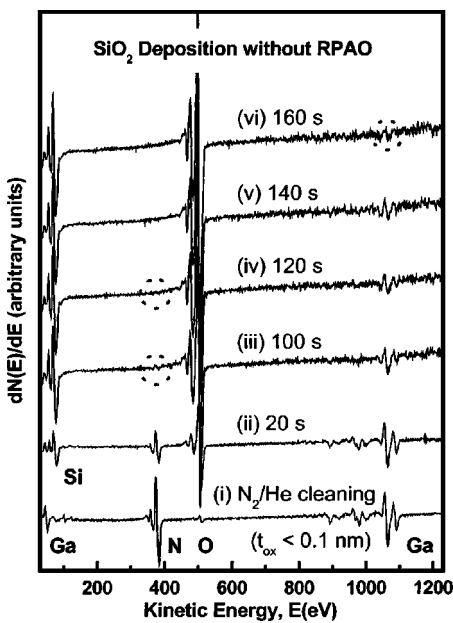


FIG. 2. Differential AES spectra for (i) *in situ* N<sub>2</sub>/He-plasma-cleaned GaN sample followed by (ii)-(vi) SiO<sub>2</sub> deposition on GaN sample for 20-160 s. Initial oxide thickness (*t<sub>ox</sub>*) prior to SiO<sub>2</sub> film deposition on GaN sample was below 0.1 nm.

Figs. 2 and 3 disappeared at nearly the same SiO<sub>2</sub> deposition time, 120 s. In addition, the Ga *LMM* features of both samples show similar intensity after the deposition of SiO<sub>2</sub> for 160 s. This indicates that oxide thickness (*t<sub>ox</sub>*) of both samples became similar after the deposition of SiO<sub>2</sub> film for 120 s.

Figure 4 shows a comparison of determined *t<sub>ox</sub>* of GaN samples shown in Figs. 2 and 3 as a function of SiO<sub>2</sub> deposition time. Assuming the negligible dependence of electron escape depth on oxide overlayer, i.e., GaO<sub>x</sub> or SiO<sub>2</sub>, oxide thickness (*t<sub>ox</sub>*) is obtained from (Ref. 18 and references therein):

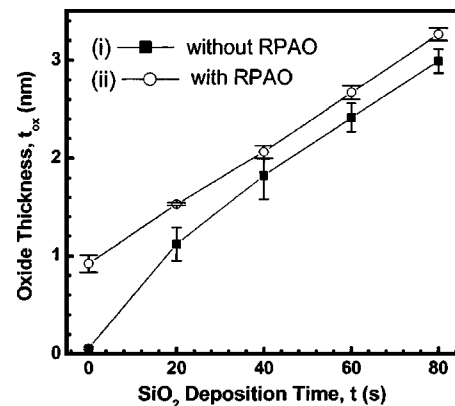


FIG. 4. Comparison of determined oxide thickness (*t<sub>ox</sub>*) of both GaN samples, shown in Figs. 2 and 3, as a function of SiO<sub>2</sub> deposition time (*t*).

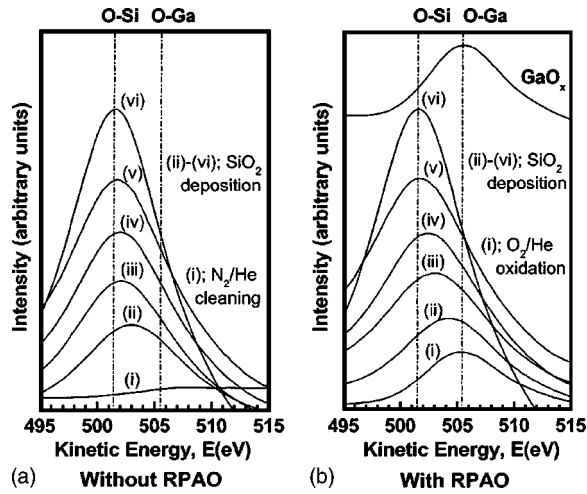


FIG. 5. Peak shift of nondifferentiated AES spectra by the SiO<sub>2</sub> deposition for (ii) 20, (iii) 40, (iv) 60, (v) 80, and (vi) 180 s on GaN samples (a) without RPAO and (b) with RPAO.

$$t_{\text{ox}} = \lambda \ln \left( 1 + \frac{I_{\text{N}}^{\text{O}}}{I_{\text{O}}^{\text{O}}} \times \frac{I_{\text{O}}}{I_{\text{N}}} \right), \quad (1)$$

where  $I_{\text{N}} = \text{N KLL}$  Auger electron intensity from the GaN substrate,  $I_{\text{N}}^{\text{O}} = \text{N KLL}$  Auger electron intensity from the clean GaN substrate,  $I_{\text{O}} = \text{O KLL}$  Auger electron intensity from the thin GaO<sub>x</sub> layer,  $I_{\text{O}}^{\text{O}} = \text{O KLL}$  Auger electron intensity from the thick GaO<sub>x</sub> layer, and  $\lambda =$  electron escape depth for O and N,  $\sim 1$  nm.

The difference of  $t_{\text{ox}}$  between two samples was gradually reduced by increasing SiO<sub>2</sub> deposition time from the initial value of  $\sim 1$  nm, and saturated to  $\sim 0.3$  nm. This reduction indicates that  $\sim 0.7$  nm of GaO<sub>x</sub> was formed during the direct SiO<sub>2</sub> deposition on the GaN sample without RPAO due to the subcutaneous oxidation process. The nearly linear SiO<sub>2</sub> deposition rate of the sample with RPAO means that negligible subcutaneous oxidation occurred, and  $\sim 1.0$  nm of GaO<sub>x</sub> using the RPAO process (or several monolayers of a sacrificial Si) can inhibit the subcutaneous oxidation process of GaN during the SiO<sub>2</sub> deposition.

Figure 5 displays the peak shift of nondifferentiated AES spectra by the SiO<sub>2</sub> deposition for (ii) 20, (iii) 40, (iv) 60, (v) 80, and (vi) 180 s on GaN samples (a) without RPAO and (b) with RPAO. The nondifferentiated AES spectrum of a thick GaO<sub>x</sub> sample, obtained by remote O<sub>2</sub>/He plasma oxidation of the GaN sample for 30 min, is included as a reference in Fig. 5(b). The AES O KLL feature at  $\sim 505.5$  eV of the GaN sample with RPAO, shown in Fig. 5(b), gradually shifts to lower energy as the SiO<sub>2</sub> deposition time increased. This gradual peak shift ( $\sim 4$  eV) of the O KLL feature indicates that O-Ga bonds change to O-Si bonds. For the direct deposition of SiO<sub>2</sub> on a cleaned GaN sample without RPAO, shown in Fig. 5(a), the O KLL feature after the deposition of SiO<sub>2</sub> for 20 s was located  $\sim 1.5$  eV higher position than that of thick SiO<sub>2</sub> films ( $> 3$  nm) and gradually shifted to lower energy as the SiO<sub>2</sub> deposition time increased. This peak shift

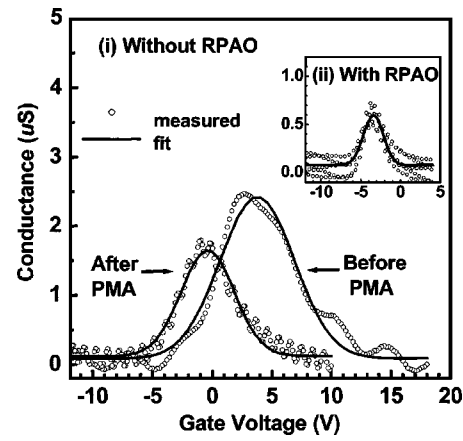


FIG. 6. Conductance-voltage ( $G$ - $V$ ) characteristics of GaN MOS capacitors (i) without RPAO before/after PMA and (ii) with RPAO measured at room temperature and 1 MHz in the dark.

demonstrates that thin GaO<sub>x</sub>, or subcutaneous oxide, was formed during the direct SiO<sub>2</sub> deposition on the GaN sample.

## B. GaN MOS system with/without RPAO

The quality of the interface and dielectric layer (i) without and (ii) with the RPAO process was compared by the fabricated GaN MOS capacitors. The RPAO process was performed for 30 s to form the RPAO oxide of  $\sim 1.0$ -nm thickness, and the RPECVD process was performed for 12 min to deposit SiO<sub>2</sub> of  $\sim 40$ -nm thickness. Note that both MOS capacitors (i) without RPAO and (ii) with RPAO have an interfacial GaO<sub>x</sub> layer below the SiO<sub>2</sub> film because subcutaneous oxide ( $\sim 0.7$  nm) was formed at the sample without RPAO. In this section, we discuss a significant role of (i) subcutaneous oxide and (ii) RPAO oxide in determining the electrical properties of the semiconductor/oxide interface. Compared to the MOS sample with RPAO, the sample without RPAO showed a large  $\Delta V_{\text{fb}}$  to the positive voltage direction and frequency dependence in the depletion region. Postmetallization annealing (PMA) was performed for the sample without RPAO at 400 °C for 30 min in forming gas (N<sub>2</sub>/H<sub>2</sub>), as well as for all of the samples with the RPAO step.

We measured conductance-voltage ( $G$ - $V$ ) characteristics of GaN MOS capacitors (i) without RPAO before/after PMA and (ii) with RPAO before PMA at room temperature and 1 MHz. Figure 6 displays the measured  $G$ - $V$  curves that have clear peaks of interface trap reduction. The value of  $R_s$  determined from measured capacitance and conductance in accumulation was  $\sim 50$ – $70$   $\Omega$ . This relatively low value of  $R_s$  for the GaN MOS system is attributed to thick ( $\sim 5$ - $\mu\text{m}$ ) GaN epilayer with high doping concentration ( $\sim 5$ – $10 \times 10^{17}$  cm<sup>-3</sup>). The low and symmetric base line of the  $G$ - $V$  curve indicates that there are no significant trapping effects and charge injection into the superficially thin RPAO oxide. For the electron-beam-deposited Ga<sub>2</sub>O<sub>3</sub> film, where the Ga<sub>2</sub>O<sub>3</sub> was used as a bulk oxide of the MOS system,<sup>19,20</sup> interface trap loss is masked by high oxide loss. The conductance peak heights of samples (i) without RPAO before

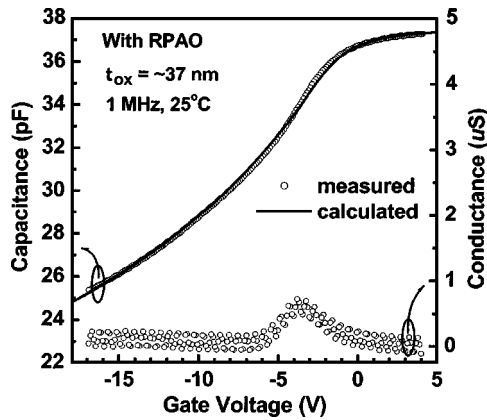


FIG. 7. Calculated and measured  $C$ - $V$  curve of the GaN capacitor with RPAO at room temperature and 1 MHz. Also shown is the measured conductance.

PMA, (ii) without RPAO after PMA, and (iii) with RPAO before PMA were  $\sim 2.4$ ,  $1.5$ , and  $0.5 \mu\text{S}$ , respectively. Because these samples have nearly similar values of  $R_s$  and oxide capacitance ( $C_{ox}$ ),  $D_{it}$  of each sample will be approximately proportional to the measured conductance peak heights.

To estimate the distribution of  $D_{it}$  using the Terman method,  $C$ - $V$  curves of each sample were measured at room temperature and 1 MHz. In the evaluation of expressions for theoretical  $C$ - $V$  curves,<sup>15,16</sup> the same fundamental constants as in a previous paper<sup>21</sup> were used. The relative dielectric constant of GaN is taken as 9.5. The intrinsic carrier concentration ( $n_i$ ) is  $2.0 \times 10^{-10} \text{ cm}^{-3}$  for GaN at room temperature. Both the electron affinity of GaN and the work function of the Al gate are assumed as 4.1 eV. Figure 7 shows the measured and calculated  $C$ - $V$  curves of the GaN MOS capacitor with RPAO. Also shown is the measured conductance. The calculated  $C$ - $V$  curve was obtained using a net donor concentration ( $N_D$ ) of  $1.7 \times 10^{18} \text{ cm}^{-3}$  and fixed oxide charge of  $3.5 \times 10^{11} \text{ cm}^{-2}$  (or  $\Delta V_{fb}$  of  $-0.6 \text{ V}$ ). These values were determined from a close fit of the measured  $C$ - $V$  curve over the entire voltage range. The measured  $C$ - $V$  curve shows a small deviation from the calculated  $C$ - $V$  curve between  $-1$  and  $-7 \text{ V}$ . Note that this deviation cannot be attributed to interface states because the measured curve is sharpened, rather than stretched. Figure 8 displays the  $1/C^2$ - $V$  characteristics. Two linear lines fit the characteristics, and  $N_D$  obtained from the slope increased from the initial value of  $1.5 \times 10^{18} \text{ cm}^{-3}$  to  $1.7 \times 10^{18} \text{ cm}^{-3}$ . It is not clear whether this result is caused by the actual change in  $N_D$  or by voltage and capacitance changes associated with interface states. Figure 9 shows the distribution of  $D_{it}$  by applying the Terman method. The minimum  $D_{it}$  was estimated as  $\sim 1 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$  at  $\sim 0.45 \text{ eV}$  below the conduction band edge. For the sample without RPAO before/after PMA, as shown in Fig. 10, there was a reduction of the stretch-out in the measured  $C$ - $V$  curves. When the measured  $C$ - $V$  curves were partially fit above  $\sim 30 \text{ pF}$ , measured curves agreed with calculated curves.  $N_D$  was  $2.7 \times 10^{18} \text{ cm}^{-3}$  for the sample before PMA

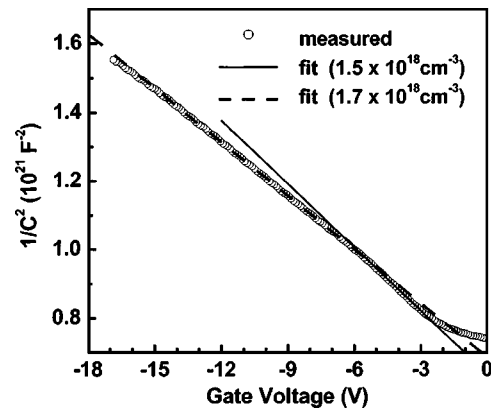


FIG. 8.  $1/C^2$  characteristics as a function of gate voltage. Net doping concentration ( $N_D$ ) obtained from the slope was  $1.5 \times 10^{18}$  and  $1.7 \times 10^{18} \text{ cm}^{-3}$ .

and  $2.0 \times 10^{18} \text{ cm}^{-3}$  for the sample after PMA. These results indicate that the  $C$ - $V$  curve stretch-out along the gate voltage axis, which is associated with interface trap occupancy changes, can sometimes be misinterpreted as an increased value of  $N_D$ .

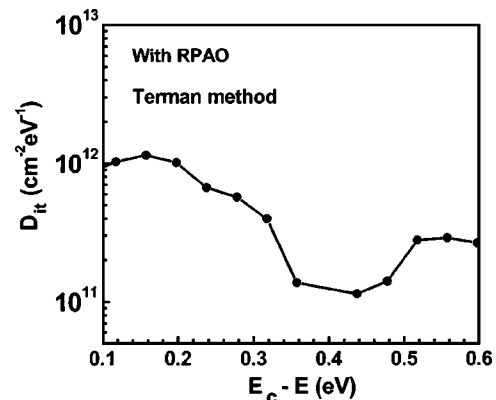


FIG. 9. Distribution of the density of interface state ( $D_{it}$ ) of GaN MOS capacitor with RPAO using Terman method.

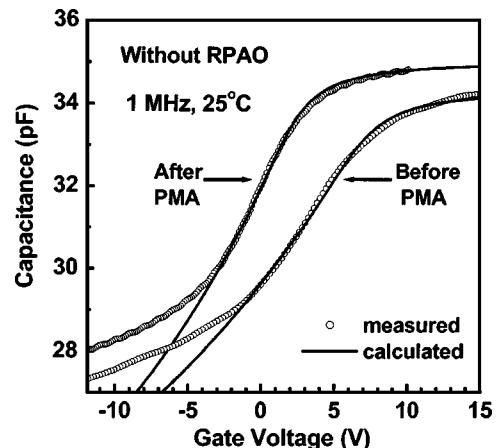


FIG. 10. Calculated and measured  $C$ - $V$  curve of the GaN capacitors without RPAO before/after PMA at room temperature and 1 MHz.

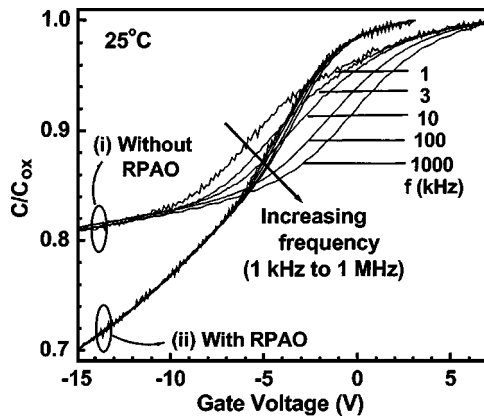


FIG. 11. Frequency dependence (1 kHz to 1 MHz) of the  $C$ - $V$  characteristics of GaN MOS capacitors (i) without RPAO after PMA and (ii) with RPAO.

Because the high-low frequency method does not require a theoretical curve to compare with the measured curve, this method can reduce the uncertainty of the extraction of  $D_{it}$  associated with doping concentration. In this study,  $C$ - $V$  curves measured at 1 MHz and 3 kHz were used as high- and low-frequency  $C$ - $V$  curves, respectively. The actual  $D_{it}$  will be higher than the estimated value using this method because the 3-kHz frequency is not sufficiently low that slow interface traps respond. In addition, the gate voltage where low and high  $C$ - $V$  curves showed the maximum capacitance difference ( $\Delta C_{max}$ ) can be used to estimate the energy level of the traps contributing to  $D_{it}$ . The capacitance difference between low and high frequency is due to the electron emission and capture by interface states. If each energy level has the same values of  $D_{it}$  and time constant of electron emission, the capacitance difference will be continuously increased with gate bias sweep from accumulation to depletion. In fact, the capacitance difference showed a maximum value and gradually decreased to a negligible value because the time constant for electron emission from interface states increased exponentially with energy from the conduction band edge. Then, a limiting energy where  $D_{it}$  can be investigated without underestimation will be obtained at the gate voltage of  $\Delta C_{max}$ . Figure 11 shows the frequency dependence (1 kHz to 1 MHz) of the  $C$ - $V$  characteristics of GaN MOS capacitors (i) without RPAO after PMA and (ii) with RPAO. The gate voltage was swept from positive to negative voltage at room temperature. Figure 12 shows the distribution of  $D_{it}$  as a function of gate voltage calculated from<sup>15,16</sup>

$$D_{it} = \frac{C_{ox}}{q} \left( \frac{C_{lf}/C_{ox}}{1 - C_{lf}/C_{ox}} - \frac{C_{hf}/C_{ox}}{1 - C_{hf}/C_{ox}} \right), \quad (2)$$

where  $C_{lf}$  is the capacitance measured at low frequency (or 3 kHz) and  $C_{hf}$  is the capacitance measured at high frequency (or 1 MHz). The minimum value of  $D_{it}$  was determined at the gate voltage where low and high  $C$ - $V$  curves showed  $\Delta C_{max}$ . For the  $C$ - $V$  curves measured at 1 MHz, shown in Fig. 11, the values of  $C/C_{ox}$  at the voltage of  $\Delta C_{max}$  were  $\sim 0.88$ – $0.89$ . This small difference in the values

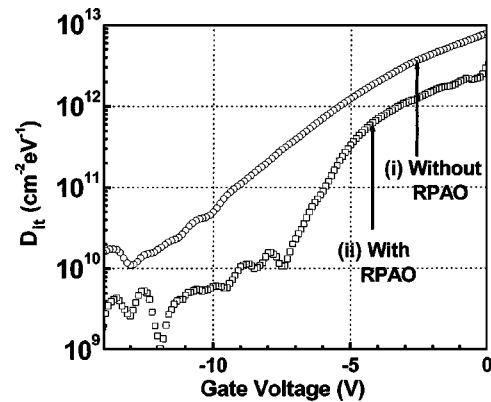


FIG. 12. Density of interface state ( $D_{it}$ ) of GaN MOS capacitors (i) without RPAO and (ii) with RPAO using the high-low frequency method. The minimum  $D_{it}$  was determined at the gate voltage where low and high  $C$ - $V$  curves showed the maximum capacitance difference ( $\Delta C_{max}$ ). Then, minimum  $D_{it}$  of (i) without and (ii) with RPAO was  $\sim 4 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$  at  $-2.5 \text{ V}$  and  $\sim 7 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$  at  $-4.1 \text{ V}$ , respectively.

of  $C/C_{ox}$  indicates that the minimum  $D_{it}$  was determined at the similar energy level. The minimum value of  $D_{it}$  (i) without the RPAO was  $\sim 4 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$  at  $-2.5 \text{ V}$ , and (ii) with RPAO was  $\sim 7 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$  at  $-4.1 \text{ V}$ . Figure 13 shows the distribution of  $D_{it}$  over the band-gap energy near the conduction band edge using the Terman method and the high-low frequency method. When the extracted values of  $D_{it}$  were compared at  $\sim 0.3 \text{ eV}$ , where  $\Delta C_{max}$  was observed,  $D_{it}$  using the Terman method is  $\sim 2$  times smaller than that using the high-low frequency method. Note that the calculated curve without  $D_{it}$  was obtained using  $N_D$  from a close fit of the  $C$ - $V$  curve, and the actual energy level for minimum  $D_{it}$  was located at a level deeper than  $\sim 0.3 \text{ eV}$ .

The conductance method was also used to clarify the estimated  $D_{it}$  using the high-low frequency method. Figures 14 and 15 show the parallel conductance loss ( $G_p/\omega$ ) versus angular frequency ( $\omega$ ) curves at selected gate voltages. Assuming negligible series resistance,  $G_p/\omega$  was obtained from<sup>16</sup>

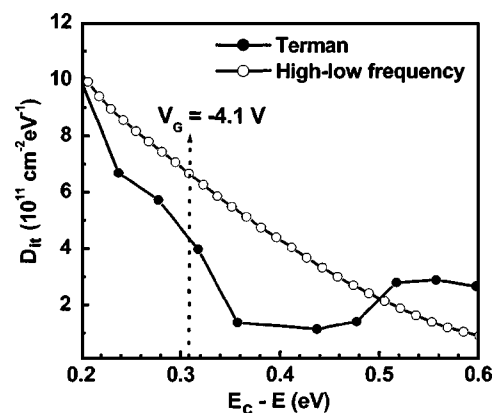


FIG. 13. Distribution of the density of interface state ( $D_{it}$ ) of GaN MOS capacitor with RPAO using the Terman method and the high-low frequency method.

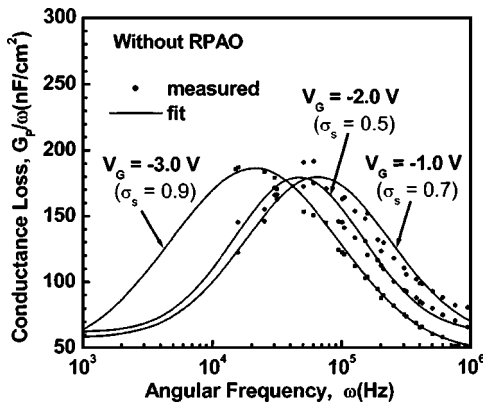


FIG. 14. Parallel conductance loss ( $G_p/\omega$ ) vs angular frequency ( $\omega$ ) curves measured at 25 °C for GaN MOS capacitor without RPAO after PMA. The graphically determined standard deviation of band bending ( $\sigma_s$ ) was 0.5–0.9 (in the unit of  $kT/q$ ).

$$\frac{G_p}{\omega} = \frac{\omega G_m C_{ox}^2}{G_m^2 + \omega^2 (C_{ox} - C_m)^2}, \quad (3)$$

where  $G_m$  is the measured conductance and  $C_m$  is the measured capacitance. From the graphically determined standard deviation of band bending ( $\sigma_s$ ) and universal function ( $f_D$ ) as a function of  $\sigma_s$ ,  $D_{it}$  of each sample was calculated from<sup>16</sup>

$$D_{it} = \left( \frac{G_p}{\omega} \right)_{f_p} [qf_D(\sigma_s)]^{-1}, \quad (4)$$

where  $f_p$  is the frequency corresponding to the peak value of  $G_p/\omega$ . The determined values of  $f_D$  were about 0.34–0.38 for the sample without RPAO and 0.24–0.26 for the sample with RPAO. Figure 16 shows  $D_{it}$  from the conductance measurements in Figs. 14 and 15, along with  $D_{it}$  from the high-low frequency method in Fig. 12. Both methods indicate well that  $D_{it}$  of (i) without RPAO after PMA is ~5 times larger compared to that of (ii) with RPAO. Therefore, it is clear that the two-step (RPAO-RPECVD) process can effectively reduce  $D_{it}$  of the GaN MOS system.

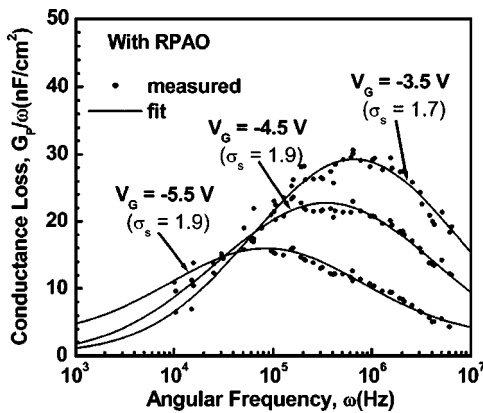


FIG. 15. Parallel conductance loss ( $G_p/\omega$ ) vs angular frequency ( $\omega$ ) curves measured at 25 °C for GaN MOS capacitor with RPAO. The graphically determined standard deviation of band bending ( $\sigma_s$ ) was 1.7–1.9 (in the unit of  $kT/q$ ).

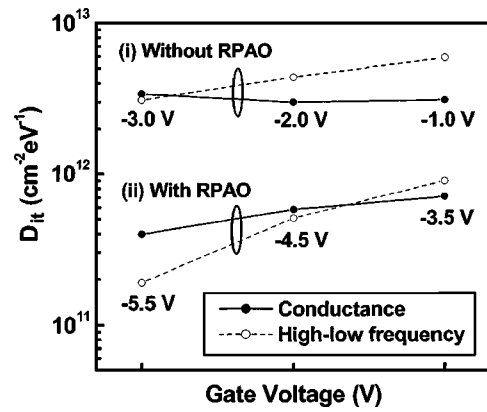


FIG. 16. Density of interface state ( $D_{it}$ ) of GaN MOS capacitors (i) without RPAO after PMA and (ii) with RPAO using the conductance method and the high-low frequency method.

### C. High-temperature and photo-assisted C-V measurements

The high-temperature C-V method<sup>22–24</sup> and photoassisted C-V method<sup>21,22,25</sup> have been used to estimate  $D_{it}$  over a significant portion of the wide band gap. The GaN MOS sample with RPAO was investigated using these two methods.

Figure 17 shows the C-V characteristics measured at 25°–200 °C in the dark. Also shown is the change in polarization charge ( $\Delta Q$ ) (Ref. 23) by increasing temperature. As reported by Matocha, Chow, and Coutmann,<sup>23</sup> our C-V curves also showed a positive shift with increasing temperature. They reported that their large positive shift (~2 V) was caused by the pyroelectric polarization of GaN because the change in the semiconductor bulk potential ( $E_c-E_f$ ) and interface trap charge ( $Q_{it}$ ) with increasing temperature make  $\Delta V_{fb}$  (below 0.1 V) negligible in the negative-voltage direction. For the capacitor with RPAO, shown in Fig. 17, calculated  $\Delta V_{fb}$  from the change in  $E_c-E_f$  was about –0.06 V with increasing temperature from 25° to 200 °C. The determined pyroelectric charge coefficient was ~4.9 × 10<sup>9</sup> q/cm<sup>2</sup> K. As shown in Fig. 17, however, C-V curves

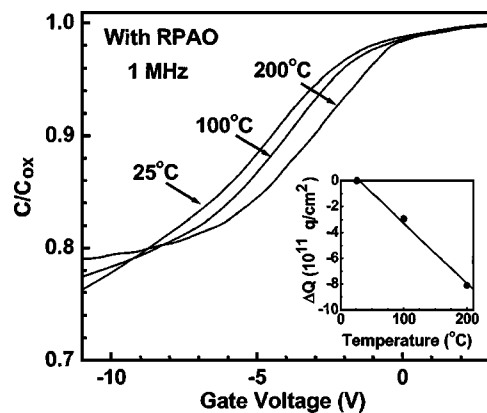


FIG. 17. C-V characteristics of GaN MOS capacitors with RPAO measured at 25°–200 °C in the dark. Also shown is the change in polarization charge ( $\Delta Q$ ) by increasing temperature Ref. 23.

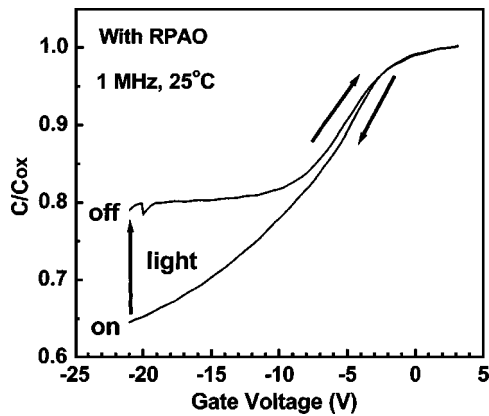


FIG. 18. Photoassisted  $C$ - $V$  characteristics of GaN MOS capacitors measured at room temperature and 1 MHz.

were stretched along the voltage axis and flatten with increasing temperature. This indicates that electron-capture/emission-associated interface traps increased at high temperature and were not negligible in the measured positive shift of  $V_{fb}$ .

Figure 18 shows the photoassisted  $C$ - $V$  characteristics measured at room temperature. The sweep rate of gate bias was 100 mV/s. From  $N_D$  of  $1.7 \times 10^{18} \text{ cm}^{-3}$ , the threshold voltage was determined as about  $-18 \text{ V}$ . The bias first swept from accumulation ( $+3 \text{ V}$ ) to deep depletion ( $-21 \text{ V}$ ) in the dark. While the bias remained at  $-21 \text{ V}$ , the sample was illuminated by ultraviolet lamp (365 nm) until the measured capacitance saturated. After the capacitance saturated, the lamp was turned off and the bias was swept back to accumulation in the dark. Due to the higher photosaturated capacitance ( $\sim 31 \text{ pF}$ ) than the expected inversion capacitance ( $\sim 25 \text{ pF}$ ), "interface state ledge"<sup>14,26,27</sup> was not observed, and photoinduced hysteresis ( $\Delta V_p$ ) was obtained within the limited voltage range. Tungsten-bulb or microscope illumination can produce the same value of photosaturated capacitance with a reduced  $\Delta V_p$ . The discrepancy between photosaturated capacitance and the expected inversion capacitance was also reported,<sup>21,22</sup> and was attributed to the small minority-carrier recombination rate, rather than to charge transfer from interface states.<sup>22</sup> In this study, the photosaturated capacitance was quite similar to the saturated capacitance measured at  $200 \text{ }^\circ\text{C}$ , as well as that of MOS samples without RPAO.

Details of high-temperature  $C$ - $V$  and photoassisted  $C$ - $V$  will be discussed in a separate paper. It would be interesting to investigate the high-temperature  $C$ - $V$  characteristics of nonpolar (or Ga- and N-terminated surface) GaN MOS structures as well as the photoassisted  $C$ - $V$  characteristics by varying the gate-voltage sweep rate, and this will be presented in a separate paper.

#### IV. CONCLUSION

A low-temperature RPAO process for interface formation and passivation has been extended from Si and SiC to GaN. The process provides the control of ultra-thin interfacial lay-

ers that passivate the GaN substrate, preventing a parasitic or subcutaneous oxidation of the substrate during plasma deposition of SiO<sub>2</sub>. Without the RPAO step, subcutaneous oxidation of GaN occurs during RPECVD deposition of SiO<sub>2</sub>, and on-line AES indicates a  $\sim 0.7$ -nm subcutaneous oxide. A two-step process (RPAO-RPECVD) has been shown to result in significantly reduced interfacial trapping compared to a single-step SiO<sub>2</sub> deposition that does not include the RPAO step. The high-low frequency method and conductance method indicate that  $D_{it}$  of a GaN MOS sample without RPAO is  $\sim 5$  times larger than that of the sample with RPAO. Improved GaN-dielectric interface properties will be obtained by changing the O<sub>2</sub>/He plasma oxidation time to minimize RPAO oxide thickness as a superficially thin ( $\sim 0.6$ – $1.0$ -nm) oxide, followed by a remote plasma-assisted interface nitridation step that introduces approximately one monolayer of nitrogen atoms at the GaN-gallium oxide interface. Also, a post-oxide-deposition anneal and forming-gas anneal need to be investigated to obtain optimized processing conditions.

The remote plasma processing can be extended to the following applications: (i) the gate dielectric insulator of a GaN MOS field-effect transistor, (ii) the passivation layer of an AlGaIn/GaN high-electron-mobility transistor (HEMT), and (iii) the intermediating layer prior to the RPAO process of other III-V materials such as GaAs and GaP. For the AlGaIn/GaN HEMT, the RPAO oxide will be a mixture of Al<sub>2</sub>O<sub>3</sub> and Ga<sub>2</sub>O<sub>3</sub> because the RPAO process will be performed on AlGaIn. For the GaAs and GaP devices, sacrificial GaN layers are formed prior to the RPAO process because the key of this study is the volatility of N-oxide species, e.g., NO and N<sub>2</sub>O. The nonvolatility of As and P oxides means that the RPAO process cannot be applied directly to GaAs or GaP.

#### ACKNOWLEDGMENT

This research is supported by the ONR, AFOSR, SRC, and i-Sematech/SRC Front End Processes Center.

- <sup>1</sup>S. J. Pearton, F. Ren, A. P. Zhang, and K. P. Lee, *Mater. Sci. Eng.*, **R**, **30**, 55 (2000).
- <sup>2</sup>R. Vetry, N. Q. Zhang, S. Keller, and U. K. Mishra, *IEEE Trans. Electron Devices* **48**, 560 (2001).
- <sup>3</sup>E. S. Aydil, K. P. Giapis, R. A. Gottscho, V. M. Donnelly, and E. Yoon, *J. Vac. Sci. Technol. B* **11**, 195 (1993).
- <sup>4</sup>M. Passlack, E. F. Schubert, W. S. Hobson, M. Hong, N. Moriya, S. N. G. Chu, K. Konstantinidis, J. P. Mannaerts, M. L. Schnoes, and G. J. Zydzik, *J. Appl. Phys.* **77**, 686 (1995).
- <sup>5</sup>J. Kwo, D. W. Murphy, M. Hong, R. L. Opila, J. P. Mannaerts, A. M. Sergeant, and R. L. Masaitis, *Appl. Phys. Lett.* **75**, 1116 (1999).
- <sup>6</sup>G. G. Fountain, S. V. Hattangady, R. A. Rudder, R. J. Markunas, G. Lucovsky, S. S. Kim, and D. V. Tsu, *J. Vac. Sci. Technol. A* **7**, 576 (1989).
- <sup>7</sup>G. Lucovsky, S. S. Kim, D. V. Tsu, G. G. Fountain, and R. J. Markunas, *J. Vac. Sci. Technol. B* **7**, 861 (1989).
- <sup>8</sup>G. Lucovsky, S. S. Kim, and J. T. Fitch, *J. Vac. Sci. Technol. B* **8**, 822 (1989).
- <sup>9</sup>T. Yasuda, Y. Ma, S. Habermehl, and G. Lucovsky, *Appl. Phys. Lett.* **60**, 434 (1992).
- <sup>10</sup>G. Lucovsky, *IBM J. Res. Dev.* **43**, 301 (1999).
- <sup>11</sup>A. Gözl, G. Lucovsky, K. Koh, D. Wolfe, H. Niimi, and H. Kurz, *J. Vac. Sci. Technol. B* **15**, 1097 (1997).



- <sup>12</sup>R. S. Johnson, H. Niimi, and G. Lucovsky, *J. Vac. Sci. Technol. A* **18**, 1230 (2000).
- <sup>13</sup>R. Therrien, G. Lucovsky, and R. Davis, *Appl. Surf. Sci.* **166**, 513 (2000).
- <sup>14</sup>J. A. Cooper, Jr., *Phys. Status Solidi A* **162**, 305 (1997).
- <sup>15</sup>D. K. Schoder, *Semiconductor Material and Device Characterization*, 2nd ed. (Wiley, New York, 1998).
- <sup>16</sup>E. H. Nicollian and J. R. Brews, *MOS (Metal Oxide Semiconductor) Physics and Technology* (Wiley, New York, 1982).
- <sup>17</sup>J. I. Izpura, *Semicond. Sci. Technol.* **16**, 243 (2001).
- <sup>18</sup>C. Bae and G. Lucovsky, *Surf. Sci.* **532–535**, 759 (2003).
- <sup>19</sup>S. Pal, S. K. Ray, B. R. Chakraborty, S. K. Lahiri, and D. N. Bose, *J. Appl. Phys.* **90**, 4103 (2001).
- <sup>20</sup>T. S. Lay, W. D. Liu, M. Hong, J. Kwo, and J. P. Mannaerts, *Electron. Lett.* **37**, 595 (2001).
- <sup>21</sup>H. C. Casey, G. G. Fountain, R. G. Alley, B. P. Keller, and S. P. Den-Baars, *Appl. Phys. Lett.* **68**, 1850 (1996).
- <sup>22</sup>B. Gaffey, L. J. Guido, X. W. Wang, and T. P. Ma, *IEEE Electron Device Lett.* **48**, 458 (2001).
- <sup>23</sup>K. Matocha, T. P. Chow, and R. J. Gutmann, *IEEE Electron Device Lett.* **23**, 79 (2002).
- <sup>24</sup>Y. Nakano and T. Jimbo, *Appl. Phys. Lett.* **80**, 4756 (2002).
- <sup>25</sup>T. Hashizume, E. Alekseev, D. Pavlidis, K. S. Boutros, and J. Redwing, *J. Appl. Phys.* **88**, 1983 (2000).
- <sup>26</sup>A. Goetzberger and J. C. Irvin, *IEEE Electron Device Lett.* **15**, 1009 (1968).
- <sup>27</sup>J. Tan, M. K. Das, J. A. Cooper Jr., and M. R. Melloch, *Appl. Phys. Lett.* **70**, 2280 (1997).