Reduction of interface state density at SiO2/InAlN interface by inserting ultrathin Al2O3 and plasma oxide interlayers

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SiO2/InAlN interfaces formed by plasma-enhanced chemical vapor deposition were investigated. X-ray photoelectron spectroscopy showed that the direct deposition of SiO2 onto an InAlN surface led to the oxidation of the InAlN surface. The interface state density, \( D_{it} \), was on the order of \( 10^{12} \) cm\(^{-2}\)eV\(^{-1}\) (5\( \times \)10\(^{12} \) cm\(^{-2}\)eV\(^{-1}\) at 0.3 eV from the conduction band edge, \( E_c \)), which indicated the possibility of improving the interface properties. Reduction of the interface state density was attempted using an Al2O3 interlayer and a plasma oxide interlayer. The insertion of a 2-nm-thick Al2O3 interlayer to prevent surface oxidation by plasma reduced \( D_{it} \) slightly. A marked reduction in \( D_{it} \) to less than \( 10^{11} \) cm\(^{-2}\)eV\(^{-1}\) deeper than 0.3 eV from \( E_c \), however, was achieved by the intentional formation of a 1-nm-thick plasma oxide layer, formed by N2O plasma oxidation, as an interlayer between SiO2 and InAlN.

1. Introduction A lattice-matched InAlN/GaN interface provides a high-density two-dimensional electron gas (2DEG) generated by the high density of polarization-induced interface charges and the large conduction band offset [1]. Therefore InAlN is a promising material for achieving a high-power and high-frequency GaN high-electron-mobility transistor (HEMT) that can switch or control a large current flow. In the actual application of InAlN to HEMTs, the utilization of an insulator is important for suppressing the gate leakage current [2], especially for a very thin barrier layer, to obtain enhancement-mode HEMTs. It has also been reported that the electron mobility in an insulated-gate HEMT is higher than that in a Schottky barrier gate HEMT [2]. Actually, the high-power and high-frequency performances of metal-oxide-semiconductor (MOS) HEMTs have been reported [2-7]. So far, several insulators have been investigated for combination with InAlN, including Al2O3 [2, 8-11], ZrO2 [9, 12, 13], GdScO3 [9], HfO2 [12], SiO2 [14], plasma oxides [3-7], and thermal oxides [15, 16]. Among these insulators, SiO2 has the largest band gap with a proven track record in Si-based electronics. However, a method for controlling the SiO2/InAlN interface has not been investigated.

Among the several deposition methods developed for SiO2, chemical vapor deposition (CVD) is the most widely used method to deposit a high-quality SiO2 film. However, the topmost surface of the host semiconductor is usually oxidized in an uncontrolled manner during the deposition of SiO2, which might lead to disorder of the interface, resulting in the generation of interface states. To reduce the interface state density, the disorder at the interface should be avoided. To clarify the effect of deposition on the interface, one of the CVD methods should be examined. Here we applied plasma-enhanced chemical vapor deposition (PECVD), which is one of the most frequently used methods for the deposition of SiO2 films. Nevertheless, the present results for the interface chemical reaction and its control can also serve a useful reference for other CVD methods.

In this study, we investigated SiO2/InAlN interfaces formed by PECVD and attempted to reduce the interface state density, \( D_{it} \). X-ray photoelectron spectroscopy (XPS) indicated that the direct deposition of SiO2 led to the oxidation of the InAlN surface. \( D_{it} \) on the order of \( 10^{12} \) cm\(^{-2}\)eV\(^{-1}\) was measured for the SiO2/InAlN interface. Then we attempted to control the interface to reduce \( D_{it} \). Compared
with the direct deposition of SiO$_2$ onto an InAlN surface, the insertion of an ultrathin Al$_2$O$_3$ interlayer reduced $D_{it}$ slightly. However, a marked reduction was achieved by using a plasma oxide interlayer.

2. Experimental

An MOVPE-grown Si-doped (2×10$^{18}$ cm$^{-3}$) thick (160 nm) In$_{0.17}$Al$_{0.83}$N/2-μm-thick GaN buffer layer on a sapphire substrate was used for MOS diodes. The structure of the fabricated MOS diodes is shown in Fig. 1. Since the InAlN layer is sufficiently thick and highly doped, the depletion layer width is smaller than the InAlN layer thickness. Therefore, this diode can be used as an ordinary MOS diode. The fabrication sequence is as follows. Before the deposition of an insulator, the surface oxide was removed by buffered hydrofluoric acid (BHF, HF:NH$_4$F=1:5). A SiN layer of 20 nm was deposited by electron cyclotron resonance chemical vapor deposition (ECRCVD) at 400 °C. An ohmic contact electrode of Ti (20 nm)/Al (50 nm)/Ni (20 nm)/Au (50 nm) was then formed by photolithography. Then the sample was annealed at 850 °C for 1 min in a nitrogen flow with the InAlN surface protected by the SiN layer, which was followed by SiN removal with BHF. A SiO$_2$ layer (20–30 nm) was deposited by plasma-enhanced chemical vapor deposition (PECVD) at 300 °C with a plasma power of 40 W using N$_2$O and SiH$_4$. Finally, a Ni/Au electrode was formed. For the samples with interlayers, prior to the SiO$_2$ deposition, an Al$_2$O$_3$ interlayer (2 nm) was deposited by atomic layer deposition (ALD) using trimethylaluminum (TMA) and H$_2$O, while a plasma oxide interlayer (1 nm) was formed by N$_2$O plasma at 300 °C with a plasma power of 40 W. A sample without an interlayer was also fabricated for comparison.

The XPS investigation of the SiO$_2$/InAlN interface was carried out using a sample with a 30-nm-thick InAlN layer grown by MOVPE on a sapphire substrate via a 2-μm-thick GaN buffer layer. A monochromated Al-κα X-ray source (1486.6 eV) was used. The charge-up error in the binding energy was corrected by setting the C 1s spectral peak to 285.0 eV. If necessary, θ was varied by rotating the sample. The photoelectron escape depth changed accordingly as

$$\lambda = \lambda_0 \sin \theta,$$

Figure 1 Structure of MOS diode.

where $\lambda_0$ is the inelastic mean free path calculated using the theory in Refs. 17 and 18. Since the material parameters for the N$_2$O plasma oxide were unknown, the escape depth for the plasma oxide layer was assumed to be the same as that for the Al$_2$O$_3$ layer as a first approximation.

Capacitance-voltage (C–V) measurement was carried out at a bias voltage sweep rate of 25 mV/s. Interface state density, $D_{it}$, distributions were derived from the 1 MHz C–V curves by using the high-frequency method described in Ref. 19. The insulator capacitance, $C_i$, was determined from the accumulation capacitance of the Si MOS diodes that were simultaneously fabricated with the same deposition sequence. The doping density was determined from the deep depletion region at the high negative bias region of the measured 1 MHz C–V curve.

3. Results and discussion

To investigate the effect of SiO$_2$ deposition on interface chemical bonding, XPS analysis was carried out. Clear evidence of oxidation at the interface was observed in the O 1s spectra. The XPS O 1s spectra obtained from the BHF-treated InAlN surface and the ultrathin (2.6 nm) SiO$_2$/InAlN interface are shown in Fig. 2 (a). Here the spectrum for the SiO$_2$/InAlN interface was obtained at $\theta = 90^\circ$, for which the photoelectron escape depth was 2.9 nm. The energy position, shape, and intensity of the O 1s spectrum from the InAlN surface before deposition, immediately after the BHF treatment, coincided with those for the O 1s spectrum from the HF-treated gold surface, which indicated that the corresponding component can be attributed to absorbed water molecules [20]. On the other hand, as shown in Fig. 2 (b), compared with the spectrum from a thick SiO$_2$ layer, the O 1s spectrum from the ultrathin SiO$_2$/InAlN sample included an additional small shoulder peak on the lower-energy side. This shoulder peak can be
mainly attributed to Al-O bonding (531 eV), while no discernible Al-O bonding component was observed before the deposition of SiO$_2$. Thus, the surface of the InAlN was oxidized during the deposition. However, as shown in Fig. 3, no oxide components were detected in the Al 2p and In 3d core-level spectra from the SiO$_2$/InAlN interface, presumably due to the sub-monolayer thickness of the native oxide layer, resulting in signals that were too faint to be detected. Therefore, the native oxide layer that formed at the interface during the SiO$_2$ deposition was very thin (0.3 nm or less). In Fig. 3 (b), the higher-energy component in the N 1s spectrum is presumably due to absorbed NO$_x$ molecules.

The C–V characteristics for the SiO$_2$/InAlN MOS diode sample without an interlayer are shown in Fig. 4 (a). The hysteresis was negligible (not shown). Here the ideal curve is calculated assuming that the flat band voltage is obtained at zero bias. It is also assumed that the polarization charge is fully compensated. This is because the origin and generation mechanism of charge at the insulator/III-nitride interface are under debate [21-24]. In particular, the interface charge density may change with the interface bonding as discussed in Ref. 21. Therefore, we cannot determine the exact ideal value of the Al$_2$O$_3$/InAlN interface polarization charge density. Here the interface polarization charge is considered to be included in the interface fixed charge to shift the measured C–V curves horizontally relative to the ideal curve. Even though the SiO$_2$ layer was directly deposited onto the semiconductor surface by PECVD, the resultant C–V characteristic did not suffer from severe Fermi level pinning. Combined with the XPS results, this result indicates the robustness of the InAlN surface to the plasma deposition process. Nevertheless, the steepness of the C–V curve is low. The $D_{ox}$ distribution derived from the C–V curve is plotted in Fig. 5. A $D_{ox}$ of $5 \times 10^{12}$ cm$^{-2}$eV$^{-1}$ at 0.3 eV from the conduction band edge,
$E_C$, was obtained for the directly deposited SiO$_2$/InAlN sample. (This energy point can be common metric for all samples.) It may be possible to improve the interface properties by controlling the oxidation at the interface. In particular, it should be clarified whether plasma oxidation has an adverse effect on the interface properties. We thus attempted to control the interface properties.

We attempted to improve the interface properties by inserting an ultrathin interlayer to minimize the plasma oxidation of the InAlN surface. An ultrathin ALD Al$_2$O$_3$ layer was chosen because an Al$_2$O$_3$/InAlN interface has been reported to show good properties [2, 8-11]. Figure 6 shows the XPS O 1s, In 3d, N 1s, and Al 2p core-level spectra obtained from the ultrathin Al$_2$O$_3$/InAlN interface. The thickness of the Al$_2$O$_3$ ultrathin layer was 2 nm. No clear sign of oxidation was observed in the In 3d and N 1s core-level spectra. The O 1s spectrum has two components, which can be attributed to Al-O-Al bonding and Al-O-H bonding [25, 26]. For Al 2p, since the chemical shift between the hydroxide and oxide components is too small to separate them [26], the oxide components merged to form one peak here. Considering the thickness of the oxidized layer discussed for Fig. 3, the oxidation of the InAlN surface is likely to have been minimized by the Al$_2$O$_3$ interlayer during SiO$_2$ deposition. The minimization of the InAlN surface oxidation should lead to a change in the interface properties. The C-V characteristic, shown in Fig. 4 (b) for the MOS diode with the ultrathin Al$_2$O$_3$ interlayer, was slightly improved. The hysteresis was negligible again (not shown). As shown in Fig. 5, a $D_{it}$ value lower than that of the SiO$_2$/InAlN sample without the interlayer was obtained for the sample with the Al$_2$O$_3$ interlayer. The minimization of the InAlN surface oxidation led to a slight improvement of the interface properties.

A significant result was obtained by the formation of a native oxide interlayer by N$_2$O plasma oxidation. Figure 7 shows the XPS spectra obtained for the plasma-oxidized InAlN surface. The oxide components can be clearly observed in the Al 2p and In 3d spectra, while no oxide components can be seen in the N 1s spectrum. Therefore, by the present plasma oxidation, an oxide layer containing no nitrogen oxide was formed. The thickness was estimated to be about 1 nm from the decay of the spectral intensity. On the other hand, the O 1s spectrum consisted of four components indicated by A to D in Fig. 7 (a). Components A and B can be attributed to the In and Al oxides, while components C and D should be attributed to the In and Al hydroxides or their oxygen-deficient region [27-29]. The completed MOS diode, after the deposition of a thick SiO$_2$ layer, exhibited a C-V curve with a steep change in capacitance as indicated in Fig. 4 (c). A markedly reduced $D_{it}$ as shown in Fig. 5, was obtained with a value on the order of $10^{11}$ cm$^{-2}$eV$^{-1}$ near $E - E_c = -0.3$ eV. Empirically, the detection limit of $D_{it}$ was found to be $1 \times 10^{11}$ cm$^{-2}$eV$^{-1}$, and the derived $D_{it}$ was lower than the detection limit deep inside the band gap ($E - E_c < -0.3$ eV). The C–V curves do not saturate at a negative bias because the band gap of InAlN is too large to allow the formation of an inversion layer. According to a simple calculation using Shockley–Read–Hall statistics, the time constant at 0.7 eV from $E_c$ is about 1 s. Since the bias voltage sweep was sufficiently slow, i.e., 25 mV/s, we can derive $D_{it}$ in the range of 0.7 eV from $E_c$ without any
effect of deep depletion when \( D_n \) is sufficiently high. Therefore, the observed rapid reduction of \( D_n \) around \( E - E_c = -0.3 \) eV is due to the low \( D_n \). The large shift of the measured C–V curves from the ideal curve is due to the difference in the work function between metal and InAlN, and the interface/oxide fixed charge including the interface polarization charge, which is independent of \( D_n \). Although the frequency dispersion is less

![Figure 7 XPS spectra for ultrathin plasma oxide/InAlN structure. (a) O 1s, (b) In 3d, (c) N 1s, and (d) Al 2p spectra.](image)

than that in other samples, the hysteresis was increased to \(-1 \) V (not shown). However, the hysteresis for the plasma oxide interlayer sample was counterclockwise, which most likely resulted from the mobile ions and not from the interface state charge [30, 31]. Although the origin of the mobile ions is not clear, they might have originated from the intermingling of extrinsic contamination during the surface chemical treatment prior to the interface formation. The residual frequency dispersion may have possibly resulted from the lateral nonuniform distribution of the interface states, which is still high near the conduction band \( (E - E_c > -0.2 \) eV). More specifically, there is a possibility that pinning spots distributed randomly where the Fermi level was pinned locally in a small (nm-size) spot [32]. Nevertheless, the average characteristics can be derived from the high-frequency C–V curve. Therefore, neither the hysteresis nor the frequency dispersion is a rebuttal of the low \( D_n \). Although the average characteristics can be derived from the interface/oxide fixed charge including the interface polarization charge, which is independent of \( D_n \). Although the frequency dispersion is less

![Figure 7 XPS spectra for ultrathin plasma oxide/InAlN structure. (a) O 1s, (b) In 3d, (c) N 1s, and (d) Al 2p spectra.](image)
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