



HOKKAIDO UNIVERSITY

Title	Chemical and Potential Bending Characteristics of SiNx/AlGaIn Interfaces Prepared by In Situ Metal-Organic Chemical Vapor Deposition
Author(s)	Ogawa, Eri; Hashizume, Tamotsu; Nakazawa, Satoshi et al.
Citation	Japanese Journal of Applied Physics. Pt. 2, Letters & express letters, 46(24), L590-L592 https://doi.org/10.1143/JJAP.46.L590
Issue Date	2007-06-25
Doc URL	https://hdl.handle.net/2115/33899
Rights	Copyright © 2007 The Japan Society of Applied Physics
Type	journal article
File Information	JJAP-ogawa.pdf



Chemical and Potential-Bending Characteristics of $\text{SiN}_x/\text{AlGaN}$ Interfaces Prepared by *In Situ* Metal-Organic Chemical Vapor Deposition

Eri Ogawa*, 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, Japa Sapporo 060-8628, Japan n

We investigate the chemical and potential-bending characteristics of *in situ* $\text{SiN}_x/\text{AlGaN}$ interfaces prepared by metal-organic chemical vapor deposition. X-ray photoelectron spectroscopy showed that the *in situ* SiN_x layer had typical chemical binding energies corresponding to the Si-N bonds. The *in situ* SiN_x deposition brought no chemical degradation on the AlGaN surface at the $\text{SiN}_x/\text{AlGaN}$ interface, whereas the *ex situ* deposition of SiN_x 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* SiN_x passivation, probably due to a decrease in the surface state density.

KEYWORDS: SiN_x , *in situ*, MOCVD, AlGaN , XPS, surface, potential

* e-mail : ogawa@rciqe.hokudai.ac.jp

Surface passivation structures using dielectric films such as SiO_2 , SiN_x , AlN , and Al_2O_3 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 SiN_x -based passivation scheme is effective in suppressing "current collapse effects" ¹⁻³⁾ due to a relatively low state density at the $\text{SiN}_x/\text{AlGaN}$ interface.⁴⁻⁶⁾ Very recently, Derluyn *et al.*⁷⁾ have reported that the *in situ* deposition of SiN_x 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* $\text{SiN}_x/\text{AlGaN}$ interfaces prepared by metal-organic chemical vapor deposition (MOCVD).

Figure 1 shows the sample structures. We grew undoped $\text{Al}_{0.4}\text{Ga}_{0.6}\text{N}$ /undoped GaN structures on sapphire substrates by MOCVD. *In situ* deposition of an ultrathin SiN_x layer (~ 1 nm) was carried out at 1000 °C, as shown in Fig. 1(a), using SiH_4 and NH_3 as precursors for Si and N atoms, respectively. For comparison, we prepared a reference structure having an *ex situ*-deposited SiN_x 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 SiN_x layer with a thickness of 3 nm was deposited on the AlGaN surface at 300 °C, using SiH_4 and NH_3 . The chemical properties of the SiN_x layers and $\text{SiN}_x/\text{AlGaN}$ 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 $K\alpha$ radiation source ($h\nu = 1486.6$ eV).

Figure 2 shows the $\text{Si}2p$ and $\text{N}1s$ core-level spectra with an electron escape angle of 15° obtained from the *in situ* SiN_x surface. Because of the ultrathin thickness of the SiN_x layer, the $\text{Ga}3p$ signal from AlGaN underneath was overlapped with the $\text{Si}2p$ line, whereas the $\text{N}1s$ spectra included other $\text{N}1s$ 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 $\text{Si}2p$ and $\text{N}1s$ levels, respectively. These energies are very similar to those of the binding energies for

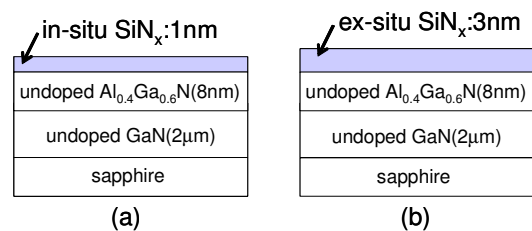


Fig. 1. Sample structures with (a) *in situ* and (b) *ex situ* SiN_x passivation layers.

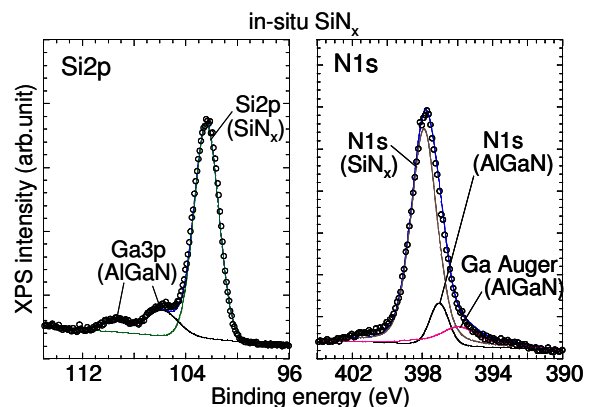


Fig.2 XPS $\text{Si}2p$ and $\text{N}1s$ spectra from the *in situ* SiN_x layer deposited on AlGaN/GaN heterostructure.

the Si-N bond.⁸⁾ The N composition of the *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 Si₃N₄ composition.

Since the expected thickness of the SiN_x film is only 1 nm, we checked whether the *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⁾

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

where S_{Si2p} and S_{Ga3p} are the XPS sensitivity factors for the Si2p and Ga3p core levels, respectively, d is the thickness of the SiN_x layer, λ is the electron escape depth in an inelastic collision process, and θ 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 *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 ± 0.3 nm.

Figure 4 shows the Al2p and Ga3d core-level spectra of the AlGaIn surfaces with the SiN_x layers prepared by *in situ* and *ex situ* processes. For the *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 AlGaIn 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 *in situ* deposition of SiN_x brought no significant effects on the chemical bonding state of the as-grown AlGaIn surface. On the other hand, the *ex situ* sample showed oxide-related peaks in the Al2p and the Ga3d spectra, as shown in Fig. 4. After the growth of the AlGaIn/GaN layer structure, the AlGaIn surface was exposed to air, resulting in the formation of natural oxide consisting of Ga₂O₃ and Al₂O₃ on the AlGaIn surface.^{5,11)} 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 AlGaIn surface. Even after the PECVD of SiN_x, such chemical degradation, including the composition change and the formation of interfacial oxides, remained on the AlGaIn surface.

Finally, we estimated surface potential on the AlGaIn surface from the core-level energy and the valence band edge. We plotted the Ga3d spectra of the SiN_x/AlGaIn samples and bare AlGaIn 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 *ex situ* SiN_x/AlGaIn sample. In the *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 AlGaIn 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 *in situ* SiN_x/AlGaIn sample. Such

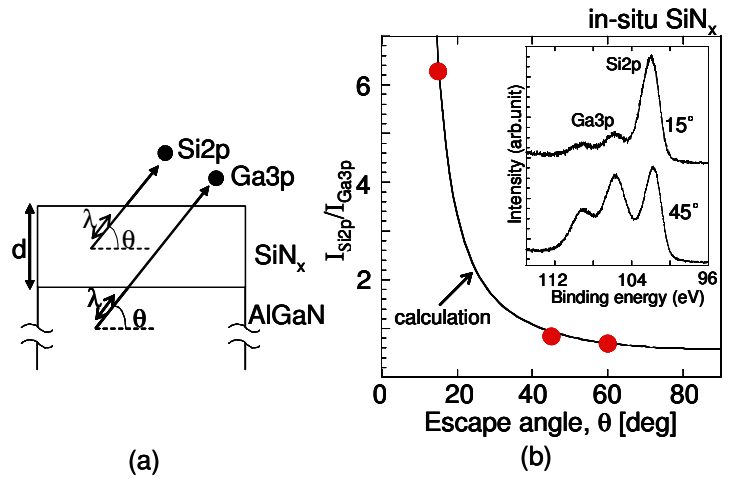


Fig.3 (a) Schematic illustration of photoelectron emission process from the SiN_x/AlGaIn layer structure. (b) XPS intensity ratio of Si2p to Ga3p as a function of electron escape angle. The solid line indicates the calculated ratio using $d = 1.2$ nm and $\lambda = 2.0$ nm. The inset shows the angle dependence of the XPS spectra.

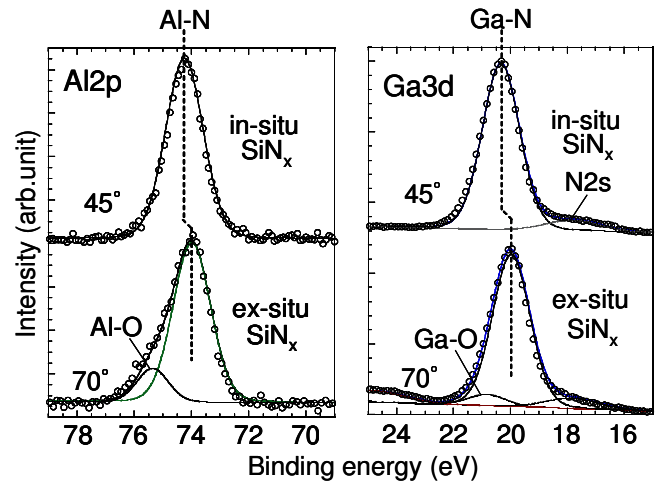


Fig.4 Al2p and Ga3d spectra for the SiN_x/AlGaIn interfaces.

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_x/AlGa_{1-x}N sample, because a thicker SiN_x layer significantly impeded the appearance of the AlGa_{1-x}N VB spectrum.

From the energy difference in the VB onset or the Ga3d peak, the surface potential (surface band bending) on the AlGa_{1-x}N surface was estimated for the air-exposed and the SiN_x-passivated samples. We defined the surface potential, E_s , on the AlGa_{1-x}N 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_g is the bandgap of Al_xGa_{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 AlGa_{1-x}N surfaces are plotted in Fig. 6. Only for the *ex situ* SiN_x/AlGa_{1-x}N 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 AlGa_{1-x}N surface. E_s values ranging from 1.3 to 1.7 eV have often been reported for Al_xGa_{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 AlGa_{1-x}N 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 AlGa_{1-x}N surface, thereby increasing the surface potential of AlGa_{1-x}N. 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 AlGa_{1-x}N 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 AlGa_{1-x}N 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 AlGa_{1-x}N 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 AlGa_{1-x}N, affecting the surface potential of the AlGa_{1-x}N surface at the SiN_x/AlGa_{1-x}N interface. Thus, further investigation is needed to obtain better insight into the passivation effects of the SiN_x deposition on the AlGa_{1-x}N surface.

In summary, we investigated the chemical and potential-bending characteristics of SiN_x/AlGa_{1-x}N interfaces. By

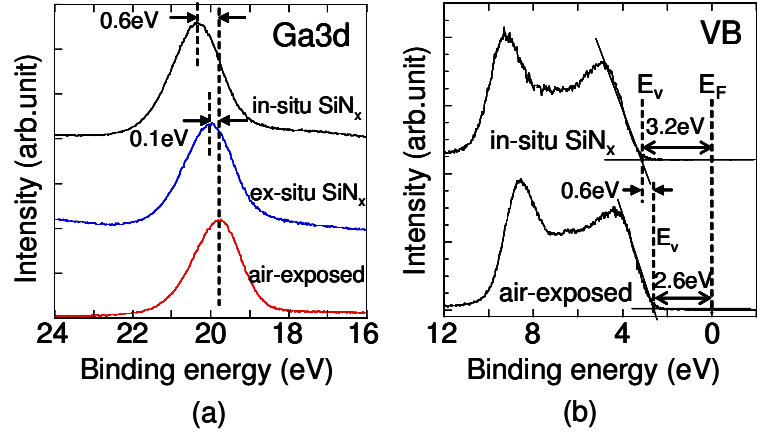


Fig.5 (a) Ga3d spectra for the air-exposed AlGa_{1-x}N surface and the SiN_x/AlGa_{1-x}N interfaces. (b) Valence band spectra for the air-exposed and *in situ* SiN_x passivated AlGa_{1-x}N surfaces.

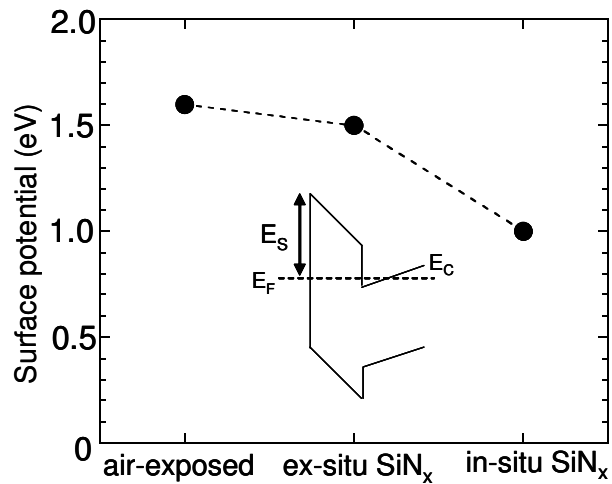


Fig.6 Surface potential values for the air-exposed and the SiN_x passivated AlGa_{1-x}N surfaces.

angle-resolved XPS, we confirmed that *in situ* SiN_x had a layer structure with a thickness of 1.2 nm. The *in situ* SiN_x deposition brought no degradation on the chemical bonding states of the AlGaN surface, whereas the *ex situ* deposition of SiN_x 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 SiN_x 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* SiN_x layer can be promising for improving the stability and reliability of GaN-based devices.

- 1) B. M. Green, K. K. Chu, E.M. Chumbes, J.A. Smart, J.M. Shealy and L.F. Eastman: IEEE Electron Device Lett. **21** (2000) 268.
- 2) Y. Okamoto, Y. Ando, T. Nakayama, Koji Hataya, H. Miyamoto, T. Inoue, M. Senda, K. Hirata, M. Kosaki, N. Shibata, and M. Kuzuhara: IEEE Trans. Electron Devices, **51** (2004) 2217.
- 3) T. Kikkawa: Jpn. J. Appl. Phys. **44** (2005) 4896.
- 4) T. Hashizume, S. Ootomo, S. Oyama, M. Konishi and H. Hasegawa: J. Vac. Sci. Technol. B **19** (2001) 1675.
- 5) T. Hashizume, S. Ootomo, T. Inagaki and H. Hasegawa: J. Vac. Sci. Technol. B **21** (2003) 1828.
- 6) T. Hashizume and H. Hasegawa: Appl. Surf. Sci. **234** (2004) 387.
- 7) J. Derluyna, S. Boeykens, K. Cheng, R. Vandersmissen, J. Das, W. Ruythooren, S. Degroote, M. R. Leys, M. Germain, and G. Borghs: J. Appl. Phys. **98** (2005) 054501.
- 8) R. Kaercher, L. Lay, and R.L. Johnson: Phys. Rev. B **30** (1984) 1896.
- 9) S. Hofman and J. M. Sanz: Surf. Interface Anal. **6** (1984) 75.
- 10) D. R. Penn: Phys. Rev. B **35** (1987) 482.
- 11) T. Hashizume, S. Ootomo, R. Nakasaki, S. Oyama, M. Kihara: Appl. Phys. Lett. **76** (2000) 2880.
- 12) H.W. Jiang, C.M. Jeon, K.H. Kim, J.K. Kim, S.B. Bae, J.H. Lee, J.W. Choi, J.L. Lee: Appl. Phys. Lett. **81** (2002) 1249.
- 13) A. Rizzi, H. Luth: Appl. Phys. A **75** (2002) 69.
- 14) S. Heikman, S. Keller, Y. Wu, J.S. Speck, S.P. DenBaars, K. Mishra: J. Appl. Phys. **93** (2003) 10114.
- 15) H. Luth: *Surfaces and Interfaces of Solids*, (Springer-Verlag, Berlin, 1993) 2nd. Ed., Chapter 6.
- 16) W. Moench, Appl. Sur. Sci. **117/118** (1997) 380.