Gallium arsenide passivation through nitridation with hydrazine

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Passivating films were grown on gallium arsenide by direct nitridation with hydrazine at 300–400 °C. Auger electron spectroscopy and x-ray photoelectron spectroscopy analysis show that the films are primarily gallium nitride with an oxide impurity. The oxide content is a function of the surface pretreatment, reaction temperature, and water concentration in the hydrazine. Improvements in the band gap photoluminescence with nitridation indicate a lower surface state density and reflect an improvement in the termination of the semiconductor lattice.

The lack of stable passivation material for III-V semiconductors impedes the development of electronic and optoelectronic devices. Surface passivation is used for electrical insulation, chemical resistance, and mechanical protection. Inadequate surface passivation results in a high density of interband energy states at the semiconductor-film interface.[1] Many of the interband energy states are attributed to oxide contamination at the interface.[2] The oxides react with the gallium arsenide (GaAs) substrate and produce metallic arsenic that degrades the electrical properties of the film.

In this communication, we report on the formation of group III nitrides as a passivating material for GaAs and other III-V semiconductors. Unlike group III oxides, nitrides are stable compounds that can chemically stabilize the semiconductor surface. In order to form the passivating nitride film, the native oxide is first removed from the surface. After oxide removal, a nitride film is grown by consuming the native semiconductor, analogous to growing silicon dioxide on silicon.[3] Unfortunately, neither oxide removal nor nitridation is easily accomplished. Several processes have been previously investigated with mixed results. High temperature (600–1000 °C) annealing in ammonia or nitrogen yielded thin nitride films;[4–6] however, GaAs has a high vapor pressure and rapidly decomposes at these temperatures.[7] Plasma-assisted decomposition of nitrogen, hydrogen, and ammonia[8,9] and exposure to nitrogen ion beams[10] also produced thin nitride films, but high energy particles in plasmas and ion beams can damage the semiconductor lattice.[11] Photon-assisted decomposition of ammonia[12,13] has also been used to form nitride films, but the high energies can damage the semiconductor surface.[14] Last, alkali metals used during catalyst-assisted nitridation[14] react with the semiconductor and contaminate the substrate.

To overcome these problems, we have investigated direct nitridation with hydrazine at low temperatures (i.e., <400 °C). Hydrazine readily generates reactive nitrogen species for nitridation, even below 100 °C.[15] In this process, high temperatures, plasmas, ion beams, photon beams, and alkali catalysts are not needed to produce reactive nitrogen species for nitridation.

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The reaction system has been described more fully elsewhere.[16] The GaAs substrate was oriented (100) $-2°$(110) and silicon doped n-type with a carrier concentration of 3×10^{16}. Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) were used for elemental analysis of the thin films. AES was performed with a Physical Electronics Model 600 scanning auger multiprobe. The base pressure inside the chamber was $\sim2.0\times10^{-9}$ Torr. A 3 keV, 1 μA electron beam was used for excitation. A 2 keV, 40 μA/cm^2 Ar^- ion beam was used for ion etching. The argon pressure was $\sim1.0\times10^{-8}$ Torr. The Surface Science SSX-100 XPS was equipped with an aluminum $K\alpha$ x-ray source and a crystalline x-ray monochromator. The operating pressure in the sample chamber was $\sim4\times10^{-9}$ Torr. the XPS system was also equipped with a 4 keV argon ion gun that was used to lightly clean the surface. The argon pressure was 3.7×10^{-7} Torr during ion etching. Photoluminescence measurements were made with a SPEX Model 1404 double spectrometer and a cooled GaAs photomultiplier detector. The excitation source was a Lexel Model[95], 514.5 nm argon laser with a power of 100 mW and a spot size of 0.5 mm. The measurements were conducted at 77 K.

Prior to nitride growth, several pretreatments of the GaAs were made. In the first phase, oxides were removed from the surface because they have deleterious effects on surface passivation.[3] The oxides were removed with acidic wet etchants and gas-phase etchants [hydrogen chloride (HCl) and hydrogen (H_2)]. Saito *et al.* showed that a HCl/H_2 etch produces an oxide-free GaAs surface.[17] The next phase was to produce a gallium-rich surface by depleting arsenic from the near-surface region. The surface was further reduced by the HCl/H_2 treatment at 300–400 °C. The intent of this process was the formation of volatile arsenic hydride and/or chloride species in order to deplete the arsenic at the surface. A gallium-rich surface is important in preventing nitride reactions which are limited by the dissociation of the GaAs. Matsuno found that nonhomogeneous, islandlike films of gallium nitride were formed after nitridation of GaAs with ammonia at 800–1000 °C.[6] They suggested that islandlike films result when the nitridation reactions are limited by GaAs dissociation. Consequently, if the surface of the GaAs is initially depleted of arsenic, the reactions will not be limited by

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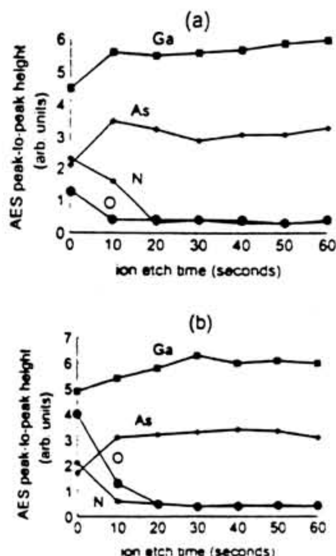

FIG. 1. AES depth profiles of GaN films grown on GaAs precleaned with 10% HCl-isopropanol, 10% HF-methanol, and 2% Br-methanol, *in situ* cleaned with 20% HCl-H_2 for 20 min, and nitrided with 99.7% hydrazine (a) at 300 °C and (b) at 400 °C.

GaAs dissociation, and uniform films of gallium nitride can be made.

Finally, after the GaAs surface has been suitably cleaned and activated, nitride growth can occur by exposure to a reactive nitrogen source. A 1% hydrazine in argon reaction at 300–400 °C for 1 h was used to form the nitride on the GaAs surface. Hydrazine is an endothermic compound that readily decomposes into reactive nitrogen and hydrogen species at low temperatures.[18]

Typically, 1 h exposure to hydrazine produced very thin nitride layers on GaAs (< 100 Å). AES depth profiles of films grown at 300 and 400 °C are shown in Figs. 1(a) and (b), respectively. The samples were precleaned with 10% hydrochloric acid (HCl)-isopropanol, 10% hydrofluoric acid (HF)-methanol, and 2% bromine (Br)-methanol, and *in situ* cleaned with 20% HCl-H_2 for 20 min at 300 °C for Fig. 1(a) and 400 °C for Fig. 1(b). Both films were a mixture of oxides and nitrides. The oxygen peak-to-peak intensity approximately doubled when the reaction temperature was increased from 300 to 400 °C, while the nitrogen intensity remained nearly the same. After correcting for atomic sensitivities, the AES results show that the gallium nitride (GaN) films are nonstoichiometric, with the gallium concentration exceeding the nitrogen concentration. The film thickness, measured by the amount of time needed to etch through the film, also increased when the reaction temperature was increased from 300 to 400 °C. The most likely sources of oxygen contamination were incomplete oxide removal during precleaning, water impurities in the hydrazine, and oxygen and water contamination of the films after the reaction was completed and the samples were transferred from the dry box to the AES chamber. Further characterization of the nitride films, including crystallinity, is proceeding.

Although thin nitride films were formed, in one case a thick film (500–1000 Å) was made by precleaning the sample in 1:1:10 sulfuric acid (H_2SO_4)/hydrogen peroxide (H_2O_2)/water (H_2O), 2% Br-methanol mechanical etch, and 1% HCl-H_2 *in situ* gas-phase etch for 5 min at 400 °C, and the nitridation with 1% hydrazine at 400 °C for 1 h. The film was orange/yellow in color and uniformly covered the entire substrate. The AES profile showed that the film was composed of gallium and equal concentrations of nitrogen and oxygen. Arsenic was depleted from the near-surface region of the film and the semiconductor-film interface. The film was formed by converting the native semiconductor to gallium oxynitride and depleting the region of arsenic. These results are similar to those of Faulkner[4] and Prochazkova[5] for the nitridation of thick oxide films on GaAs. They found that thick nitride films could be grown on GaAs if it was first thermally or anodically oxidized. After nitridation with ammonia at 800–1000 °C, their films were orange/yellow in color, consisted primarily of gallium nitride and gallium oxide, and were arsenic-deficient. These reports raise the possibility that the oxide in the film originates from undissolved oxide during the pretreatment.

XPS analysis was used to examine the oxidation state of the elements in the film. The carbon 1*s* binding energy for adventitious carbon was referenced to 284.6 eV for all samples. The binding energies for the oxidation states of the Ga 3*d* and N 1*s* XPS spectra were identified from literature.[19–21] The XPS results show that the nitrogen in the films was primarily gallium nitride. The amount of oxide impurity was a function of the precleaning and the reaction temperature. For example, the Ga 3*d* XPS spectra for the 500–1000 Å film shows that the film was primarily gallium nitride with a small amount of gallium oxide. A large peak for the N 1*s* spectra was at 397 eV and shows that the oxidation state of the nitrogen was nitride and not nitrite or nitrate. This suggests that the oxygen impurity remains as an oxide and does not combine with the nitrogen to form a nitrite or nitrate.

The precleaning treatment and the hydrazine purity were investigated as possible sources of oxide in the films. First, a reduced factorial experiment was used to understand the effects of precleaning on the N/N+O ratio in the film. The 2% Br-methanol and acid wet etch had the largest effect on the results. For the 2% Br-methanol etch, a light mechanical rubbing for 30 s was better than a free etch for 30 s. Likewise, an etch in 10% HCl-isopropanol and 10% HF-methanol for 30 s increased the N/N+O ratio more than a 30 s etch in 1:1:10 $H_2SO_4/H_2O_2/H_2O$.

Second, the water impurity in the hydrazine was investigated as a possible source of oxygen contamination. Activated alumina can improve the purity of the hydrazine to greater than 99.99%.[18] Powdered activated alumina (particle diameter 0.125–0.25 mm) was vacuum-dried at 1×10^{-6} Torr for four days at 120 °C. The dried alumina was mixed with Olin ultrapure hydrazine (as received

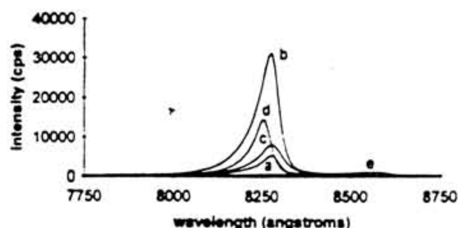

FIG. 2. Photoluminescence of GaAs samples at 77 °K: (a) precleaned with 10% HCl-isopropanol, 10% HF-methanol, 2% Br-methanol, and 20% HCl/H_2 (clean 1), and reacted with 99.7% hydrazine at 300 °C; (b) precleaned with clean 1 and reacted with purified hydrazine at 300 °C; (c) precleaned with 1:1:10 $H_2SO_4/H_2O_2/H_2O$, 2% Br-methanol, and 1% HCl/H_2 (clean 2), and reacted with 99.7% hydrazine at 400 °C; (d) precleaned with clean 2 and reacted with purified hydrazine at 400 °C, and (e) untreated control.

99.7%) and allowed to sit for seven days. Gallium arsenide samples were precleaned and reacted with either as-received hydrazine or purified hydrazine. The AES results showed that purification with alumina decreased the amount of oxide but resulted in a thinner film. It appears that the water impurity and subsequent oxide content of the film compromises the quality and density of the film, allowing easy penetration of the reactants to the interface.

Photoluminescence has been used to measure the relative quantity of surface states.[22] The photoluminescence of five gallium arsenide samples were measured, including an untreated control sample, two samples cleaned with 10% HCl-isopropanol, 10% HF-methanol, 2% Br-methanol, and 20% HCl/H_2 (clean 1) and reacted with either 99.7% or purified hydrazine at 300 °C, and two samples cleaned with 1:1:10 $H_2SO_4/H_2O_2/H_2O$, 2% Br-methanol, and 1% HCl/H_2 (clean 2) and reacted with either 99.7% or purified hydrazine at 400 °C. The results in Fig. 2 show that photoluminescence substantially increased after nitridation with hydrazine. There was more surface state mediated recombination seen with the untreated sample than with the hydrazine treated samples. Further increases in the photoluminescence intensity were observed when purified hydrazine was used. These results show that further gains in the photoluminescence and purity of the film may be possible by reducing the oxygen contamination in the film. The median wavelength for photoluminescence of the hydrazine-treated samples also shifted to higher energies, closer to that of band edge radiation. The cause of the wavelength shift with nitridation is under further investigation.

In conclusion, the direct nitridation of gallium arsenide with hydrazine at 300–400 °C to produce gallium nitride has been demonstrated. The films were grown by consuming the gallium arsenide substrate and depleting the surface region of arsenic. The films contained some oxygen impurities, but the N/N+O ratio was improved by using a 10% HCl-isopropanol, 10% HF-methanol, and 2% Br-methanol preclean and by drying the hydrazine. Last, the photoluminescence intensity of untreated GaAs was significantly improved by nitridation with hydrazine. The water impurity of the hydrazine adversely affected the quality of the films and the photoluminescence from the gallium arsenide substrates.

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