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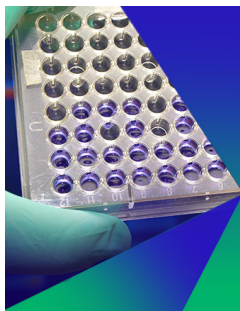
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Ultraviolet photochemical nitridation of GaAs

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Monolayer nitridation of Ga-rich GaAs(100) is achieved at 100 K by simultaneous exposure to ammonia and 6.4 eV photons in a vacuum environment. This process is a result of nonthermal photodissociation of adsorbed ammonia. Surface NH_2 is identified as an important intermediate in nitridation.

Surface processing is a fundamental aspect of electronic device fabrication. Because high-temperature activation is nonselective and may induce unwanted side reactions, such as dopant diffusion or destruction of nanoscale quantum structures, it is becoming increasingly important to develop more selective nonthermal activation processes.

Nitridation GaAs is an interesting and technologically relevant material. Two preparation methods have been explored: (1) exposure of GaAs at ~ 500 °C to activated N sources, e.g., nitrogen or ammonia plasmas,[1-3] and (2) surface activation, using white light synchrotron radiation.[4] In this report, we demonstrate that monolayer nitridation of GaAs(100) surfaces can be achieved by photolyzing adsorbed ammonia with 6.4 eV photons in a vacuum environment.

All experiments were conducted in a vacuum chamber (base pressure $< 2 \times 10^{-10}$ Torr) and involved high resolution electron energy loss spectroscopy (HREELS), quadrupole mass spectroscopy (QMS), x-ray photoelectron spectroscopy (XPS), and low energy electron diffraction (LEED). Photons, 6.4 eV (193 nm) from a pulsed (11–20 ns) excimer laser were used. After passing through a series of prisms and apertures, the photons entered the chamber through a CaF_2 window. Normally, the full front surface of the substrate was uniformly illuminated, and the transient substrate temperature increased no more than 10 K. The GaAs(100) substrate ($15 \times 10 \times 1$ mm, $10^{15}/cm^3$ Si-doped) was cooled by liquid nitrogen to 102 K and resistively heated (through a 4000 Å Ta backing) to 900 K. Cleaning the sample was achieved by Ar ion sputtering, annealing (773 K), and flashing (823 K) cycles. Surface cleanliness was verified by XPS and LEED. The latter showed a (4×6) LEED pattern, which corresponds to a Ga-rich (×70% Ga) surface.[5,6] To minimize adsorption on surfaces other than the sample, ammonia was directed through an 8 mm diam tube that terminated between 1 and 8 mm from the GaAs surface, depending on the experiment. The tube contained a 2 μm pinhole and the dose rate was determined by the pressure established behind it.

Figure 1 shows a set of N(1s) XP spectra taken after dosing at 102 K. In each, the clean surface spectrum was subtracted. It showed some broad features from substrate Auger transitions. The remaining secondary electron background in each spectrum was subtracted by a smoothed step-function fit to the binding energy (BE) region above and below the peak. For NH_3 covered GaAs(100) at 102 K (a), the result (dots) can be fit nicely with a single

mixed-Gaussian–Lorentzian function (solid line) peaked at 400.1 eV, as expected for molecular ammonia,[7,8] with a full width at half maximum (FWHM) of 1.9 eV. Quantitative analysis gives a coverage of 0.5 ± 0.1 ML (adsorbate to surface atom ratio) for saturation NH_3 on GaAs(100) at 102 K. Heating to above 350 K eliminates the N(1s) XPS peak leaving a clean surface spectrum, i.e., no thermal decomposition.

When GaAs(100)-(4×6) at 102 K is exposed *simultaneously* to NH_3 ($\sim 10^{14}$ molecules cm^{-2} s^{-1}) and 6.4 eV photons (5×10^{15} photons cm^{-2}, 50 pulses per second) at 102 K for 60 min, a broader N(1s) XPS peak at lower BE appears (curve b), indicating the formation of new N-containing species. The data (dots) can be deconvoluted into two peaks with binding energies at 398.5 and 397.0 eV, respectively. We assign these two peaks to surface GaN (397.0 eV) with a coverage of 1.1×0.2 ML, and AsN combined with NH_x ($x = 1, 2$) (398.5 eV) with a coverage
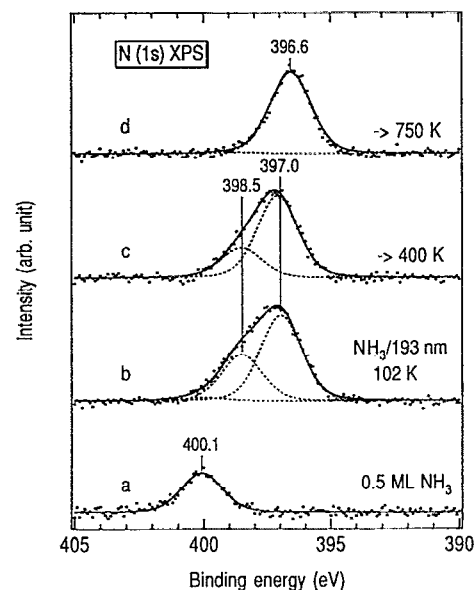

FIG. 1. N(1s) x-ray photoelectron spectra (XPS, Mg $K\alpha$, $h\nu = 1253.6$ eV) taken after the GaAs(100)-(4×6) surface was exposed simultaneously to NH_3 ($\sim 10^{14}$ molecules/cm^2 s) and 6.4 eV photons (5 mJ/ $cm^2 \cdot$ pulse, 50 Hz, incident at 60° off surface normal) for 60 min at 102 K (b), and heated to 400 K (c) and 750 K (d), respectively. 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).
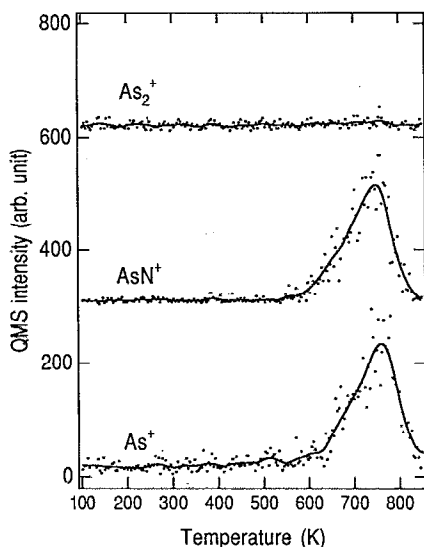
FIG. 2. TPD spectra (from bottom to top, $m/e=75$, 89, and 150 for As$^+$, AsN$^+$, and As$_2^+$, respectively) taken after the GaAs(100)-(4×6) surface was exposed simultaneously to NH$_3$ ($\sim 10^{14}$ molecules/cm^2 s) and 6.4 eV photons (5 mJ/cm^2 pulse, 50 Hz, incident at 60° off surface normal) for 60 min at 102 K.
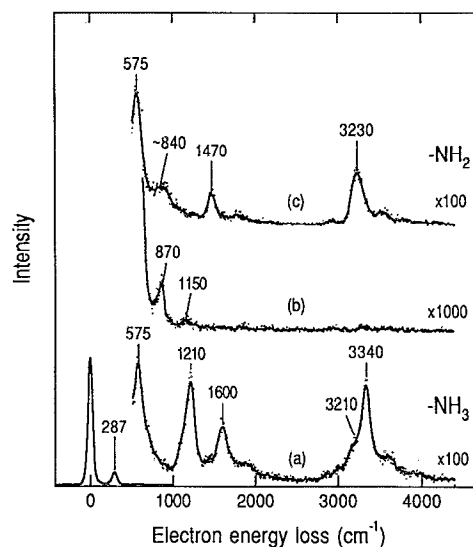
FIG. 3. HREEL spectra taken after the GaAs(100) surface was: (a) saturated with NH$_3$ at 105 K and (b) annealed to 350 K. Spectrum (c) was taken after the NH$_3$-saturated surface was irradiated with 5×10^{19} photons/cm^2 (1 mJ/cm^2 pulse, 6.4 eV) at 105 K and annealed to 400 K. All spectra were taken at 105 K with a primary electron energy of 3 eV. All spectra are normalized to the elastic peak; the multiplication factor with respect to the elastic peak is 100 for spectra (a) and (c) and 1000 for spectrum (b).

of 0.6×0.1 ML.[7,8] The intensity of molecular NH$_3$ at 400.1 eV in spectrum (b) is negligible. Since the starting surface is Ga-rich, it is sensible that the surface nitride layer is mainly GaN, as observed in ammonia plasma treatment.[1]

After photolysis, heating to 400 K (curve c) results in a slight depletion of the 398.5 eV peak, a result of a small amount of recombinative NH$_3$ desorption from NH$_x$ ($x = 1,2$), as observed in temperature programmed desorption.[9] Further flashing to 750 K removes the AsN peak (398.5 eV). This is due to the thermal desorption of AsN, as shown below. The resulting spectrum (curve d) 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 700 K, the N (1s) binding energy for GaN in spectrum (d) is 0.4 eV lower than those in spectra (b) and (c). This is related to the desorption of arsenic nitride which changes the local electronic structure of GaN.

Volatile AsN species[1] are detected by temperature programmed desorption (TPD) mass spectroscopy. Figure 2 shows spectra for three masses, $m/e=75$ (As$^+$), 89 (AsN$^+$), and 150 (As$_2^+$). While no Ga containing species desorb below 850 K (not shown), AsN desorbs at 750 K. The As$^+$ ($m/e=75$) spectrum tracks that of AsN$^+$ and is assigned electron-induced cracking of AsN. In addition to the above products, the presence of some surface NH$_x$ ($x = 1,2$) species also gives rise to a small amount of NH$_3$ and H$_2$ desorption between 300 and 700 K.[9] Since only tiny amounts of dihydrogen desorb during heating, we conclude that most of the photon-driven N—H bond breaking leads to H atom desorption during photolysis.

The above results show conclusively that both arsenic nitride and gallium nitride are formed on GaAs(100)-(4×6) at 102 K by simultaneous exposure to NH$_3$ and 6.4

eV photons. While gallium nitride is thermally stable, arsenic nitride desorbs between 600 and 800 K. In the following, we turn to the mechanism of photoassisted nitridation.

The low ammonia flux used in the simultaneous dosing and irradiation experiments assures insignificant gas phase optical absorption at 6.4 eV.[10] Confirming this, we found that, with the same photon and molecular ammonia fluxes, surface nitride was not formed when the substrate temperature was 400 K, i.e., above the thermal desorption temperature of ammonia. The photochemistry, therefore, must occur at the adsorbate-substrate interface.

To probe reaction paths, we studied the photolysis of *preadsorbed*, saturation coverage ammonia by HREELS, i.e., no dosing during irradiation. With no irradiation (curve a in Fig. 3), the adsorbate-related losses are assigned to the symmetric/asymmetric deformations and symmetric/asymmetric stretching vibrations of molecular NH$_3$, respectively.[11] The intense losses at 287 (v_p) and 575 cm^{-1} ($2v_p$) are surface optical phonons.[12] These assignments are supported by isotope labeling using ND$_3$. After heating to 350 K or higher, all vibrational features assigned to NH$_3$ are gone and the clean surface spectrum is recovered (spectrum b in Fig. 3). The losses at 870 and 1150 cm^{-1} are optical phonons ($3v_p$ and $4v_p$) of the GaAs(100) surface.[12] In agreement with XPS, these HREELS results unambiguously prove that ammonia does not thermally decompose on the Ga-rich GaAs(100) surface.

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 for NH$_3$ at 1470 and 3230 cm^{-1}. These become cleaner after desorbing the remaining molecular NH$_3$ [Fig. 3(c)]. The weak

shoulder at ~ 840 cm^{-1} cannot be accounted for by the fourth phonon overtone, and is assigned to the Ga-NH$_2$ stretch. Finally, the photodissociation of surface NH$_2$ results in nitridation. Some NH might be present at 102 K following irradiation, but cannot be resolved from the dominating NH$_2$ species.

Photodissociation accounts for $< 10\%$ of the total photolysis of adsorbed ammonia. The major channel is molecular NH$_3$ photodesorption, characterized by a mean translational energy of 52 meV, or $\langle E_{trans}/2k \rangle = 300$ K, independent of the laser pulse energy/cm^2 used (0.5–11 mJ/cm^2).[9] The photodesorption yield depends *linearly* on laser pulse energy. Both these observations indicate a *nonthermal* mechanism.

There are two well-established[13] general excitation mechanisms: (i) direct absorption of an ultraviolet photon by the adsorbate; and (ii) indirect adsorbate excitation via the adsorbate, i.e., adsorption of a photon by the substrate followed by hot carrier (electron or hole) transfer and attachment to the adsorbate. Molecular ammonia does not absorb 3.5 eV photons but, adsorbed on GaAs, photodissociation and photodesorption do occur at this energy.[9] Since all evidence from spectroscopy and thermal desorption indicates only slight perturbation of molecular ammonia upon adsorption, we must turn to substrate mediated hot carrier excitation at this wavelength. At 6.4 eV, the situation is different; molecular ammonia absorbs strongly, substrate absorption is weaker than at 3.5 eV, and the cross section for ammonia loss is at least tenfold higher (10^{-20} compared to 10^{-21} cm^2). At both wavelengths, hot electrons will be formed well above the conduction band minimum (band gap $= 1.42$ eV). For these to be effective, we suppose they must arrive at the ammonia before relaxing to the conduction band edge because electron attachment to molecular ammonia occurs at 5.7 eV in the gas phase and it is unlikely that the resonance will be lowered sufficiently upon weak adsorption. A similar argument can be made for the holes; holes, relaxed to the valence band maximum, will not accept charge because they lie above the highest occupied orbitals of adsorbed ammonia. Thus, we propose that unrelaxed hot carriers, with energies well away from the band edges, where band bending effects are not important, must be considered at 6.4 eV. The sharp increase in the dissociation cross section in passing from 3.5 to 6.4 eV points in one or both of two directions which we cannot distinguish in our experiments. First, direct photon absorption by the ammonia at 6.4 eV; second, the substrate mediated excitation probability may increase as compared to 3.5 eV. After the initial excitation, the excited state can evolve to desorption or dissociation by numerous paths.

Direct excitation, forming an excited state neutral molecule, can lead to desorption or dissociation along the excited state potential energy surface, but, because of the proximity of the substrate, charge transfer, on a femtosecond time scale, to and from the substrate may also be involved. The same kind of charge transfers are expected in the case of substrate-mediated excitation. Generically, the time evolution leading to dissociation and desorption can be described in terms of the Antoniewicz[14] or Menzel–Gomer–Redhead[15] mechanisms, modified to include the effects of intramolecular conversion of electronic-to-vibrational energy transfer.[16]

To summarize, monolayer nitridation of the Ga-rich GaAs(100)-(4×6) surface is achieved at 100 K 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$_2$ is an important intermediate in nitridation.

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