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Nitridation of GaAs surfaces stimulated by nitrogen glow discharge

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Abstract

Nitridation of a GaAs surface can be realized simply by exposing the substrate to a windowless-connected nitrogen glow discharge light source. The photoemission data measured in situ show that both GaN and AsN species have been formed during the exposure process. In addition, it is found that nitridation can result in a 0.3 eV reduction of surface band bending.

1. Introduction

Nitridation of GaAs surfaces is of great interest to the device technology of III–V semiconductors. For GaAs-based devices, the existence of a thin nitride layer can effectively reduce the high surface state density and hence improve surface quality and device performance. A thin GaN film may also be used as an in situ mask for selective-area epitaxy of GaAs [1]. Furthermore, III–V nitrides themselves are promising optoelectronic materials and GaAs is one of the substrates often used for their heteroepitaxy [2–4].

Recent studies show that thin nitride layers can be formed on GaAs surfaces by simultaneous exposure of the substrate to ammonia [5] (or hydrazoic acid [6]) and UV photons in an ultrahigh vacuum environment. While photodissociation of the N-containing species plays a key role in the nitride formation process, to keep the substrate at low temperatures during the exposure seems important to ensure a high coverage of the adsorbate.

In this paper, we report that photodissociation-induced nitridation can also be achieved with the GaAs substrate kept at room temperature. The key feature here is the use of a windowless-connected nitrogen glow discharge light source, acting both as a nitrogen plasma beam directed to the GaAs surface and as a stimulus to the dissociation of pure nitrogen near the surface. Besides its simplicity, the present approach has the potential to be further developed as a technique for the growth of a thick GaN film if a gallium source is attached.

2. Experimental

The experiment was carried out in a home-made sample preparation chamber attached to a VG ADES-400 electron spectrometer, as has been de-

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scribed elsewhere [4]. The base pressure of the 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}. After routine chemical treatment, the substrate surface was first bombarded by 1 keV argon ions and then annealed at above 500°C for 30 min. Several cycles of such an ion bombardment and annealing (IBA) process would result in the appearance of a (4×1) low-energy electron diffraction (LEED) pattern, indicating that the surface was an ordered Ga-rich one [7,8].

Nitrogen glow discharge was set in a differentially pumped, standard UV lamp. Under the conditions for maintaining a steady discharge, the nitrogen pressure in the sample preparation chamber was on the order of 10^{-8} Torr. Nitrogen exposure times in the present study were typically a few hours.

Both X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS) were used to examine the variations in composition and electronic state of the GaAs surface upon the nitrogen exposures. An Al X-ray source ($h\nu = 1486.6$ eV) was chosen for XPS measurements. The 2p peaks instead of the 3d peaks of Ga and As were measured to raise the relative intensities of the surface components. For UPS, He I ($h\nu = 21.2$ eV) was adopted. The photoelectron exit angle is 45° for XPS and 0° for UPS with respect to the surface normal.

3. Results and discussion

During the nitrogen exposure process, the LEED pattern changed gradually from (4×1) to (1×1), accompanied by a considerable increase in background intensity. This is evidence that nitrogen molecules do dissociate and adsorb on the GaAs surface when the glow discharge light source is on. It is generally accepted that there exist both Ga and As dangling bonds on the GaAs(100)(4×1) surface [7,9]. So a gradual LEED pattern change means that the photodissociated nitrogen atoms may bond randomly to the surface Ga and As atoms. Such an explanation is consistent with the previous results that both surface GaN and AsN species are present after a Ga-rich GaAs(100) surface has been exposed to N-containing species and photons at low temperatures [5,6]. More direct support of the above deduction is of course from the photoemission measurements.

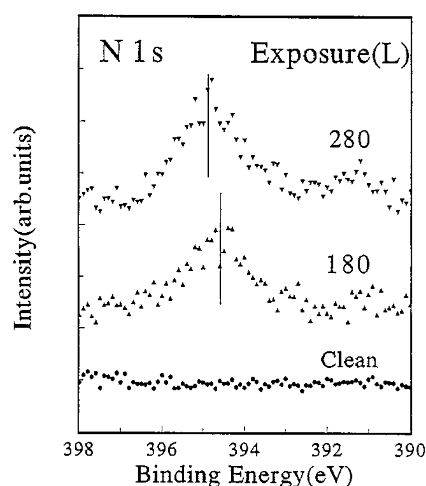

Fig. 1. N 1 s XPS spectra taken after the GaAs(100)(4×1) surface was exposed to a windowless-connected nitrogen glow discharge light source. The sample was kept at room temperature during the exposure.

Fig. 1 shows the N 1s XPS spectra measured following different nitrogen-photon exposures (in units of L, 1 L = 10^{-6} Torr · s). Since the N 1s peak is close to the Ga LMM Auger peaks and hence difficult to distinguish from the latter, the spectra given in the figure are not those originally measured but the difference curves between the N-exposed and clean ones. As is immediately evident, increase in nitrogen exposure results not only in an intensity increase but also in a position shift of the N 1s peak. Meanwhile, the full width at half maximum (FWHM) of the peak remains unchanged. This is a strong hint that the surface Fermi level, E_F, which is always pinned in the band gap for non-cleaved III–V semiconductors, may change its position to some extent during the N-exposure process. If this is the case, the substrate core-level spectra should show the same rigid shift. Shown in Fig. 2 and Fig. 3 are Ga 2p and As 2p spectra, respectively. Now both FWHM and peak position are changed. Each Ga and As peak, which has been broadened upon exposure, can be fitted by two components, as shown in the figures. Obviously, the main component here corresponds to Ga or As in GaAs and the minor one corresponds to surface Ga or As bonded to N. The shift of the main

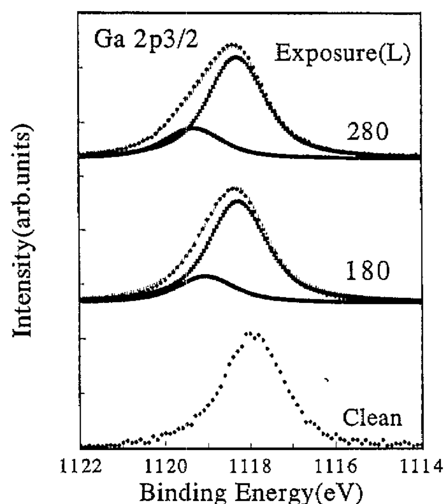

Fig. 2. Ga 2p XPS spectra taken after the same treatments as in Fig. 1.

component following a 280 L exposure is 0.3 eV towards the higher binding energy side, independent of whether it is Ga or As. In other words, the shift is rigid and surface band bending is reduced by 0.3 eV during the process. The maximum shifts of the minor components in the present experiment, which can be read directly from the 280 L spectra, are 0.9 eV for Ga 2p and 1.5 eV for As 2p, consistent with those previously observed [6]. It is thus clear that exposing

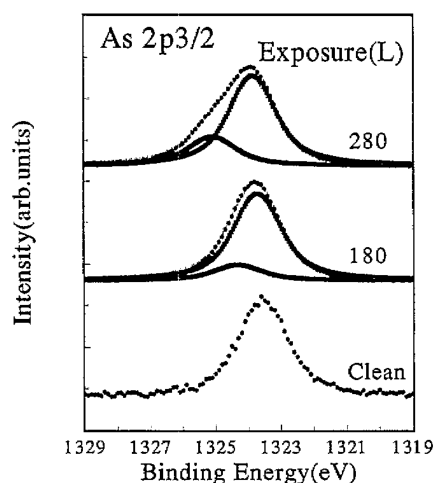

Fig. 3. As 2p XPS spectra taken after the same treatments as in Fig. 1.

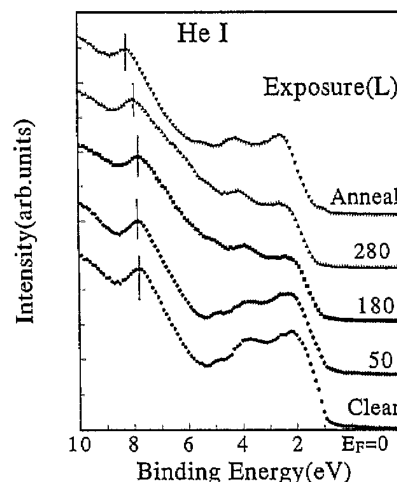

Fig. 4. UPS spectra of clean and N-covered GaAs(100) surfaces.

a GaAs surface to N_2-photon can result in nitridation of the surface and a shift of E_F.

From the variation of valence band spectra upon N-exposure one can come to the same conclusion. Fig. 4 shows the UPS spectra measured from various N-covered GaAs surfaces as noted. The top spectrum was taken after the 280 L exposed surface had been annealed at 500°C for 10 min. The common energy reference for all the spectra here is E_F ($=0$ eV), which is 0.8 eV above the valence band maximum (VBM) of the clean surface. The strong peak at 6.9 eV below VBM is a well-known bulk structure, related to the transition from the X_3 critical point [10]. Similar to what observed in XPS, this peak, and the VBM as well, shift to higher binding energies during the N-exposure process. It is thus further confirmed that band bending is reduced in the process of nitridation.

Besides the shift of the bulk-related band structures, uptake of nitrogen on the GaAs surface leads to a quenching of surface peaks, and to the emergence of a broad N-induced peak. To show this effect in a more straight manner, we plot in Fig. 5 the difference spectra between the clean and N-covered surfaces taken by aligning and normalizing their X_3 peaks. It is well established that the peaks in a difference spectrum obtained so can unambiguously be attributed to surface-originating effects. In other words, a positive peak in the spectrum must result from a complete or partial quenching of a

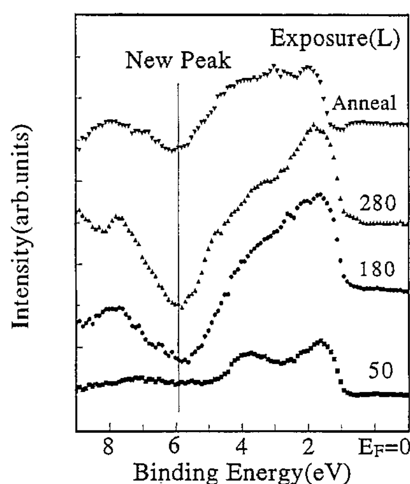

Fig. 5. Difference spectra between clean and N-covered GaAs(100) surfaces taken by aligning and normalizing their X_3 bulk structures.

surface state which existed initially at the clean surface, while a negative peak should be due to the emergence of a new state associated with uptake of foreign atoms or molecules on the surface. Thus, the positive and negative peaks in the present case should originate from the Ga- and/or As-related surface states and the N 2p valence states respectively. One can also see from the figure that although annealing can make the surface recover from nitridation to some extent, a relatively strong N 2p peak remains. This is understandable as the GaN species should still be on the surface after annealing.

Both XPS and UPS spectra also reveal that only limited Ga and As atoms are involved in the nitridation process under the experimental conditions we use. That means what happens on the surface is probably the saturation of the Ga and As dangling bonds by N atoms. It is likely that the process continues if extra Ga and/or As is supplied. We hope therefore that, with a gallium source attached, the present method can be used for the growth of thick GaN films.

4. Conclusion

A GaAs surface can be nitrided by using a nitrogen glow discharge light source to dissociate nitrogen molecules near the surface. As a result of nitridation, surface band bending can be reduced to some extent.

Acknowledgements

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References

[1] S. Yoshida, M. Sasaki and H. Kawanishi, J. Cryst. Growth 136 (1994) 37.
[2] S. Strite, J. Ruan, Z. Li, A. Salvador, H. Chen, D.J. Smith, W.J. Choyke and H. Morkoc, J. Vac. Sci. Technol. B 9 (1991) 1924.
[3] H. Okumura, S. Misawa and S. Yoshida, Appl. Phys. Lett. 59 (1991) 1058.
[4] Z.Q. He, X.M. Ding, X.Y. Hou and X. Wang, Appl. Phys. Lett. 64 (1994) 315.
[5] X.Y. Zhou, M. Wolf and J.M. White, J. Vac. Sci. Technol. A 11 (1993) 838.
[6] Y. Bu and M.C. Lin, Surf. Sci. 317 (1994) 152.
[7] Y.B. Xu, G.S. Dong, X.M. Ding, S. Yang and X. Wang, Chin. Phys. 4 (1984) 189.
[8] N.K. Singh, A.T. Murrell and J.S. Foord, Surf. Sci. 274 (1992) 341.
[9] D.K. Biegelsen, R.D. Bringans, J.E. Northrup and L.E. Swartz, Phys. Rev. B 41 (1990) 5701.
[10] T.C. Chiang, J.A. Knapp, M. Aono and D.E. Eastman, Phys. Rev. B 21 (1980) 3513.