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Discrete surface state related to nitrogen-vacancy defect on plasma-treated GaN surfaces

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Detailed studies on the defect-related surface states of plasma-exposed *n*-GaN surfaces were carried out. An anomalous flat portion appeared in the metal–insulator–semiconductor capacitance–voltage characteristics for the sample exposed to H₂ plasma, corresponding to a localized peak at $E_C - 0.5$ eV in the surface state density distribution. Atomic-force microscope and x-ray photoemission studies revealed the formation of Ga droplets on H₂-plasma-treated GaN surfaces, caused by the desorption of nitrogen atoms in the form of NH_x. These results suggested that a nitrogen-vacancy-related state near the conduction-band edge was introduced on the H₂-plasma-treated GaN surface. No such effects took place on the N₂-plasma-treated GaN surfaces.
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Recent progress in high-power/high-frequency field-effect transistors based on GaN and its related heterostructures has demonstrated that they are key devices for next-generation high-density communication systems. However, these devices still have surface/interface-related problems, including frequency dispersion in drain current,¹ large gate leakage current,^{2,3} and lack of suitable surface passivation structure.⁴ Furthermore, the device processing involves various kinds of surface treatments and junction formation steps, which may introduce defects on processed GaN surfaces. To control these surface issues effectively, systematic investigation of the properties of defect-related surface states becomes inevitable. However, experimental confirmation on the chemical and electrical identity of surface defects on GaN has been largely lacking.

In this letter, we report the identification of a defect-related state on a GaN surface exposed to electron–cyclotron-resonance (ECR) excited H₂ plasma. Schottky-junction-type structures are often used for the detection of deep levels in bulk materials. However, they are not suitable for the assessment of surface states located near the band edges because of the large leakage near the flatband condition. Thus, a metal–insulator–semiconductor (MIS) structure was employed in the present investigation.

The sample structure is schematically shown in Fig. 1. We used a Si-doped *n*-type GaN layer ($n = 1 - 2 \times 10^{17} \text{ cm}^{-3}$) grown on a sapphire substrate by metal–organic vapor-phase epitaxy (MOVPE). The typical value of electron mobility at room temperature (RT) was about 500 cm²/V s. GaN surfaces were treated in NH₄OH solution at 50 °C for 10 min,⁵ followed by treatment in N₂ or H₂ plasma excited by the ECR source with a microwave (2.75 GHz) power of 50 W at 280 °C for 1–15 min. In the same chamber, a SiN_x film was subsequently deposited on the plasma-treated GaN surfaces at 280 °C by ECR-assisted chemical-vapor deposition (ECR CVD) using N₂ and SiH₄ with a mi-

crowave power of 100 W. The deposition rate was 1.0 nm/min. The thickness and refractive index of the deposited films, determined by ellipsometric measurements, ranged from 40 to 60 nm and 1.9 to 2.0, respectively. A ring-shaped Ohmic contact was formed on the GaN surface where the deposited SiN_x was removed using buffered hydrofluoride (BHF) solution (Fig. 1). Ti/Al (20/80 nm) alloy was annealed at 600 °C for 2 min. Then, an Al gate electrode with a diameter of 400 μm was formed on the SiN_x layer by a conventional vacuum deposition process. An HP 4192A LF impedance analyzer was used for *C*–*V* measurements, with a measurement frequency and a bias sweep rate of 100 kHz and 100 mV/s, respectively. The surface chemistry of the plasma-treated GaN surface was studied using an x-ray photoelectron spectroscopy (XPS) system (PHI 1600C) with a monochromated Al *Kα* x-ray source ($h\nu = 1486.6$ eV).

Figure 2 shows the measured MIS *C*–*V* curves and corresponding surface Fermi-level positions at a given gate bias for the SiN_x/GaN samples. Dotted lines indicate the calculated *C*–*V* curves based on the accumulation, depletion, and inversion behavior for the interface-trap free MIS structure.⁶ An effective electron mass of 0.2 *m*₀, an effective hole mass of 0.8 *m*₀, a dielectric constant of 9.5, and an energy gap of 3.39 eV were used in the calculation for GaN at room temperature. It is noted that the difference in the calculated curves is due to the difference in the thickness of SiN_x films. The SiN_x/GaN structures showed good *C*–*V* characteristics, consistent with the previous results.⁵ As shown in Figs. 2(a) and 2(b), the measured *C*–*V* curves for the samples with N₂

FIG. 1. Schematic illustration of the MIS structure.

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FIG. 2. Measured and ideal C - V curves of the $\text{SiN}_x/\text{n-GaN}$ samples. The solid lines indicate surface Fermi level (E_{fs}) positions.

and H_2 plasma treatments for 1 min were very close to the calculated ones. Furthermore, a clear, deep depletion behavior was observed at room temperature. This deep depletion feature without inversion characteristics is typical for wide-gap semiconductor MIS structures such as SiO_2/SiC (Ref. 7) and AlN/SiC ,⁸ since the generation rate of the minority carriers (holes) is extremely low at room temperature. In fact, the deep depletion behavior disappeared when the sample was illuminated by an UV lamp. In this case, the saturation behavior of capacitance was clearly observed due to the photoexciting minority carriers.^{9,10} These results indicated that control of the surface potential of GaN over a remarkably wide range was achieved on surfaces treated in N_2 and H_2 plasma for 1 min.

On the other hand, the long-time H_2 plasma treatment caused anomalous C - V behavior, as shown in Fig. 2(c). A flat portion appeared in the C - V curve in the bias ranging from -5 to 0 V, probably due to the pinning of the surface Fermi level. This strongly indicates the existence of a localized interface state near $E_c - 0.5$ eV, which could supply excess positive charges and block the gate control of the surface potential. The interface state density (D_{it}) distributions of the fabricated $\text{SiN}_x/\text{n-GaN}$ structures were estimated by applying the Terman method to the measured C - V curves,⁶ and the results are plotted in Fig. 3. The interfaces treated in the N_2 plasma showed continuous D_{it} distribution with a relatively low density (less than $1 \times 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$). In particular, the minimum D_{it} value of $1 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$ was obtained in the 1 min treatment process. The control sample surface (not exposed to plasma)

FIG. 3. Interface state density (D_{it}) distributions of the $\text{SiN}_x/\text{n-GaN}$ structures calculated by the Terman method.

showed similar D_{it} distributions with minimum values ranging from 3×10^{11} to $5 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$.⁵ The long-time N_2 -plasma treatment increased the density of continuous interface states. On the other hand, a localized surface state was found at approximately $E_c - 0.5$ eV for H_2 -plasma-treated surfaces, as shown in Fig. 3. The density of the discrete defect state was increased with treatment time. The total density of the defect state was estimated to be $2.1 \times 10^{12} \text{ cm}^{-2}$ for the 5 min treated sample.

In order to investigate the origin of this discrete state, atomic-force-microscope (AFM) observation and *in situ* XPS analysis were performed on the plasma-treated GaN surfaces. Figure 4 shows AFM images of GaN after treatment in H_2 plasma. As-grown MOVPE GaN exhibited a smooth surface with a root-mean-square (rms) roughness of 0.28 nm . The H_2 plasma treatment for 1 min maintained the surface morphology, showing the characteristic feature dominated by monolayer steps, as shown in the left image in Fig. 4. Many of the steps were terminated by the large dark pits at the edges, which could be correlated to the surface termination of the edge-screw-mixed dislocations.¹¹ A comparable rms roughness value of 0.31 nm to the as-grown sample was obtained. Similar AFM images were observed for the N_2 -plasma treated surface. After the 5-min H_2 -plasma treatment, however, the surface feature changed drastically. Large numbers of bright particles with a diameter of about 20 – 30 nm were found on the treated GaN surface, as shown in the right-hand

FIG. 4. AFM images of the H_2 -plasma-treated GaN surfaces.

FIG. 5. XPS Ga 3d core-level spectra of the GaN surfaces after the treatments in NH_4OH solution and H_2 plasma.

image in Fig. 4. In addition, smaller dark pits also appeared at the terraces away from the steps, which seems to be related to the pure edge dislocations.¹¹

Figure 5 shows the XPS Ga 3d core-level spectra taken from the GaN surfaces treated in NH_4OH solution and H_2 plasma. Photoemission from the GaN surface was detected using an electron escape angle of 15° , implying that the obtained spectra reflected information from the topmost region (within 1.5–2.0 nm). It was found that three spectra have the same Ga–N bonding component. However, the enlarged portion of the spectra shows that the higher intensity of photoemission was obtained in the binding energy range of 18.0–19.0 eV for the sample treated with H_2 plasma for 5 min. This energy range corresponds to the binding energy of metallic Ga bonding (typically, 18.5 eV), showing that the GaN surface after the H_2 plasma treatment for 5 min has a considerable amount of metallic Ga component. This result explicitly suggests that a large number of particles observed at the H_2 -plasma-treated surface (Fig. 4) are Ga droplets.

Based on the C – V , AFM, and XPS results, possible origins of the discrete defect state are discussed below. During the H_2 -plasma treatment, it is expected that highly active hydrogen-plasma species such as hydrogen radicals react with the GaN surface to form volatile NH_x products, namely, NH_3 . This process leaves Ga droplets and leads to N depletion at the topmost GaN surface. Separate experiments on ECR-excited reactive-ion-beam etching of n -GaN using a CH_4/H_2 gas mixture showed that the etched surface also exhibited a Ga-rich phase including a large metallic Ga component.¹² Such a surface reaction process in H_2 plasma could introduce a N-vacancy-related defect state. The reason for the appearance of the smaller dark pits on the surface exposed to H_2 plasma for 5 min is not yet clear, but the preferential desorption of N atoms may modify the surface structure including the pure edge dislocations.

Neugebauer and Van de Walle¹³ and Boguslawski, Briggs, and Bernholc¹⁴ have calculated energy levels of native point defects in GaN using the first-principle supercell method, and concluded that the simple nitrogen vacancy (V_N) creates resonant levels in the conduction band and con-

tributes to the conduction-band edge, supplying free electrons in GaN. On the other hand, recent results of calculations using the Green's function method by Yamaguchi and Junnarkar¹⁵ predicted that the V_N defect can form an s-like discrete deep level at $E_c - 0.3$ eV. Thus, these suggest the possibility that V_N -related clusters and/or defects may act as donor-type deep levels. In fact, we observed clockwise C – V hysteresis with a large voltage shift towards the negative bias only for the sample treated in the H_2 plasma for 5 min, supporting the assumption that a V_N -related state is donor type and supplies excess positive charges at the GaN surface in the deep-depletion condition. From this voltage shift and the value of insulator capacitance, the defect state density was estimated to be $1.4 \times 10^{12} \text{ cm}^{-2}$, reasonably in agreement with the value calculated from the D_{it} distribution shown in Fig. 3.

In summary, a discrete defect state was detected on H_2 -plasma-treated GaN surfaces using a MIS structure. An anomalous flat portion appeared in the C – V curve, corresponding to a clear discrete peak at $E_c - 0.5$ eV in the D_{it} distributions at the insulator–GaN interface. AFM and XPS results revealed the formation of Ga droplets on H_2 -plasma-treated GaN surfaces due to the desorption of nitrogen atoms in the form of NH_x . Such surface reactions could introduce a V_N -related donor state around 0.5 eV below the conduction-band edge. No such effects took place on N_2 -plasma-treated GaN surfaces.

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