

## Wet chemical nitridation of GaAs (100) by hydrazine solution for surface passivation

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A mild wet nitridation procedure using hydrazine-based solutions has been developed for GaAs (100) surface passivation. Both x-ray photoelectron spectroscopy and spectroscopic ellipsometry show that this nitridation procedure results in a very thin, coherent, and homogeneous GaN layer that is very stable in air. Photoluminescence data show a strong enhancement of the intensity as compared to that of an as-cleaned GaAs sample, indicating that this nitrated layer provides both chemical and electronic passivation of GaAs surfaces. The chemical mechanism of nitridation is discussed. © 2002 American Institute of Physics. [DOI: 10.1063/1.1479212]

Potential applications of III–V semiconductors are dramatically restricted by an inevitable presence of surface native oxide films. Therefore, chemical stabilization (passivation) of the crystalline semiconductor surface in air as well as in process environment through a thin film of an inert material is an important issue in the GaAs semiconductor technology.

Thin films of nitrides of the third group and, specifically, GaN, are very interesting for GaAs surface passivation because of their high thermal and chemical stability. Nevertheless, because of the high value of GaAs/GaN lattice mismatch (~20%), nitride films loose mechanical stability and coherency with the substrate lattice when their thickness becomes almost two complete monolayers.<sup>1</sup>

Recently, a number of nitridation procedures for the GaAs surface have been studied. Among others, the N<sub>2</sub> plasma nitridation,<sup>2,3</sup> the thermal nitridation by NH<sub>3</sub>,<sup>4,5</sup> N<sub>2</sub>H<sub>4</sub>,<sup>6</sup> or by N<sub>2</sub>H<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub> vapor,<sup>7</sup> and the photochemical dissociation of physisorbed NH<sub>3</sub> molecules<sup>8</sup> have been studied. However, all these treatments disrupt the surface crystal order and result in thick amorphous layers of complex composition<sup>6</sup> or strongly defected GaN layers<sup>4</sup> instead of a coherent film of monolayer thickness.

In this letter, nitridation of GaAs (100) surfaces is effectively produced by a wet chemical treatment via chemisorption of nitrogen-related species from hydrazine solutions.

Undoped GaAs (100) wafers with a concentration of residual impurities on the level of 10<sup>16</sup> cm<sup>-3</sup> were used as substrates. Before chemical nitridation, the GaAs substrates were degreased and etched by a H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O = 6:1:1 solution. Then, the substrates underwent to a short treatment into a HF-water solution for 10 h. Afterwards, GaAs substrates were nitrated by a concentrated hydrazine-water solution. A Na<sub>2</sub>S concentration of 0.01 M was added to

the solution to have sulfide anions active in the removal of arsenic from the GaAs surface. After wet treatment, samples were rinsed in de-ionized water and dried in air. Some samples were annealed in UHV in the range 250–350 °C after the nitridation treatment.

*Ex situ* x-ray photoelectron spectroscopy (XPS) was used for the chemical analysis of the nitrated surface. High-resolution XPS spectra of the Ga 3*d*, As 3*d*, N 1*s*, O 1*s*, and C 1*s* core levels were acquired at the grazing take-off angle of 15° using both the Al *Kα* and Mg *Kα* sources with a pass energy of 17.90 eV (this was because using the Al *Kα* source; the Auger L<sub>2</sub>M<sub>45</sub>M<sub>45</sub> line of Ga could interfere with the N 1*s* peak, while using the Mg *Kα* source, the L<sub>3</sub>M<sub>23</sub>M<sub>45</sub> Auger line of Ga could interfere with the C 1*s* peak). Core levels spectra were fit to different components using hybrid Lorentian–Gaussian functions. The binding energies for the various chemical states in the Ga 3*d*, As 3*d*, and N 1*s* spectra were identified from literature.<sup>9</sup> Spectroscopic ellipsometry (SE) measurements were performed in the energy range 1.5–5.0 eV to measure film thickness and the optical quality of the surface. SE spectra were analyzed by an optical model based on the Bruggeman effective medium approximation (BEMA).<sup>10</sup> Surface roughness and morphology were checked by atomic force measurements. Room temperature photoluminescence (PL) measurements were made using as excitation source an Ar ion laser (λ = 514 nm).

Figure 1 shows the results of the fitting applied to the XPS spectra of the Ga 3*d*, As 3*d*, N 1*s*, and O 1*s* photoelectron peaks recorded after the nitridation treatment and after annealing in UHV conditions. For comparison, the spectra of the GaAs substrate before the nitridation treatment are also shown. Any sulfur signal has not been detected by XPS, indicating that its adsorption on the GaAs surface is below the XPS detection limit for the optimized Na<sub>2</sub>S concentration of 0.01 M in the hydrazine solution. The presence of strong bulk GaAs components in both the Ga 3*d* (at binding energy, BE = 19.0 eV) and As 3*d* (at BE = 40.1 eV)<sup>9</sup>

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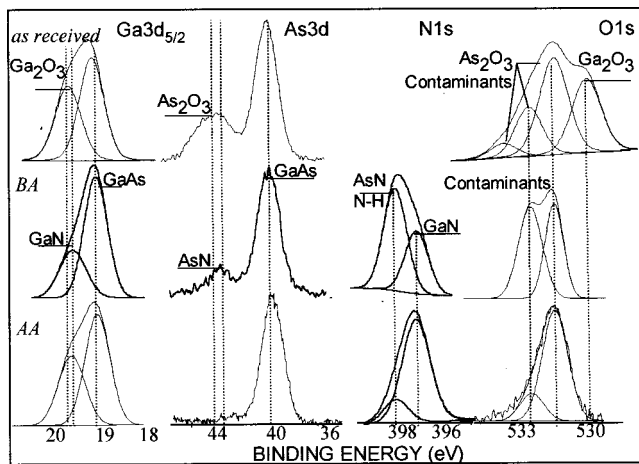


FIG. 1. XPS high-resolution spectra of the Ga  $3d_{5/2}$ , As  $3d$ , N  $1s$ , and O  $1s$  photoelectron core level acquired, at the take-off angle of  $15^\circ$ , for the as-received GaAs (001) substrate before the nitridation treatment, and for the nitrided sample by hydrazine solution before (BA) and after (AA) annealing at  $350^\circ\text{C}$  in UHV.

spectra indicates that the nitrided layer has a thickness of few tens of angstroms. Since the O  $1s$  spectrum of the nitrided sample does not show any contribution due to metallic oxide, i.e.,  $\text{Ga}_2\text{O}_3$ , and/or to As oxide (only contaminations from air exposure are seen), the components at higher BE in the Ga  $3d$  and As  $3d$  spectra have been assigned to GaN (BE =  $19.6\text{ eV}$ ) and AsN (BE =  $43.5\text{ eV}$ ), respectively. This is also consistent with the two fit components present in the N  $1s$  spectra at BE =  $397\text{ eV}$  (GaN) and at BE =  $399\text{ eV}$  (AsN). However, the component at higher BE in the N  $1s$  includes also the contribution of N–H bonds from undecomposed hydrazine adsorbed on the GaAs surface.<sup>9</sup> The nitrided surface is stable over months, since XPS spectra acquired after two months of air exposure do not show any significant variation and, hence, Ga and/or As oxidation. The As–N component can be selectively desorbed by annealing in UHV at  $300\text{--}350^\circ\text{C}$ ,<sup>5</sup> as indicated by the spectra in Fig. 1, which show only the GaAs component in the As  $3d$  spectrum, a relative enhancement of the GaN component in the Ga  $3d$  spectrum and a strong decrease of the high BE in the N  $1s$  spectrum. The small fit component still present in the N  $1s$  spectrum after annealing can be due to the contribution of outmost surface N–H bonds terminating the N atoms. Therefore, after annealing a thin GaN covers the GaAs substrate.

The oxidation resistance of GaAs after the nitridation and annealing treatments can also be evaluated from the *ex situ* XPS spectra in Fig. 1, since there is no signal due to oxide in the As  $3d$  spectrum.

Figure 2 shows the experimental and calculated SE spectra of the imaginary part,  $\langle\epsilon_2\rangle$ , of the GaAs (100) surface after the wet nitridation treatment and the annealing step. The best-fit to the ellipsometric spectrum of the “as-nitrided” GaAs surface has been obtained by a  $12\pm 1\text{ \AA}$ -thick single layer, whose dielectric response could not be described by that of GaN, because of the additional presence of AsN, as detected by XPS. Hence, a dispersion relation based on Lorentzian oscillators has been used to describe the dielectric response of the nitrided layer. In contrast, after annealing the best-fit to the annealed nitrided sample has been obtained by a  $8\pm 1\text{ \AA}$  layer which is de-

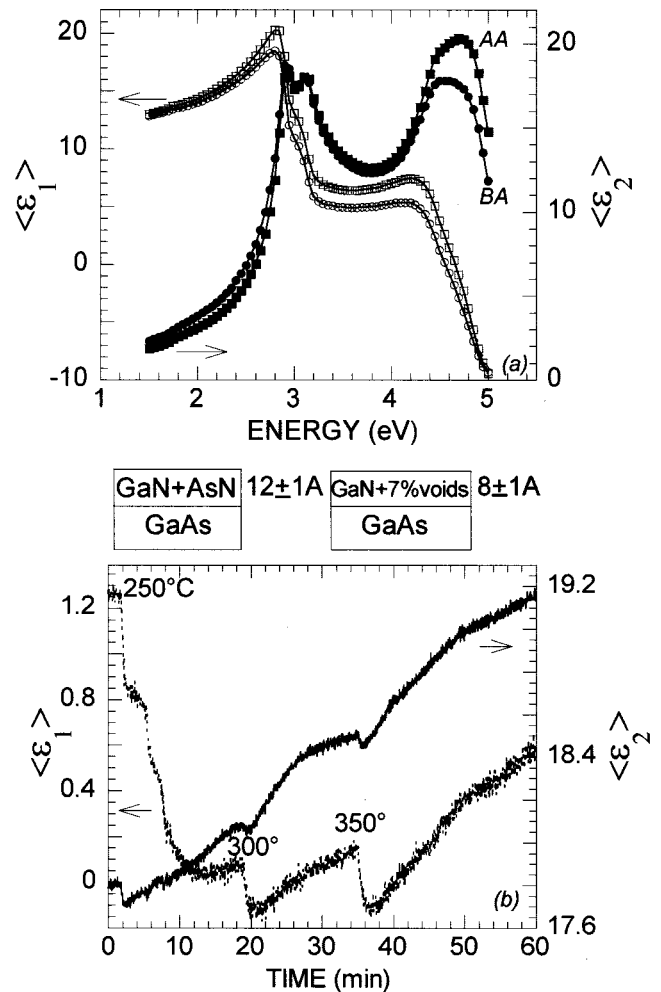


FIG. 2. (a) Ellipsometric spectra of the imaginary part,  $\langle\epsilon_2\rangle$ , acquired before and after annealing at  $350^\circ\text{C}$  in UHV of a GaAs (001) surface nitrided by hydrazine solution. (b) Time evolution of the real,  $\langle\epsilon_1\rangle$ , and imaginary,  $\langle\epsilon_2\rangle$ , parts at the  $E_2$  critical point of GaAs recorded during annealing in UHV at increasing temperatures up to  $350^\circ\text{C}$ .

scribed by a BEMA mixture of 93% GaN+7% voids. The presence of voids is because the very thin surface GaN layer has a density lower than that of a GaN bulk crystal (the GaN dielectric function of a  $5\text{ }\mu\text{m}$  epitaxial hexagonal film grown by metalorganic chemical vapor deposition has been used in the ellipsometric analysis). Therefore, the desorption of AsN upon annealing is also found by spectroscopic ellipsometry. In fact, the annealing step has been monitored in real time by ellipsometry as shown in Fig. 2(b), where the time profile of the  $\langle\epsilon_1\rangle$  and  $\langle\epsilon_2\rangle$  value at the  $E_2$  critical point of GaAs, which is highly sensitive to the surface state, are reported for annealing temperatures in the range  $250\text{--}350^\circ\text{C}$ . The increase of both  $\langle\epsilon_1\rangle$  and  $\langle\epsilon_2\rangle$  indicates desorption of species that XPS analysis indicates to be AsN (the decrease of  $\langle\epsilon_1\rangle$  when the temperature is increased is due to thermal effect). Destruction of nitride film and surface damage by incongruent decomposition of GaAs has been found to commence at  $630^\circ\text{C}$ . Any damage of the GaAs surface during the nitridation and annealing treatments was avoided, since a surface roughness of  $\text{rms}=6\text{ \AA}$  has been measured by AFM.

The prepared surfaces have been stable over months, attesting the validity of the  $\text{N}_2\text{H}_4$  wet treatment for the chemical passivation of the GaAs surface.

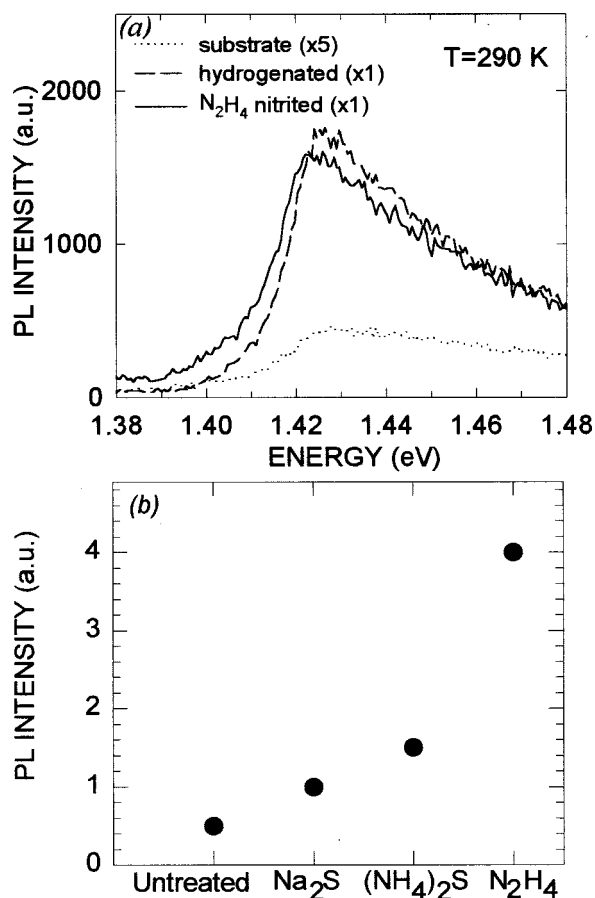


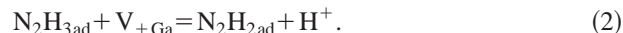
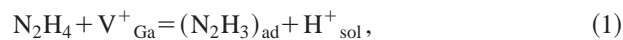
FIG. 3. Room temperature PL spectra of (a) a GaAs substrate after native oxide removal (dotted line), a GaAs surface nitrided by hydrazine solution (continuous line), and a GaAs substrate after conventional passivation by  $H_2$  plasmas (dashed line). (b) Comparison of the PL intensity for GaAs samples passivated by the present hydrazine solution and that obtained by conventional sulfur passivation procedures.

The electronic passivation of GaAs surfaces through the  $N_2H_4$  wet nitridation has also been checked by PL measurements. Figure 3(a) shows a strong increase in the intensity of the room temperature PL spectrum for a semi-insulating GaAs (100) substrate upon hydrazine treatment that is comparable to that obtained by a conventional GaAs passivation by an hydrogen plasmas.<sup>11</sup> Nevertheless, it is worthy to note that the treatment with hydrazine yield to a very thin surface passivating layer, while passivation with hydrogen is a bulk passivation. Furthermore, it has been also found that the surface electronic passivation of GaAs (100) produced by the wet nitridation is higher and more stable than that produced by the sulfide passivation,<sup>12</sup> as shown in Fig. 3(b).

In order to explain the formation of a uniform and stable passivation nitride layer on GaAs (100) surfaces the following stages have been considered:

- (i) removal of the native oxide layer in alkaline ambient;
- (ii) formation of As- and Ga-related adsorption electrophilic centers as a result of establishment of the electronic equilibrium between the semiconductor and the hydrogen Red-Ox system in the solution;<sup>13,14</sup>
- (iii) removal of As lattice atoms, in forms of soluble thioarsenic acid, by  $SH^-$  anions. It has been shown<sup>13</sup> that the probability of adsorption of  $SH^-$  anions on As-

- related adsorption centers is much higher than of others nucleophilic components in the solution; and
- (iv) dissociative adsorption of the nucleophilic nitrogen-containing species on the Ga-surface adsorption centers according to the reactions



The irreversible reaction (2) is responsible for accumulation of the N-NH<sub>2</sub> fragments with a nitrogen atom bonded in the bridge configuration Ga-N-Ga on the GaAs surface, already evidenced by XPS. The nitride layer assumes its final configuration after dissociation of the N-N bonds in the chemisorbed hydrazine molecules. The final chemisorbed layer should consist of NH groups, as confirmed indeed, by observation of N-H component in the XPS spectra. Furthermore, the relatively low temperature of the removal of the As-N component indicates that the corresponding species are situated in the external physisorbed overlayer, and apparently originate from chemical interaction between thioarsenic acid and  $N_2H_4$  molecules.

In conclusion, direct nitridation of GaAs (001) surfaces via hydrazine solution at room temperature has been demonstrated. A very thin ( $\sim 8 \text{ \AA}$ ) GaN layer results in chemical passivation, i.e., chemical stability against oxidation, and electronic passivation of GaAs surface.

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