

Molecular-beam-epitaxy growth of GaN on GaAs(100) by using reactive nitrogen source

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By using a cold cathode ion gun to ionize the nitrogen gas, the molecular-beam-epitaxy growth of GaN is carried out. The zinc-blende structure GaN epilayer grown on the GaAs(100) substrate with a narrow x-ray diffraction peak width (FWHM) of 23 min and a low carrier concentration of 10^{17} cm^{-3} is achieved. The surface optical phonon energies of cubic and hexagonal GaN are experimentally determined to be 82 and 90 meV, respectively.

GaN is one of the most promising wide-gap III-V semiconductor materials in optoelectronics and thus has attracted a great deal of attention recently. Many efforts have been made to develop a unique growth technique for preparing high quality GaN films on different substrates. Due to the inactivity of nitrogen gas, the first task in growing GaN and other nitrogen-containing compound semiconductors is to develop a good reactive N source. In the metalorganic chemical vapor deposition (MOCVD) technique, the nitrogen source was provided by hydrazine¹ and ammonia.²⁻⁴ In the molecular-beam-epitaxy (MBE) growth, the ionization of nitrogen gas was achieved either by glow discharge⁵ or electron cyclotron resonance (ECR).⁶⁻⁹ High quality wurtzite-type (hexagonal) GaN films grown on sapphire substrates could be obtained by MOCVD, however, the more important zinc-blende structure (cubic) GaN epilayers grown on GaAs or Si substrates have not been achieved by this technique. MBE is known as the most advanced thin film deposition method, which has been used to grow both hexagonal and cubic GaN films on various substrates, such as SiC,⁵ Si,⁷ GaAs,^{6,10} MgO,¹¹ etc., but the crystalline quality of the cubic GaN epilayers was not satisfactory as the peak widths (FWHM) of x-ray diffraction (XRD) rocking curves were rather large and the unintentional doping concentration was too high to be of practical use. The high doping concentration is supposed to originate from the N vacancies which are caused by the insufficient activation of the N source.¹² In this work, we develop a new reactive nitrogen source in which the nitrogen gas is ionized by a conventional cold cathode ion gun rather than the ECR facility. The cubic as well as hexagonal GaN films are successfully grown on the GaAs(100) substrates. XRD measurement shows a narrow GaN(200) peak with the FWHM of only 23 min for cubic GaN and the unintentional doping concentration down to 10^{17} cm^{-3} is reached.

The MBE growth was carried out in a homemade MBE chamber attached to a VG ADES-400 electron spectrometer equipped with the x-ray photoelectron spectroscopy (XPS) and high-resolution electron energy loss spectroscopy (HREELS). The base pressure of the growth chamber was 5×10^{-10} Torr. The substrate used was an *n*-type GaAs(100) single crystal wafer with the carrier concentration of 10^{17} cm^{-3} . The substrate surface after treatment by routine chemical method was first cleaned in the growth chamber by 1 keV

argon ion bombardment followed by heat annealing at 650 °C for 30 min. A clean and ordered GaAs(100)(4×1) surface which is believed to be a Ga-rich one was obtained. A conventional Kundsen cell was used to evaporate Ga. The source temperature was kept at around 750 °C. In order to produce the reactive nitrogen source, high purity nitrogen gas was admitted into a cold cathode sputtering ion gun (VG AGS2) which is attached to the growth chamber and placed close to the sample. A voltage of 3 kV was applied between the anode and the cathode of the gun, resulting in the discharge of nitrogen gas. The gas pressure in the vacuum chamber to sustain the discharge was 3.5×10^{-5} – 1.0×10^{-4} Torr. The accelerating power supply of the ion gun was turned off, but the nitrogen ions still suffered an accelerate voltage of 400–600 V caused by the glow discharge around the opening of the anode.

It was found that the ion species produced by the ion gun are mostly N^+ . The mass spectroscopic measurement of the nitrogen beam by a quadrupole mass spectrometer without the ionization chamber is shown in Fig. 1, where the peak at mass charge ratio of 28 is attributed to the ionized nitrogen molecules N_2^+ and the peak at 14 is the ionized atoms N^+ . The possibility of ionizing N_2 molecules into doubly charged nitrogen molecules N_2^{2+} which also have a mass charge ratio of 14 is expected to be neglected.¹³ From the relative peak intensities in Fig. 1, it could be estimated that a very high percentage (about 90%) of the ionized species are N^+ , while

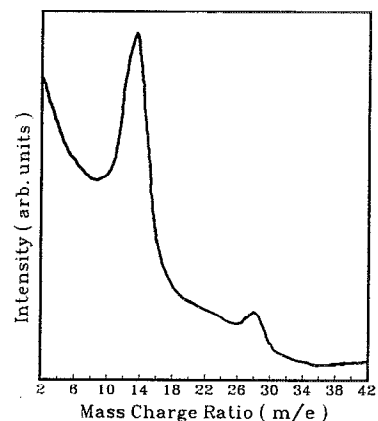


FIG. 1. Quadrupole mass spectrum of the nitrogen ion source.

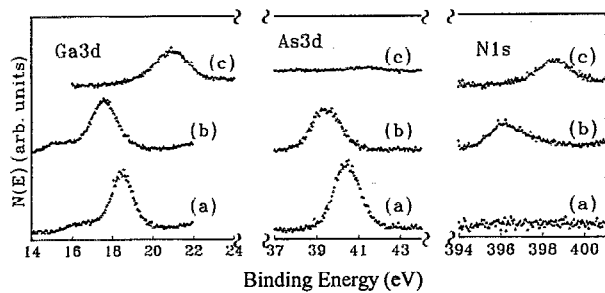


FIG. 2. XPS core-level spectra for (a) clean, (b) activated nitrogen exposed, and (c) thick GaN covered GaAs samples.

for the best ECR nitrogen source, only 15%–20% of N^+ was achieved.⁸ The reason for this difference lies in the different ionization processes. For microwave discharge, the nitrogen gas is ionized by the hot electrons with a kinetic energy of around 10 eV, which is not sufficient to effectively break the chemical bond between two N atoms in a N_2 molecule, since the bonding energy of N—N is 9.80 eV.¹⁴ In the cold cathode ion gun, however, the nitrogen gas is discharged at very high energy (3 keV). It is thus expected that the N—N bonds in N_2 molecules are broken with a high efficiency.

Prior to MBE growth, the substrate was exposed to a nitrogen beam at 400 °C for a few minutes to make the surface Ga atoms fully react with the N atoms. The surface nitridation carried out with the nitrogen beam flux hit the surface grazingly (near 90°) so that the sputtering effect by the ion beam could be minimized. The purpose of this nitridation process is to improve the epilayer/substrate interface by reducing the nitrogen vacancies. After that, a two-stage epitaxial process was carried out. The first step was a low temperature (400–500 °C) epitaxy with the growth rate of 2–5 Å/min. The nitrogen beam was still kept at a grazing angle of nearly 90° and the substrate was negatively biased from –20 to –50 eV in order to get sufficient nitrogen flux. The purpose of the first-step growth is to accumulate the large lattice misfit between GaN and GaAs by releasing the strain in the low temperature epitaxial buffer layer and also to prevent the possible out-diffusion of As. The optimum thickness of this low temperature epitaxial film was found to be about 500 Å with regard to its surface morphology and electronic properties. The second-step growth was performed at 650 °C with the growth rate of 6–9 Å/min. The sample surface directly faced the nitrogen beam and was at zero bias or biased positively. The epilayer grown at the second stage was usually as thick as 4000–5000 Å.

The compositions of the epilayers were measured by XPS. Figure 2 shows the core level spectra of Ga3d, As3d, and N1s for (a) clean, (b) activated nitrogen exposed, and (c) thick nitride covered GaAs samples. There exist different rigid shifts of the spectra in (b) and (c), which is due probably to the different combinations of band bending and/or band offset in the two cases and will be discussed in detail elsewhere. The complete disappearance of the As signal in (c) gives clear evidence that the nitride grown by the present method is pure GaN rather than the ternary compound GaAsN. By using the relative atomic sensitivity factors of Ga3d and N1s, a rough estimation of the atomic ratio of N to

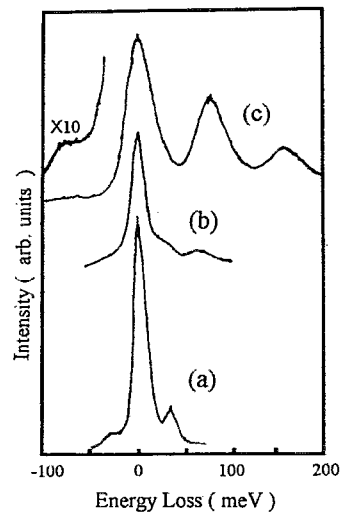


FIG. 3. HREELS spectra with primary beam energy of 3 eV for (a) clean, (b) activated nitrogen exposed, and (c) thick GaN covered GaAs samples.

Ga in the epilayer from the peak intensities gives the value of 0.95, which agrees with the stoichiometric composition of GaN within the experimental error.

For the activated nitrogen exposed GaAs, Fig. 2(b) illustrates that the signal intensities of As3d and N1s are comparable. The broad As3d peak implies that the As species might exist in two different chemical states: one is the state of anions bonded with Ga, another is the state of free As atoms resulting from the exchange reaction between N and GaAs. Such an anion exchange was recently observed by Berger *et al.*¹⁵ upon exposure of GaAs(110) to activated nitrogen. It is not known from the XPS measurements whether the As signal corresponding to the chemically bonded component comes from the bulk GaAs underlying a very thin GaN overlayer or the overlayer itself. That is, whether the activated nitrogen exposure treats the GaAs surface into a thin binary GaN or ternary GaAsN overlayer.

To answer the above question, the surface optical phonon [Fuchs–Kliwer (FK) phonon] energy was measured using HREELS. Shown in Fig. 3 are the HREELS spectra measured under the same conditions as those in Fig. 2. The clean substrate shows a loss peak at 36 meV which is the FK phonon energy of GaAs as expected. For thick GaN film, two loss peaks at 82 and 164 meV are believed to correspond to the FK phonon mode and its second harmonic of GaN. A gain peak at the left-hand side of the elastic peak could be clearly seen in Fig. 3(c). To our knowledge, this is the first time that the FK phonon is observed from GaN. The optical data for cubic GaN are not available from the literature, while for hexagonal GaN, the energies of TO and LO phonons are known as $\hbar\omega_{TO}=69$ meV (Ref. 16) and $\hbar\omega_{LO}=90$ meV,¹⁷ respectively. Its high frequency (optical) dielectric constant is $\epsilon_\infty=5.8$ (Ref. 16) and the electrostatic dielectric constant is derived from the Lyddane–Sachs–Teller relationship. The frequency of FK phonon could be obtained by the following expression:

$$\omega = \omega_{TO} [(\epsilon_0 + 1)/(\epsilon_\infty + 1)]^{1/2}.$$

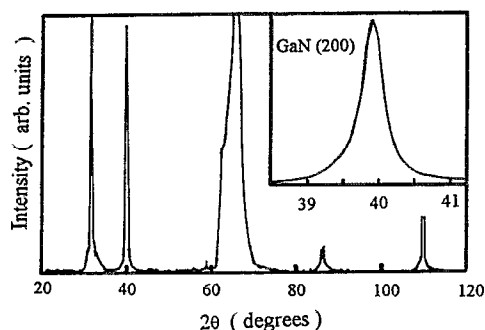


FIG. 4. XRD spectrum for the thick GaN covered sample.

The predicted value for hexagonal GaN is $\hbar\omega = 87$ meV. Our experimental measurement on hexagonal GaN shows a loss peak at 90 meV. These two values coincide well with each other within the experimental error. For activated nitrogen exposed surface, the 82 meV loss peak is not observed. Instead, a two-peak structure is shown in Fig. 3(b), which is the typical feature of energy loss spectra for ternary III-V compounds. A peak at 70 meV and a broad shoulder at 30–40 meV corresponds to dispersed GaN-like and GaAs-like phonons in the ternary compound $\text{GaAs}_{1-x}\text{N}_x$, respectively. With x approaching 1, the GaN-like phonon peak would ultimately reach the position of the GaN phonon peak at 82 meV. However, by simply exposing the GaAs substrate to nitrogen beam, the highest loss energy of GaN-like phonon peak we observed is 74 meV. It is thus concluded that pure GaN film cannot be grown without the Ga source involved.

The crystalline structure of epilayer was detected by XRD as shown in Fig. 4. Besides the peaks located at the $2\theta = 31.63^\circ$, 66.07° , and 109.71° , which correspond to the GaAs (200), (400), and (600), respectively, there are peaks at 39.94° and 86.34° originated from GaN (200) and (400) planes. The structure of the GaN epilayer is thus verified to be the cubic single crystal with the orientation of (100). The lattice constant derived thereby is 4.51 \AA , consistent with the value previously reported of cubic GaN.^{5–7,10} The inset of Fig. 4 shows that the FWHM of the GaN(200) peak is quite narrow, i.e., only 23 min, as compared with 49 min by gas source MBE on GaAs(100),⁶ and 37.5 min by ECR plasma assisted MBE on Si(100).⁷ The narrow peak width is an indication of the good crystalline quality of the GaN epilayer.

The carrier concentration of the epilayer was measured by using a C - V technique. A Schottky contact was formed by

evaporating an aluminum dot on the top of the GaN. The experimental result shows that the carrier concentration is less than 10^{17} cm^{-3} , which is smaller than the previously reported value. The lower carrier concentration implies that there are less nitrogen vacancies created in the grown film.

In summary, the cubic GaN epitaxial layer was grown on GaAs(100) by using a reactive nitrogen source. A FWHM of 23 min for the GaN(200) XRD peak was obtained. The FK phonon modes of cubic and hexagonal GaN at 82 and 90 meV were measured for the first time. The unintentional doping concentration of 10^{17} cm^{-3} was obtained. The good qualities of GaN epilayers are attributed to the fairly effective ionization of N_2 gas into single charged nitrogen ion N^+ rather than N_2^+ by the cold cathode sputtering ion gun.

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- ¹M. Mizuta, S. Fujieda, Y. Matsumoto, and T. Kawamura, *Jpn. J. Appl. Phys.* **25**, L945 (1986).
- ²S. Nakamura, *Jpn. J. Appl. Phys.* **30**, L1705 (1991).
- ³S. Nakamura, M. Senoh, and T. Mukai, *Jpn. J. Appl. Phys.* **30**, L1708 (1991).
- ⁴S. Nakamura, T. Mukai, and M. Senoh, *Jpn. J. Appl. Phys.* **30**, L1998 (1991).
- ⁵M. J. Paisley, Z. Sitar, J. B. Posthill, and R. F. Davis, *J. Vac. Sci. Technol.* **A 7**, 701 (1989).
- ⁶S. Strite, J. Ruan, Z. Li, A. Salvador, H. Chen, D. J. Smith, W. J. Choyke, and H. Morkoç, *J. Vac. Sci. Technol. B* **9**, 1924 (1991).
- ⁷T. Lei, M. Fanciulli, R. J. Molnar, T. D. Moustakas, R. J. Grcham, and J. Scanlon, *Appl. Phys. Lett.* **59**, 944 (1991); T. Lei, T. D. Moustakas, R. J. Graham, Y. He, and S. J. Berkowitz (unpublished).
- ⁸Z. Sitar, M. J. Paisley, D. K. Smith, and R. F. Davis, *Rev. Sci. Instrum.* **61**, 2407 (1990).
- ⁹Z. Sitar, M. J. Paisley, B. Yan, J. Ruan, W. J. Choyke, and R. F. Davis, *J. Vac. Sci. Technol. B* **8**, 316 (1990).
- ¹⁰H. Okumura, S. Misawa, and S. Yoshida, *Appl. Phys. Lett.* **59**, 1058 (1991).
- ¹¹R. C. Powell, G. A. Tomsch, Y. W. Kim, J. A. Thornton, and J. E. Greene, *Mater. Res. Soc. Symp. Proc.* **162**, 525 (1990).
- ¹²S. Strite and H. Morkoç, *J. Vac. Sci. Technol. B* **10**, 1237 (1992), and references therein.
- ¹³S. V. Dlisven, *Physics and Technique of Low Temperature Plasma* (Moscow Atomic, Moscow, 1972) (in Russian).
- ¹⁴*CRC Hand Book of Chemistry and Physics*, edited by Robert C. Weast (Chemical Rubber, Boca Raton, FL, 1983–1984), p. 180.
- ¹⁵A. Berger, D. Troost, and W. Mönch, *Vacuum* **41**, 669 (1990).
- ¹⁶D. D. Manchon, Jr., S. A. Barker, Jr., P. J. Dean, and R. B. Zetterstrom, *Solid State Commun.* **8**, 1227 (1970).
- ¹⁷R. Dingle and M. Ilcgems, *Solid State Commun.* **9**, 175 (1971).