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Nitridation of GaP Surfaces by Rf Nitrogen Radicals and by ECR Nitrogen Plasma

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1. Introduction

Recently, GaN has turned out to be the most attractive material for short-wavelength optoelectronic devices as well as for high-temperature and high-power electronic devices. From the viewpoint of device fabrication technologies, it is desirable to grow GaN with a cubic crystal structure on other III-V substrates. For this reason, GaAs substrates have received a significant amount of attention, and a number of efforts have been made for nitridation of GaAs surfaces using various processing techniques in order to achieve nucleation suitable for subsequent epitaxial growth of cubic GaN.

In this paper, we successfully achieved nitridation of GaP(100) surfaces by exposing surfaces either to rf-assisted nitrogen radicals, or to ECR-assisted N_2 plasma. As compared with GaAs, GaP has a closer lattice constant to GaN than GaAs. Thermal mismatch between GaN and GaP is also smaller than that between GaN and sapphire. However, there has been only very little study on nitridation of GaP substrates.

2. Experimental

Nitridation was performed in an ultra-high vacuum (UHV) based multiple chamber system containing a GSMBE chamber, an ECR-CVD chamber, an XPS/AES chamber and others, as shown in **Fig. 1**. A nitrogen radical cell was equipped in the GSMBE chamber.

S-doped ($n=5\times10^{17}$ cm^{-3}) n-GaP(100) substrates were used. Before loading substrates into the UHV transfer chamber, GaP surfaces were cleaned in organic solvents and etched in an $HF:H_2O=1:4$ solution for 1 min. In the GSMBE chamber, natural oxide layer on GaP surfaces was removed by UHV thermal cleaning at 600°C under P-overpressure (a chamber pressure of 1.0×10^{-5} Torr) obtained by cracking of tertiarybutyl-phosphine (TBP). Nitridation of GaP surfaces was attempted either using rf-assisted nitrogen radicals, or using ECR-assisted N_2 plasma with a microwave power of 100W. The substrate temperature was 400-500°C. The partial pressure of nitrogen gas was in the range of $1.0\text{-}5.0\times10^{-4}$ Torr. Nitrided GaP surfaces were systematically characterized by *in-situ* reflection high energy electron diffraction (RHEED), *in-situ* Auger electron spectroscopy (AES), *in-situ* x-ray photoemission spectroscopy (XPS), *ex-situ* cathodoluminescence (CL) and *ex-situ* atomic force microscopy (AFM).

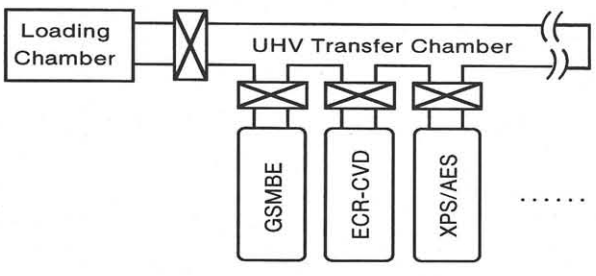

Fig.1. UHV-based multi-chamber system used in the study.

3. Results and Discussion

Figures 2(a) and **(b)** show RHEED patterns observed before and during nitridation using rf nitrogen radicals. As shown in **Fig. 2(a)**, clear streaky patterns were seen on the thermally cleaned GaP(100) surface. After 10 min nitridation, we observed weak streaky patterns from GaP substrate (indicated by -1, 0, +1 in **Fig. 2(b)**) and the additional spotty patterns (indicated by -1′, 0, +1′ in **Fig. 2(b)**). The spacing between +1′ and -1′ order of the spotty patterns was about 1.2 times wider than the spacing between the +1 and -1 order of GaP diffraction patterns. According to a similar work reported by Hauenstein, *et al.* on GaAs(100) surface exposed to ECR-assisted N_2 plasma[1], the lattice constant corresponding to the spacing between +1′ and -1′ spots is 4.54 Å. This value is smaller than the lattice constant of GaP of 5.45 Å. Therefore, the spotty patterns can be assigned as the diffraction pattern of cubic GaN.

Figure 3(a) shows AES survey spectrum obtained from the GaP surface after UHV thermal cleaning. No noticeable oxygen peak was detected. Nitridation for 10 min using rf nitrogen radicals resulted in decrease of the P-LMM signal, as well as in appearance of the N-KLL signal at about 389 eV (**Fig. 3(b)**). After nitridation for 60 min, P-LMM signal almost disappeared (**Fig. 3(c)**), indicating that P atoms were replaced with N atoms on surfaces. This slow replacement is probably due to the large difference between Ga-N and Ga-P bond strengths.

The XPS P2p and Ga3d spectra of the nitrided GaP

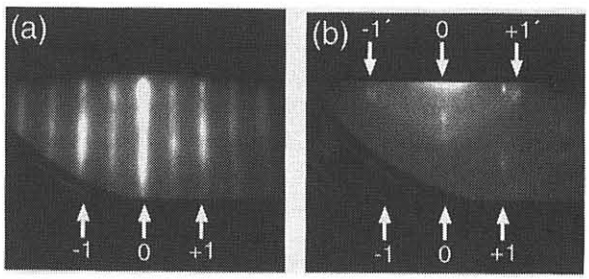

Fig.2. RHEED patterns along [011] azimuth : (a) the thermally cleaned GaP surface and (b) the GaP surface after 10 min nitridation by nitrogen radicals.

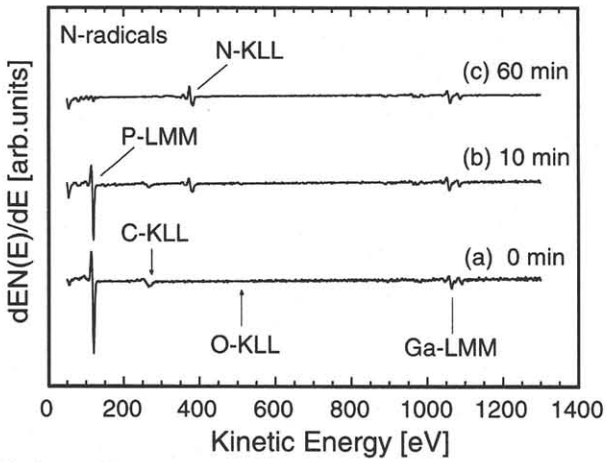

Fig.3. AES survey spectra from the GaP surface (a) after UHV thermal cleaning, (b) after nitridation for 10 min, and (c) after nitridation for 60 min.

surfaces are shown in **Fig. 4**. After nitridation for 10 min, the P-N bonding peak appeared in the P2p spectrum, accompanying broadening of the Ga3d spectrum, as shown in the middle trace (b) of **Fig. 4**. In addition, the N1s peak appeared. After nitridation for 60 min, the P2p peaks disappeared, and a clear peak shift toward the position of Ga-N bonding peak took place in the Ga3d spectrum, as seen in the trace (c) of **Fig. 4**. The integrated intensity ratio of Ga3d to N1s (Ga3d/N1s), obtained from the GaP surface after nitridation for 60 min, became approximately equal to that of an MBE-grown GaN layer. Thus, near-stoichiometric GaN layer was obtained after nitridation for 60 min. The average thickness of GaN layer on the GaP surfaces was estimated to be 5 nm from the escape depth of the P2p peak.

Although not shown here, nitridation using ECR-assisted N_2 plasma gave similar AES and XPS results.

Figure 5 shows the CL spectra of the GaP surfaces after nitridation by both (a) radicals and (b) plasma processes

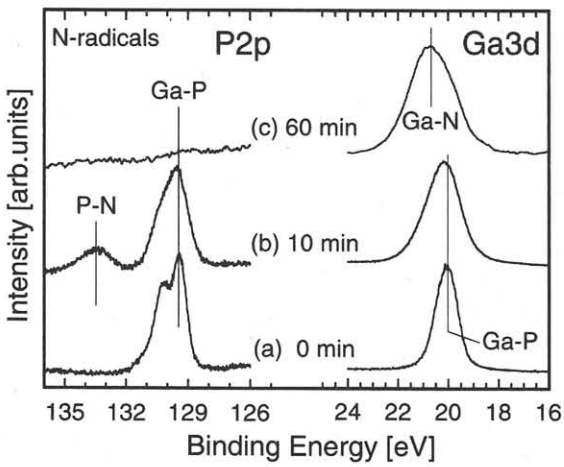

Fig.4. XPS P2p and Ga3d spectra obtained from (a) the UHV thermally cleaned GaP surface, (b) the nitrided GaP surface for 10 min, and (c) the nitrided GaP surface for 60 min.

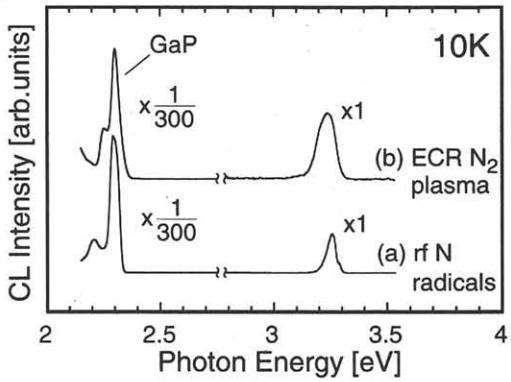

Fig.5. CL spectra from GaP surfaces after nitridation for 60 min by (a) rf nitrogen radicals and (b)ECR N_2 plasma.

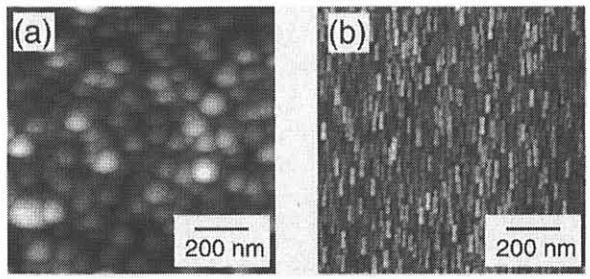

Fig.6. AFM images of GaP(100) surface after nitridation for 60 min (a) using rf nitrogen radicals and (b) using ECR N_2 plasma.

for 60 min. The main emission peak at photon energy of about 2.3 eV comes from the GaP substrate. In addition, clear CL peaks were detected at higher energies around 3.2-3.3 eV in both cases. According to Menniger *et al.*[2], micron-size single crystals of cubic GaN grown by MBE on GaAs(100) surfaces show CL lines near 3.2 eV at low temperature which is due to the near band- edge emission of GaN. Thus, peaks in **Fig. 5** at around 3.2-3.3 eV seem to originate from the thin cubic GaN layer produced on GaP surface by nitridation.

Figures 6(a) and **(b)** show AFM images of the GaP surfaces after nitridation for 60 min using (a) rf nitrogen radicals and (b) ECR N_2 plasma. The nitrided surfaces were covered with the grains of quasi-circular and rectangular features, respectively, due to nucleation of cubic GaN crystals. This is consistent with the observed complex RHEED patterns.

These results indicate that GaP substrates nitrided by the present two processes are promising for use as templates for growth of cubic GaN. Further epitaxial growth study is, however, necessary to determine which of the radicals and the ECR plasma processes produces a better template for successful growth of cubic GaN on GaP.

References

[1] R. J. Hauenstein, D. A. Collins, X. P. Cai, M. L. O'Steen, and T. C. McGill, Appl. Phys. Lett. **66** (1995) 2861.

[2] J. Menniger, U. Jahn, O. Brandt, H. Yang, and K. Ploog, Appl. Phys. Lett. **69** (1996) 836.