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Laser-assisted nitridation of GaAs: Mechanisms

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A nitride layer can be formed at low temperatures on GaAs(100) by simultaneous exposure to ammonia and UV photons in an ultrahigh vacuum environment. This process is a result of nonthermal photodissociation of adsorbed ammonia, initiated both by direct photon absorption and by attachment of hot substrate carriers. The nitride layer consists of a mixture of thermally stable GaN and volatile AsN; the latter desorbs below 800 K.

Growth of a nitride passivation layer is a vital step in controlling interface states and fabricating GaAs-based metal–insulator–semiconductor (MIS) devices.[1–3] Several schemes have been developed to achieve this, including exposing GaAs to activated nitrogen sources, such as a N_2 plasma,[4] N atoms,[5] and a reactive N_2^+ ion beam,[6] irradiating condensed NH_3 by white light synchrotron radiation,[7] and catalyzing N_2 dissociation by alkali metals.[8] In addition, various high-temperature metalorganic chemical vapor desposition (MOCVD) and molecular beam epitaxy (MBE) methods have been used to grow GaN films on GaAs.[9,10] In this report, we demonstrate a novel approach to nitride films on GaAs(100). The process relies on nonthermal photodissociation of *adsorbed* ammonia at low temperature during simultaneous exposure to ammonia and UV photons in an ultrahigh vacuum (UHV) environment. In contrast to conventional nitridation processes, the low-temperature photochemical process described here requires neither activated nitrogen sources nor elevated surface temperatures. This method has obvious technological applications, such as selective area passivation via direct laser writing and low-temperature photoassisted growth of single crystal GaN. Details of this study have been published elsewhere;[11] we briefly summarize the results as follows.

Nitridation involved simultaneously and uniformly exposing a Ga-rich GaAs(100)-(4×6) surface at 100 K to both a collimated NH_3 beam and a pulsed UV photon beam in a UHV chamber (base pressure $<2\times10^{-10}$ Torr). For comparison, the photochemistry of monolayer ammonia preadsorbed on the GaAs surface was also studied. The clean GaAs(100) surface ($10^{15}/cm^3$ Si doped) was prepared by Ar ion sputtering and annealing to yield a (4×6) low-energy electron diffraction (LEED) pattern, which corresponds to a Ga-rich (~70% Ga) surface. Low power (0.5–5 mJ/cm^2, 2–50 Hz) UV light from a pulsed (11–20 ns) excimer laser (193, 248, and 351 nm) was used in both nitridation and monolayer photodissociation experiments. Since the power was low and the full surface was uniformly irradiated, the temperature rise was negligible. Following nitridation or monolayer photolysis, the surface was analyzed by x-ray photoelectron spectroscopy (XPS), high resolution electron energy loss spectroscopy (HREELS), temperature-programmed desorption (TPD) mass spectroscopy, and low-energy electron diffraction (LEED).

Figure 1 shows three XP spectra (N 1*s*) taken at 102 K. In each, the clean surface spectrum and the secondary electron background were subtracted. As a reference, spectrum (a) shows the NH_3 covered GaAs(100) at 102 K with no light irradiation. It can be fit nicely with a single mixed-Gaussian–Lorentzian function (solid line) peaked at 400.1 eV, as expected for molecular ammonia,[12,13] with a full width at half-maximum (FWHM) of 1.9 eV. Quantitative analysis of XPS intensities yields a coverage of 0.5 ± 0.1 *monolayer*, ML, (adsorbate to surface atom ratio) for saturation NH_3 on GaAs(100) at 102 K. Heating to above 350 K eliminates this N (1*s*) XPS peak and the clean surface spectrum is obtained, i.e., negligible thermal decomposition.[11]

Following nitridation ($\leqslant$2 ML) of the GaAs(100)-(4×6) surface at 102 K for 60 min (simultaneous exposure to NH_3: ~10^{14} molecules $cm^{-2}\,s^{-1}$ and 6.4 eV photons: 5×10^{15} photons cm^{-2}, 50 Hz), a broader N(1*s*) XPS peak at lower binding energy (BE) appeared (b). Assuming this spectrum consists of individual N species with the same FWHM (1.9 eV), the data can be deconvoluted into two peaks with binding energies at 398.5 and 397.0 eV, respectively. Comparing to literature for surface nitrides and NH_x ($x=1,2$) species,[12–14] we assign these two peaks to surface GaN (397.0 eV, 1.1 ± 0.2 ML), AsN and NH_x ($x=1,2$) (398.5 eV, 0.6 ± 0.1 ML) species. As shown below, both AsN and NH_x ($x=1,2$) are present after the GaAs surface is exposed to NH_3/photon at 102 K, but their binding energies are indistinguishable by the deconvolution procedure.

Heating the NH_3/photon exposed GaAs(100) surface to 750 K removes the AsN/NH_x peak at 398.5 eV, due to the thermal desorption of AsN and NH_3. The resulting spectrum (c) can be fit with a single mixed-Gaussian–Lorentzian function (solid line) peaked at 396.6 eV with a FWHM of 1.9 eV. While the intensity of the GaN peak remains unchanged between 100 and 750 K, the N (1*s*) binding energy for GaN in spectrum (c) is 0.4 eV lower than that in spectra (b). This is probably related to the desorption of arsenic nitride which changes the local electronic structure of GaN. LEED measurements are consis-

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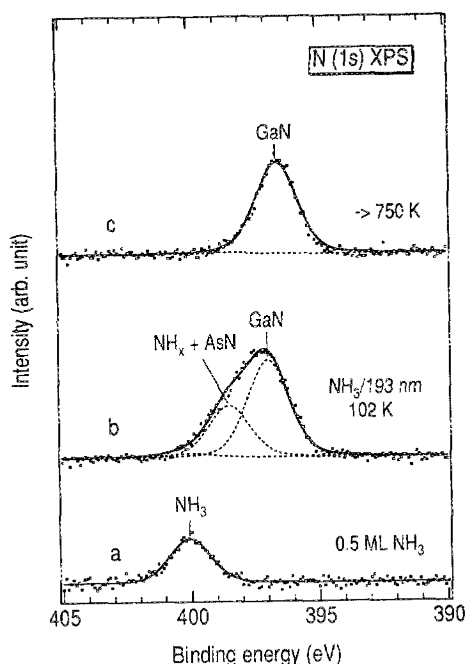

FIG. 1. N(1*s*) x-ray photoelectron spectra (XPS, Mg $K\alpha$, $h\nu = 1253.6$ eV) taken after the GaAs(100)-(4×6) surface was exposed simultaneously to NH_3 ($\sim 10^{14}$ molecules/cm^2 s) and 6.4 eV photons (5 mJ/cm^2 pulse, 50 Hz) for 60 min at 102 K (b), and heated to 750 K (c). The bottom spectrum (a) was taken after the clean GaAs surface was saturated (no photons) with NH_3 at 102 K. The dashed curves are individual peaks obtained from deconvolution and the solid curves are overall fits to the experimental data (dots).

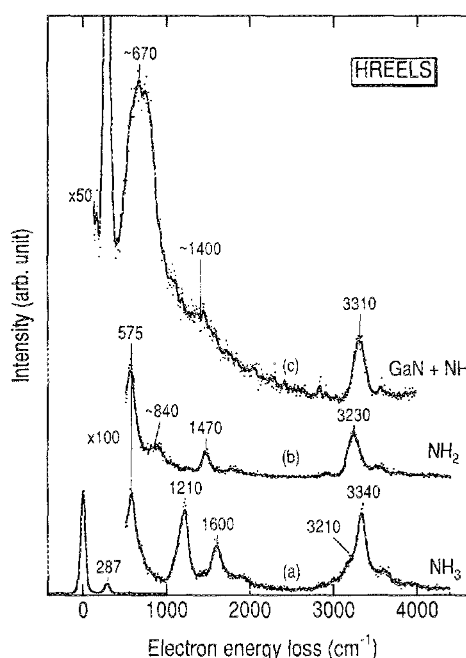

FIG. 2. HREEL spectra taken after (a) the GaAs(100) surface was saturated with NH_3 at 105 K; (b) the NH_3-saturated surface was irradiated with 5×10^{19} photons/cm^2 (1 mJ/cm^2 pulse, 6.4 eV) at 105 K and annealed to 400 K; and (c) the GaAs(100)-(4×6) surface was exposed simultaneously to NH_3 ($\sim 10^{14}$ molecules/cm^2 s) and 6.4 eV photons (5 mJ/cm^2 pulse, 50 Hz) for 60 min at 102 K and heated to 750 K. All spectra were taken after recooling, used a primary electron energy of 3 eV, and are normalized to their elastic peaks. The multiplication factor with respect to the elastic peak is 100 for spectra (a) and (b), and 50 for spectrum (c).

tent with an amorphous GaN layer. In a separate TPD measurement following nitridation, AsN desorption was indeed observed to occur at 750 K. In addition, the presence of surface NH_x ($x = 1,2$) species also gave rise to a small amount of NH_3 and H_2 desorption between 300 and 700 K.[11]

To further identify the surface species following nitridation and monolayer photolysis, we have measured HREEL spectra (Fig. 2). For a NH_3-saturated GaAs(100)-(4×6) surface at 105 K with no irradiation (curve a), the adsorbate-related losses are at 1210, 1600, 3210, and 3340 cm^{-1}, and can be assigned to the symmetric/asymmetric deformations and symmetric/asymmetric stretching vibrations of molecular NH_3, respectively.[15] The intense losses at 287 (ν_p) and 575 cm^{-1} ($2\nu_p$) are surface optical photons.[16] The weak features on the high frequency side of all losses (ν_i) are photon overtones ($\nu_i + \nu_p$). Upon heating to 350 K, or higher, all vibrational features assigned to NH_3 are gone and the clean surface spectrum is recovered, again indicating negligible thermal decomposition.

When the NH_3-covered surface is irradiated with 6.4 eV photons at 105 K, HREELS shows, in addition to losses assigned to molecular NH_3, new loss peaks at 1470 and 3230 cm^{-1}. These new losses become clearer when the irradiated surface is flashed to 400 K to desorb remaining molecular NH_3. The resulting spectrum (b) is dominated by losses at 1470 and 3230 cm^{-1}, which are the deformation and stretching vibrations of surface NH_2 species.[15] The weak shoulder feature at ~ 840 cm^{-1} is assigned to Ga–NH_2 stretch. This result indicates that the first step in photodissociation and nitridation is the formation of surface NH_2 groups, which further photodissociate to give NH (see below), and finally nitride.[11]

Following the much higher photon and NH_3 exposure in the nitridation experiment described above, HREELS shows, in addition to NH_x ($x = 1,2$) species, broad and intense losses between 600 and 800 cm^{-1} which can be assigned to the overlaping features due to surface GaN and AsN species.[11] When the NH_3 dose is terminated and this nitride-covered surface is heated to 750 K to remove NH_2 and most of the AsN, the HREEL spectrum (c) is dominated by a broad loss feature at ~ 670 cm^{-1}, the stretch vibration of GaN. For comparison, the vibrational modes of single crystal GaN are at 560 and 744 cm^{-1}, respectively.[17] In addition, the surface NH group is also present, with a stretch vibration at 3310 cm^{-1} and a weak bending loss at ~ 1400 cm^{-1}. This NH group does not result from the thermal dissociation of NH_2, but is mainly formed photochemically at 105 K.[11]

As we demonstrate in the companion article,[18] the observed photodissociation channel accounts for only $\sim 10\%$ of the total photolysis. Photon-driven molecular NH_3 photodesorption dominates (90%). The photodesorption yield depends linearly on laser pulse energy, clearly indicating a nonthermal mechanism. From the depletion of molecular ammonia TPD area as a function

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of photon fluence, we obtained initial cross sections for the photolysis (desorption + dissociation) of NH_3 on GaAs(100)-(4×6) at three photon energies: $\sigma_{6.4eV} = 5.4 \pm 0.6 \times 10^{-20}$ cm^2, $\sigma_{5.0eV} = 9.4 \pm 0.9 \times 10^{-21}$ cm^2, and $\sigma_{3.5eV} = 7.6 \pm 0.8 \times 10^{-21}$ cm^2.

The low ammonia flux used in the nitridation process assures insignificant gas phase absorption at 6.4 eV. Nitridation at the adsorbate–substrate interface is confirmed since we observed nitridation, but with slower rates, using photon energies of 5.0 and 3.5 eV, which lie well below the UV absorbance threshold (~6.0 eV) for gas or solid ammonia.[19]

Having established the photoassisted nitridation pathway, we now discuss the origin of electronic excitation(s) that leads to N–H bond breaking and parent desorption. Two excitation mechanisms are well documented in surface photochemistry:[20,21] (i) direct absorption of a UV photon by the adsorbate; and (ii) photoassisted charge transfer from the substrate to the adsorbate. The direct mechanism is not important at $h\nu = 3.5$ eV, which is 2.5 eV below the gas phase absorption threshold. It is unlikely that the UV absorption threshold of ammonia is redshifted by more than 2 eV through adsorption while its vibrational frequencies remain very close to those of gas phase or solid ammonia. Therefore, at $h\nu = 3.5$ eV, the initial excitation step must originate in the substrate and most likely involves the attachment of photoexcited substrate electrons, a process similar to gas phase dissociative electron attachment.[22] At 6.4 eV, in addition to substrate-mediated excitation, direct photon absorption by the adsorbate may also contribute. The photolysis cross section remains nearly constant at $h\nu = 3.5$ and 5.0 eV, but increases by a factor of 6 at $h\nu = 6.4$ eV where molecular ammonia absorbs relatively strongly.[11]

To summarize, nitridation of the Ga-rich GaAs(100)-(4×6) surface is achieved at low temperatures by simultaneous exposure to ammonia and UV photons in a UHV environment. This process is a result of nonthermal photodissociation of adsorbed ammonia. Surface NH_2 and NH groups are intermediates in nitridation.

ACKNOWLEDGMENT

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