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Epitaxial growth of high-quality GaN on appropriately nitridated Si substrate by metal organic chemical vapor deposition

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Abstract

Single-crystalline GaN films were grown on Si(1 1 1) substrates by metal organic chemical vapor deposition (MOCVD) using a silicon nitride (SiN_x) buffer achieved through the nitridation of substrate. The effect of in situ substrate nitridation on the GaN crystalline quality was investigated with the nitridation being performed at 750, 950 and 1120 °C, respectively. It demonstrates that the nitridation temperature greatly influences the surface morphology and PL spectra of GaN grown atop SiN_x buffer. The surface roughness of GaN film grown atop the Si substrate nitridated at 950 °C exhibited a root mean square (RMS) value of 5.057 nm for surface roughness evaluated by atomic force microscopy (AFM). Additionally, a strong photoluminescence (PL) emission at 365 nm (3.4 eV) with the full-width at half-maximum (FWHM) of 61.1 meV was achieved at room temperature. Particularly, a yellow luminescent band that was observed when the nitridation was performed at 750 °C was greatly reduced to a degree that could hardly be recognized. Alternatively, nitridating the substrate at 1120 °C resulted in a strong but much wider PL spectrum. Accordingly, an effective buffer of SiN_x for the growth of GaN on Si substrates can be formed by introducing the substrate nitridation at a due temperature around 950 °C before the commencement of epitaxial growth.
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1. Introduction

In recent years, the GaN compound semiconductor has attracted much attention because of its

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large, direct band-gap and high thermal stability. III-nitride-based semiconductors have become very important materials for light-emitting diodes (LEDs) and laser diodes under continuous wave operation in the visible spectrum region ranging from green to blue colors [1–4]. Nevertheless, there is still a lack of a suitable substrate for GaN-based devices to develop their superiorities fully. So far, there have been a number of studies concerned with the growth of GaN films on a variety of substrates, such as sapphire [5], SiC [6], GaAs [7], and Si [8–11]. Among these materials, Si is regarded as a relatively promising substrate for GaN epitaxy because it promises two advantages: low cost and large areas. Besides, this material system will make the integration of Si-based microelectronics with GaN-based optoelectronics possible. Nevertheless, it is still difficult to grow device-quality GaN on Si substrate due to a large lattice mismatch of 17% and a thermal expansion coefficient incompatibility of 56%. Otherwise, GaN cannot be grown as a buffer layer directly on Si substrates due to poor nucleation of GaN on Si [12]. Therefore many other kinds of buffers have previously been used, such as AlN [13], AlGaN/AlN [14,15] and SiC [16]. Although there have been some reports on the successful growth of GaN on Si, a defect-induced broad yellow luminescence (YL) band was not easy to be removed from the photoluminescence (PL) spectra [9,15,17]. On the other hand, it has recently been demonstrated that no YL was present when a Si_3N_4 buffer was used for the GaN grown by hot wall chemical vapor deposition [18]. This buffer was achieved by nitridating the Si substrate with N_2 flow at 900 °C. Besides, a double-buffer structure of AlN/β-Si_3N_4 was used by molecular beam epitaxy [19] where single-crystalline β-Si_3N_4 was obtained by introducing the active nitrogen plasma to the Si(1 1 1) surface at 900 °C for about 30 s. Here, the β-Si_3N_4 was shown to be a very effective diffusion barrier and the epitaxial quality of GaN film was also significantly improved.

In the present study, an SiN_x layer accompanied by $Al_{0.15}Ga_{0.85}N$/AlN double-buffer are used to form a triple-buffer structure for GaN epitaxially grown on Si substrate. The SiN_x layer was attained easily by a nitridation process in the metal organic chemical vapor deposition (MOCVD) reactor. To the best of our knowledge, this is the first time nitridation was performed by introducing NH_3 flow solely to the Si(1 1 1) surface with MOCVD. The nitridation temperature was varied to optimize the growth of GaN on Si. In this paper, the effect of substrate nitridation on the GaN epilayer is analyzed and an appropriate nitridation temperature is determined.

2. Experiment procedure

GaN epilayers were grown by a home-made atmospheric pressure MOCVD system with a vertical reactor. The liquid MO compounds of TMGa, TMAl and gaseous NH_3 were employed as the reactant source materials for Ga, Al and N, respectively and H_2 was used as the carrier gas. The substrates used in this experiment were cut from (1 1 1)-oriented Si wafers offset by 4° off toward ⟨0 1 1⟩ direction. These wafers show *n*-type conductivity with the carrier concentration around $10^{18}\,cm^{-3}$. Prior to growth, the Si(1 1 1) substrate was etched by boiling it in $H_2SO_4 : H_2O_2 = 3 : 1$ for 15 min and then dipped in HF solution ($HF : H_2O = 1 : 10$) for 15 s to remove native oxide formed on the surface. Fig. 1 shows the temperature program of our growth experiment. The Si substrate after loading was first heated to 1120–1135 °C under an $H_2 + HCl$

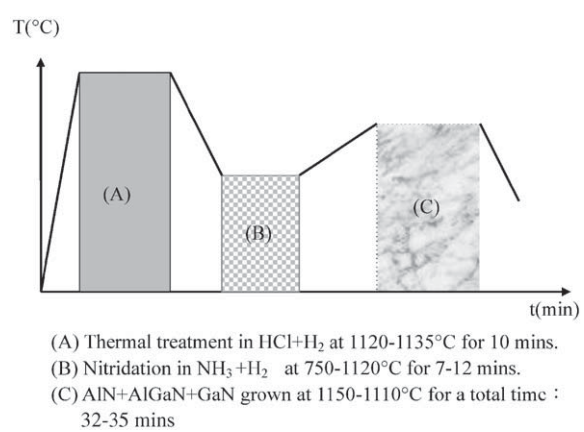

Fig. 1. The temperature program used in our growth experiment.

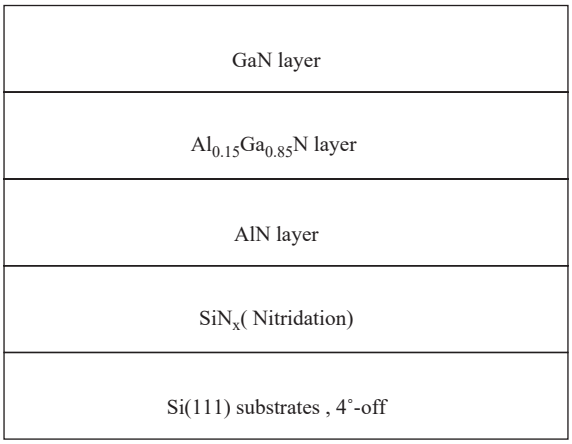

Fig. 2. A schematical view of GaN/Si (1 1 1) with an $Al_{0.15}Ga_{0.85}N/AlN/SiN_x$ buffer system.

ambient for 10 min to remove the surface passivated layer. Following the thermal etching, the substrate was nitridated by exposing it to the NH_3 flow of 0.889 slm for 7–12 mins at 750, 950 and 1120 °C, respectively. Then, AlN, $Al_{0.15}Ga_{0.85}N$ and GaN were grown in sequence at 1110–1130 °C for a total growth time of 35 min using a TMA flow of 19 sccm, a TMG flow of 13.4 sccm and an NH_3 flow of 1.963 slm, respectively. Finally, about 1-μm-thick GaN epilayer was grown atop. Fig. 2 shows the schematic of our epitaxial structure. The surface morphology of the top GaN layer was observed by atomic force microscopy (AFM). Crystalline quality was evaluated by powder X-ray diffraction (XRD) and Cu K_α radiation was used as the X-ray source. The optical properties were investigated by PL measurements performed at room temperature. PL spectra were excited with the 325 nm line of a He–Cd laser at excitation power densities of 0.1–0.25 kW/cm^2. The luminescence was dispersed by a 1 m monochromator and detected by a cooled GaAs photomultiplier. The spectral resolution of the measurement was 11 meV in the region from 1.95 to 3.65 eV.

3. Results and discussion

Fig. 3 presents the AFM images of surface morphologies of GaN/Si with the substrates being

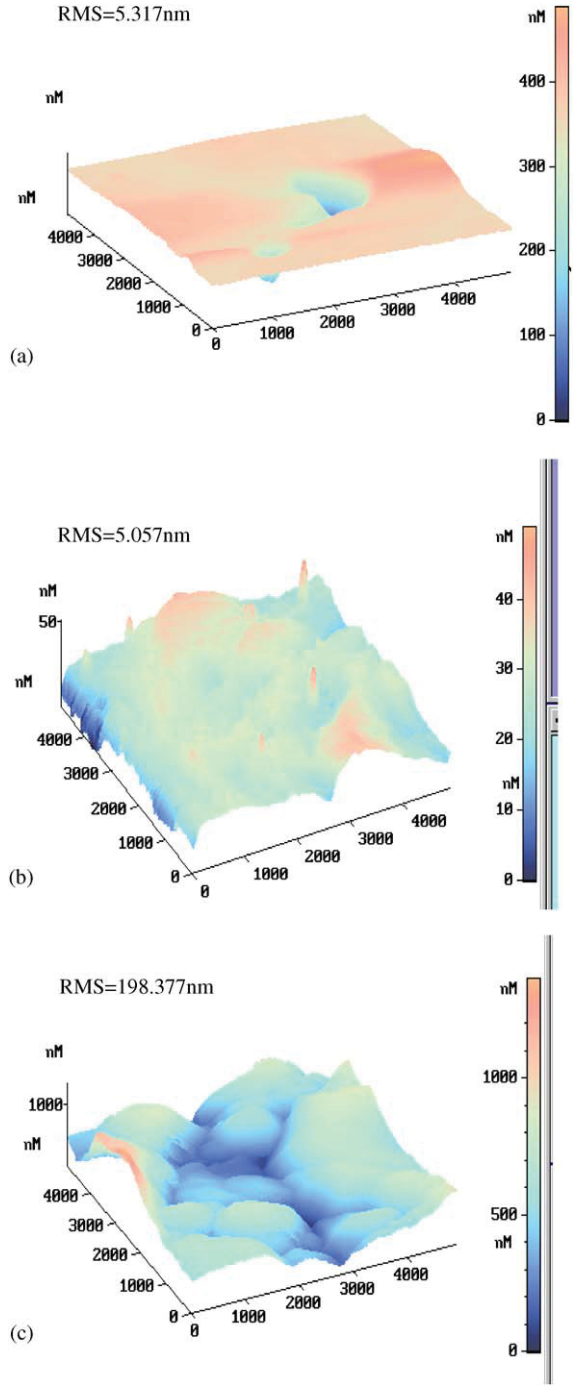

Fig. 3. AFM images of GaN/Si surface morphologies with the substrate being nitridated for 10 min at (a) 750 °C (b) 950 °C and (c) 1120 °C.

nitridated for 10 min at (a) 750 °C (b) 950 °C (c) 1120 °C, respectively. As can be seen, the root mean square (RMS) value of surface roughness decreases from 5.317 to 5.057 nm when the nitridation temperature was changed from 750 to 950 °C. However, when the temperature was raised to 1120 °C, the surface becomes rough as shown in Fig. 3(c) where the RMS value of surface roughness increases to 198.377 nm. Additionally, many dot-like crystallites are found on this rough surface. The problem of cracks was relieved compared with those species grown on unnitridated Si substrate. Particularly, performing the substrate nitridation at 950 °C had relatively reduced the number of cracks and resulted in a smoother surface.

Fig. 4 shows the XRD patterns of the GaN films grown on Si substrate. Patterns (b), (c) and (d) were obtained from the cases with substrate nitridation performed at 750, 950 and 1120 °C, respectively. Alternatively, pattern (a) corresponds to the case without substrate nitridation. Obviously beside the Si(1 1 1) peak at $2\theta = 28°$, only a weak (0 0 0 4) peak of GaN ($2\theta = 73°$) and a strong (0 0 0 2) GaN diffracted peak at $2\theta = 34.5°$ can be identified, indicating the epitaxial GaN thin film to be highly oriented along the [0 0 0 1] direction of the wurtzite GaN. The Si(1 1 1) diffracted peak is weak compared with that of GaN due to the misorientation of the substrate itself. The full-width at half-maximum (FWHM) of GaN(0 0 0 2) peak for the GaN films grown on the substrate without nitridation is 1.759°, while those for the cases with nitridation at 750, 950 and 1120 °C are 0.464°, 0.279° and 0.408°, respectively. The XRD peaks for all the samples grown on nitridated substrates show lower FWHM values, indicating improved crystalline structures compared with that of the sample without substrate nitridation.

Fig. 5 shows the room temperature PL spectra of GaN epilayers grown on Si(1 1 1) with the silicon substrates being nitridated for 10 min at (a) 750 °C, (b) 950 °C and (c) 1120 °C, respectively. For comparison, the PL spectrum obtained from GaN layer grown on Si substrate with AlGaN/AlN double buffers but without substrate nitridation is also demonstrated in part (d) of the same figure. A very strong band-edge emission peak at 3.397 eV (~364 nm) with a FWHM of only 61.1 meV (~7.13 nm) was observed for the GaN epilayer buffered by SiN_x obtained from the nitridation of Si substrate at 950 °C. The intensity and the FWHM of the band-edge emission are comparable to those samples grown on the

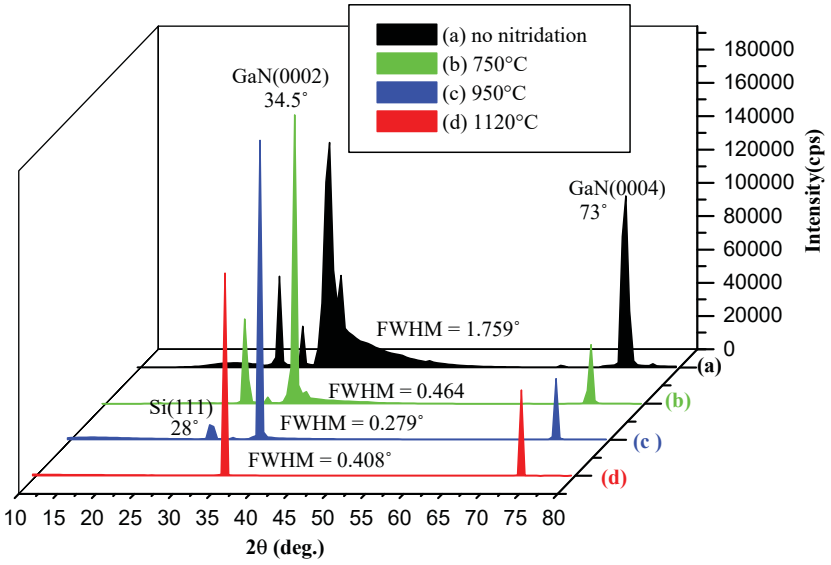

Fig. 4. XRD curves of GaN/Si (a) without nitridation and with nitridation being performed at (b) 750 °C (c) 950 °C (d) 1120 °C for 10 min.

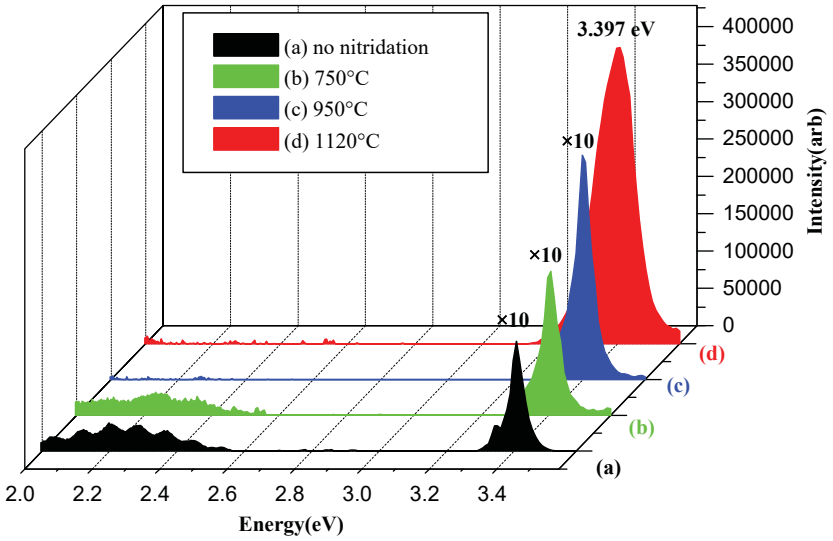

Fig. 5. Room temperature PL spectra of GaN epilayer (a) without nitridation and with substrate nitridation at (b) 750 °C (c) 950 °C (d) 1120 °C.

sapphire substrate. In particular, a defect-induced broad emission, YL was not observed. The YL has been attributed to a shallow donor-deep acceptor transition [20]. It should be noted that the YL, which was observed in the GaN epitaxially grown on Si substrate without nitridation, was absent in the GaN epilayers buffered by SiN_x obtained from an appropriate nitridation temperature higher than 950 °C. This result is very encouraging because this kind of broad emission band can alter the optical performance of related devices greatly, especially for laser diodes.

Nevertheless, the YL band was observed when the nitridation temperature was lowered to 750 °C. On the other hand, when the nitridation was performed at 1120 °C, the 3.397 eV luminescent band became much stronger but wider than those from other samples. Consequently, the nitridation condition of silicon substrate is considered to be very critical for achieving high-quality GaN epilayer on Si, which is free of YL in its PL spectra.

It is worth mentioning that even without the intentional substrate nitridation, a thin amorphous layer (6–10 Å thick) was observed at the AlN/Si interface by transmission electron microscopy [21,22], which was usually interpreted by assuming the formation of a thin amorphous SiN_x layer. The GaN films grown atop AlN/Si were surprisingly single crystalline but with YL band in its PL spectrum [22] similar to that of (d) demonstrated in Fig. 5. Otherwise, SiN_x grown on the sapphire substrate at 500–650 °C by diluted SiH_4 gas exposure was reported to be a porous structure with many nanometer-sized holes in it [15]. Two possible bases are therefore plausible to be responsible for the effects of SiN_x buffer for the crystallinity and quality improvement of the GaN top layer. First, because of its porous structure SiN_x probably regulates its lattice to relieve the strain caused by the thermal expansion coefficient incompatibility between GaN epilayer and Si substrate and lessens the crack formation. Secondly, after nitridation, the nanometer-sized holes in SiN_x possibly play a role in masking, which may change the initial growth mode, different from that of the growth on the unnitridated substrate. For example, with this porous structure the SiN_x buffer can be effectively used as a mask for selective growth, and what is more, there is the realization of an epitaxial overgrowth technique to achieve high-quality GaN overgrown atop. Some papers have discussed the above-mentioned possibilities for the epitaxial growth of GaN on sapphire buffered by SiN_x [23,24]. As for GaN epitaxy on the Si(1 1 1) substrate, the correlation

between the substrate nitridation and GaN epitaxial quality is still left to be analyzed. The crystallinity and detailed structure of SiN_x layer formed by substrate nitridation are considered to be dependent on the nitridation conditions including the parameters, such as nitridation temperature, nitridation time and NH_3 flow rate. To clarify the causes and mechanism of our results, further studies are therefore necessary and they are in progress now.

4. Conclusions

In summary, single-crystalline GaN films have been deposited successfully on Si(1 1 1) using silicon nitride as the first buffer layer. The root mean square value of surface roughness of the GaN film grown on appropriately nitridated Si is around 5.057 nm as obtained by atomic force microscopy. X-ray diffraction pattern shows good crystallinity of GaN films grown on nitridated silicon substrates. Room temperature PL spectrum exhibits a strong emission from GaN epilayer at the wavelength of 3.397 eV with a FWHM of only 61.1 meV. No YL is present when the silicon substrates are nitridated at the temperatures higher than 950 °C.

According to our investigation, it is concluded that performing a simple nitridation of silicon substrate at an appropriate temperature of 950 °C for 10 min by MOCVD makes it possible to grow high-quality GaN on Si, suggesting an effective way to eliminate the YL in GaN luminescent spectra.

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References

[1] S. Nakamura, T. Mukai, M. Senoh, Appl. Phys. Lett. 64 (1994) 1867.
[2] S. Guha, N.A. Bojarczuk, Appl. Phys. Lett. 72 (1998) 415.
[3] S. Nakamura, M. Senoh, S. Nagahama, T. Matsushita, H. Kiyoku, Y. Sugimoto, T. Kozaki, H. Umemoto, M. Sano, M. Mukai, Jpn. J. Appl. Phys. 38 (1999) L226.
[4] S. Nakamura, M. Senoh, S.-I. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku, Y. Sugimoto, T. Kozaki, H. Umemoto, M. Sano, K. Chocho, J. Crystal Growth 189/190 (1998) 820.
[5] W.A. Melton, J.I. Pankove, J. Crystal Growth 178 (1997) 168.
[6] V.A. Joshkin, C.A. Parker, S.M. Bedair, L.Y. Krasnobaev, J.J. Cuomo, R.F. Davis, A. Suvkhanov, Appl. Phys. Lett. 72 (1998) 2838.
[7] H. Nagano, Z.X. Qin, A. Jia, Y. Kato, M. Kobayashi, A. Yoshikawa, K. Takahashi, J. Crystal Growth 189/190 (1998) 265.
[8] Z.C. Feng, X. Zhang, S.J. Chua, T.R. Yang, J.C. Deng, G. Xu, Thin Solid Films 409 (2002) 15.
[9] J.R. Gong, M.F. Yeh, C.L. Wang, J. Crystal Growth 247 (2003) 261.
[10] Y. Lu, X. Liu, D.-C. Lu, H. Yuan, G. Hu, X. Wang, Z. Wang, X. Duan, J. Crystal Growth 247 (2003) 91.
[11] H. Zhang, Z. Ye, B. Zhao, J. Crystal Growth 210 (2000) 511.
[12] S. Zamir, B. Meyler, E. Zolotoyabko, J. Salzman, J. Crystal Growth 218 (2000) 181.
[13] S.-H. Jang, S.-J. Lee, I.-S. Seo, H.-K. Ahn, O.-Y. Lee, J.-Y. Leem, C.-R. Lee, J. Crystal Growth 241 (2002) 289.
[14] M.-H. Kim, Y.-G. Do, H.C. Kang, D.Y. Noh, S.-J. Park, Appl. Phys. Lett. 79 (2001) 2713.
[15] S.-E. Park, S.-M. Lim, C.-R. Lee, C.S. Kim, O. Byungsung, J. Crystal Growth 249 (2003) 487.
[16] A. Yamamoto, T. Yamauchi, T. Tanikawa, M. Sasase, B.K. Ghosh, A. Hashimoto, Y. Ito, J. Crystal Growth 261 (2004) 266.
[17] P. Chen, S.Y. Xie, Z.Z. Chen, Y.G. Zhou, B. Shen, R. Zhang, Y.D. Zheng, J.M. Zhu, M. Wang, X.S. Wu, S.S. Jiang, D. Feng, J. Crystal Growth 213 (2000) 27.
[18] J. Huang, Z. Ye, L. Wang, J. Yuan, B. Zhao, H. Lu, Solid-State Electron. 46 (2002) 1231.
[19] C.-L. Wu, J.-C. Wang, M.-H. Chan, T.T. Chen, S. Gwo, Appl. Phys. Lett. 83 (2003) 4530.
[20] P. Perlin, T. Suski, H. Teisseyre, M. Leszezynski, I. Grzegory, J. Jun, S. Porowski, P. Boguslawski, J. Bernholc, J.C. Chervin, A. Polian, T.D. Moustakas, Phys. Rev. Lett. 75 (1995) 296.
[21] L. Dobos, B. Pécz, E. Feltin, B. Beaumont, P. Gibart, Vacuum 71 (2003) 285.
[22] M.-H. Kim, Y.-C. Bang, N.-M. Park, C.-J. Choi, T.-Y. Seong, S.-I. Park, Appl. Phys. Lett. 78 (2001) 2858.
[23] S. Sakai, T. Wang, Y. Morishima, Y. Naoi, J. Crystal Growth 221 (2003) 334.
[24] T. Wang, Y. Morishima, Y. Naoi, S. Sakai, J. Crystal Growth 213 (2003) 188.