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Author(s)
Ogawa, Eri; Hashizume, Tamotsu; Nakazawa, Satoshi; Ueda, Tetsuzo; Tanaka, Tsuyoshi

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Chemical and Potential-Bending Characteristics of SiNₓ/AlGaN Interfaces Prepared by In Situ Metal-Organic Chemical Vapor Deposition

Eri Ogawa*¹, Tamotsu Hashizume, Satoshi Nakazawa¹, Tetsuzo Ueda¹ and Tsuyoshi Tanaka¹

Research Center for Integrated Quantum Electronics (RCIQE) and Graduate School of Information Science and Technology, Hokkaido University,
¹Semiconductor Devices Research Center, Matsushita Electric Industrial Company
Takatsuki, Osaka 569-1193, Japan Sapporo 060-8628, Japan

We investigate the chemical and potential-bending characteristics of in situ SiNₓ/AlGaN interfaces prepared by metal-organic chemical vapor deposition. X-ray photoelectron spectroscopy showed that the in situ SiNₓ layer had typical chemical binding energies corresponding to the Si-N bonds. The in situ SiNₓ deposition brought no chemical degradation on the AlGaN surface at the SiNₓ/AlGaN interface, whereas the ex situ deposition of SiNₓ by a plasma process induced chemical disorder on the AlGaN surface including a composition change and the formation of interfacial oxides. A significant reduction in the surface band bending was observed on the AlGaN surface after the in situ SiNₓ passivation, probably due to a decrease in the surface state density.

KEYWORDS: SiN, in situ, MOCVD, AlGaN, XPS, surface, potential
* e-mail: ogawa@rciqe.hokudai.ac.jp

Surface passivation structures using dielectric films such as SiO₂, SiNₓ, AlN, and Al₂O₃ among others, are very important for the realization of operation stability and reliability for various kinds of semiconductor devices. For GaN field-effect transistors (FETs), in particular, it has been reported that the SiNₓ-based passivation scheme is effective in suppressing “current collapse effects” due to a relatively low state density at the SiNₓ/AlGaN interface. Very recently, Derluyn et al. have reported that the in situ deposition of SiNₓ on the AlGaN surface significantly improved the DC performance of AlGaN/GaN high-electron mobility transistors (HEMTs). However, the physical mechanism of its passivation effects on the HEMT characteristics is not yet known. In this paper, we investigate the chemical and potential-bending characteristics of the in situ SiNₓ/AlGaN interfaces prepared by metal-organic chemical vapor deposition (MOCVD).

Figure 1 shows the sample structures. We grew undoped AlₓGa₁₋ₓN/undoped GaN structures on sapphire substrates by MOCVD. In situ deposition of an ultrathin SiNₓ layer (~ 1 nm) was carried out at 1000 °C, as shown in Fig. 1(a), using SiH₄ and NH₃ as precursors for Si and N atoms, respectively. For comparison, we prepared a reference structure having an ex situ-deposited SiNₓ layer, as shown in Fig. 1(b). After the MOCVD growth of the AlGaN/GaN heterostructures, the samples were transferred to a plasma-enhanced chemical vapor deposition (PECVD) chamber through air. Then, a SiNₓ layer with a thickness of 3 nm was deposited on the AlGaN surface at 300 °C, using SiH₄ and NH₃. The chemical properties of the SiNₓ layers and SiNₓ/AlGaN interfaces were characterized using an X-ray photoelectron spectroscopy (XPS) system (Perkin-Elmer PHI 1600C) equipped with a spherical capacitor analyzer and a monochromated Al Kα radiation source (hν = 1486.6 eV).

Figure 2 shows the Si2p and N1s core-level spectra with an electron escape angle of 15° obtained from the in situ SiNₓ surface. Because of the ultrathin thickness of the SiNₓ layer, the Ga3p signal from AlGaN underneath was overlapped with the Si2p line, whereas the N1s spectra included other N1s and Ga Auger signals from the AlGaN bond, even when using a very shallow detection angle. Thus, we deconvoluted both spectra using a combination of Gaussian and Lorentzian functions. The solid lines in Fig. 2 indicate the deconvoluted spectra. We found that the energy positions were 102.2 and 397.8 eV for the Si2p and N1s levels, respectively. These energies are very similar to those of the binding energies for
the Si-N bond.\(^\text{8)}\) The N composition of the \textit{in situ} SiN\(_x\) film, estimated from the integrated XPS intensities of the Si2p and N1s core levels, was 1.25, indicating a slightly Si-rich film in reference to a standard SiN\(_x\) composition.

Since the expected thickness of the SiN\(_x\) film is only 1 nm, we checked whether the \textit{in situ}-deposited SiN\(_x\) had a layer structure or an island structure by angle-resolved XPS. If the sample has a layer structure, as shown in Fig. 3(a), the intensity ratio of Si2p to Ga3p is given by the following equation:\(^{9)}\)

\[
\frac{I_{\text{Si2p}}}{I_{\text{Ga3p}}} = \frac{S_{\text{Si2p}}}{S_{\text{Ga3p}}} \left[ \exp \left( \frac{-d}{\lambda \sin \theta} \right) - 1 \right]^{-1}
\]

where \(S_{\text{Si2p}}\) and \(S_{\text{Ga3p}}\) are the XPS sensitivity factors for the Si2p and Ga3p core levels, respectively, \(d\) is the thickness of the SiN\(_x\) layer, \(\lambda\) is the electron escape depth in an inelastic collision process, and \(\theta\) is the electron escape angle. Since the electron kinetic energies from the Si2p and Ga3p levels are about 1400 eV, we used \(\lambda = 2.0\) nm for the calculation.\(^{10}\) Figure 3(b) shows the experimental and calculated ratios as a function of the escape angle. The angle dependence of the Si2p and Ga3p spectra is shown in the inset of Fig. 3(b). The measured ratio was in excellent agreement with the calculated curve, indicating that the \textit{in situ} deposited SiN\(_x\) film has a layer structure with high uniformity. The best fitting result allowed \(d = 1.2 \pm 0.2\) nm, which is very similar to that expected by the deposition rate. For the PECVD SiN\(_x\) film, the thickness was estimated to be \(2.5 \pm 0.3\) nm.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{(a) Schematic illustration of photoelectron emission process from the SiN\(_x\)/AlGaN layer structure. (b) XPS intensity ratio of Si2p to Ga3p as a function of electron escape angle. The solid line indicates the calculated ratio using \(d = 1.2\) nm and \(\lambda = 2.0\) nm. The inset shows the angle dependence of the XPS spectra.}
\end{figure}

Figure 4 shows the Al2p and Ga3d core-level spectra of the AlGaN surfaces with the SiN\(_x\) layers prepared by \textit{in situ} and \textit{ex situ} processes. For the \textit{in situ} sample, both the Al2p and Ga3d spectra were represented by each single component arising from the Al-N bond and Ga-N bond, respectively, in the AlGaN lattice. From the integrated XPS intensity, we found an Al composition of 39 %, which is very similar to the expected value by the growth condition.

Thus, the \textit{in situ} deposition of SiN\(_x\) brought no significant effects on the chemical bonding state of the as-grown AlGaN surface. On the other hand, the \textit{ex situ} sample showed oxide-related peaks in the Al2p and the Ga3d spectra, as shown in Fig. 4. After the growth of the AlGaN/GaN layer structure, the AlGaN surface was exposed to air, resulting in the formation of natural oxide consisting of Ga\(_2\)O\(_3\) and Al\(_2\)O\(_3\) on the AlGaN surface.\(^{5,6,11)}\) In particular, the formation of Al oxide was more enhanced than that of Ga oxide, due to the highly reactive property of Al with oxygen, probably causing a composition change on the AlGaN surface. Even after the PECVD of SiN\(_x\), such chemical degradation, including the composition change and the formation of interfacial oxides, remained on the AlGaN surface.

Finally, we estimated surface potential on the AlGaN surface from the core-level energy and the valence band edge. We plotted the Ga3d spectra of the SiN\(_x\)/AlGaN samples and bare AlGaN surface exposed to air in Fig. 5(a). In comparison to the peak position of the air-exposed sample, a slight shift toward higher energies was observed in the Ga3d peak of the \textit{ex situ} SiN\(_x\)/AlGaN sample. In the \textit{in situ} sample, we observed a large peak shift of about 0.6 eV, as shown in Fig. 5(a). Similar peak-energy shifts were confirmed in the Al2p and N1s core levels. Then, we estimated the energy position of the valence band (VB) maximum from the onset of the VB spectra, as shown in Fig. 5(b). The air-exposed AlGaN surface exhibited a VB maximum energy of 2.6 eV from the Fermi level, \(E_F\). A higher onset energy of 0.6 eV was obtained for the \textit{in situ} SiN\(_x\)/AlGaN sample. Such
difference in the onset energy was consistent with the energy difference in the Ga3d peaks. Note that such analysis was impossible on the VB spectrum for the ex situ SiN/AlGaN sample, because a thicker SiN$_x$ layer significantly impeded the appearance of the AlGaN VB spectrum.

From the energy difference in the VB onset or the Ga3d peak, the surface potential (surface band bending) on the AlGaN surface was estimated for the air-exposed and the SiN$_x$-passivated samples. We defined the surface potential, $E_S$, on the AlGaN surfaces as follows:

$$E_S = E_C - E_F = E_G - (E_F - E_V) \quad (2),$$

where $E_C$ is the energy at the conduction band minimum, $E_F$ is the bandgap of Al$_x$Ga$_{1-x}$N ($E_G = 4.2$ eV for x=0.4), and $E_V$ is the energy at the valence band maximum. The estimated $E_S$ values of the air-exposed and SiN$_x$-passivated AlGaN surfaces are plotted in Fig. 6. Only for the ex situ SiN$_x$/AlGaN sample, $E_S$ was determined from the Ga3d peak energy relative to that of the air-exposed sample, as mentioned above.

We obtained an $E_S$ of 1.6 eV on the air-exposed AlGaN surface. $E_S$ values ranging from 1.3 to 1.7 eV have often been reported for Al$_x$Ga$_{1-x}$N surfaces (x: 0.24–0.41).\(^6\)\(^,\)\(^12\)\(^,\)\(^14\) Originating from the termination of crystalline periodicity, the composition change, and the formation of an interfacial transition layer on the semiconductor surfaces, the separation of the density of states into the conduction and valence bands becomes insufficient at the insulator-semiconductor interfaces, generally inducing the so-called interface states. This suggests that the upper half of the state continuum has a conduction-band character with an acceptor-like charging nature, whereas the lower-half one is derived from the valence-band states with a donor-like charging nature.\(^15\)

The branching point between the two kinds of state continuum can act as a charge neutrality level.\(^16\) It is likely that the air-exposed AlGaN surface has high-density interface states due to chemical degradation as mentioned above. The acceptor-like states occupied with electrons can induce a large amount of negative charge on the AlGaN surface, thereby increasing the surface potential of AlGaN. The surface passivation structure utilizing the ex situ deposition of SiN$_x$ may slightly reduce the surface states. After the in situ SiN$_x$ passivation, we observed a pronounced reduction in surface potential down to 1.0 eV, as shown in Fig. 6. As shown in Fig. 4, no chemical degradation was brought on the AlGaN surface after the in situ deposition of SiN$_x$. The in situ CVD provided no interfacial composites such as oxides and less processing energy to the AlGaN surface than the plasma-assisted process. Thus, the surface passivation structure having in situ-deposited SiN$_x$ could be effective in reducing the electronic states on the AlGaN surface.

There remains a possibility that the difference in the passivation effect between the in situ and ex situ SiN$_x$ layers comes from the difference in their insulating film quality. The ex situ SiN$_x$ layer was deposited at a relatively low temperature (300 °C). In this case, the film usually includes many H atoms and becomes coarse. In comparison with the in situ SiN$_x$ layer deposited at 1000 °C, such an inferior film quality of the ex situ SiN$_x$ can cause a reduction in its bandgap and/or a change in its band alignment to AlGaN, affecting the surface potential of the AlGaN surface at the SiN$_x$/AlGaN interface. Thus, further investigation is needed to obtain better insight into the passivation effects of the SiN$_x$ deposition on the AlGaN surface.

In summary, we investigated the chemical and potential-bending characteristics of SiN$_x$/AlGaN interfaces. By
angle-resolved XPS, we confirmed that in situ SiNₓ had a layer structure with a thickness of 1.2 nm. The in situ SiNₓ deposition brought no degradation on the chemical bonding states of the AlGaN surface, whereas the ex situ deposition of SiNₓ by a plasma process induced chemical degradation on the AlGaN surface including a composition change and the formation of interfacial oxides. In addition, the in situ deposition of SiNₓ resulted in a significant reduction in surface potential bending on the AlGaN surface, probably due to a decrease in the surface state density. A surface passivation structure utilizing an in situ SiNₓ layer can be promising for improving the stability and reliability of GaN-based devices.