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Effect of hydrogen in dilute $\text{InN}_x\text{Sb}_{1-x}$ alloys grown by molecular beam epitaxy

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The electronic properties and nitrogen bonding configurations are investigated in dilute $\text{InN}_x\text{Sb}_{1-x}$ alloys grown by molecular beam epitaxy using a mixed nitrogen and hydrogen plasma. High-resolution electron-energy-loss spectroscopy is used to observe annealing-induced changes in the conduction band electron plasma frequency and plasmon lifetime. X-ray photoelectron spectroscopy of the N 1s core level indicates that a large proportion of the nitrogen in the $\text{InN}_x\text{Sb}_{1-x}$ alloy is contained within neutral N-H complexes. Annealing at 300 °C removes hydrogen from these complexes, increasing the concentration of isoelectronic nitrogen acceptors. This increases the ionized impurity scattering and reduces the background conduction electron density. © 2003 American Institute of Physics. [DOI: 10.1063/1.1604463]

The substitution of nitrogen onto a few percent of the group V lattice sites in conventional III-V semiconductors results in a large reduction in the band gap.¹ Extensive research has recently been focused on the quaternary alloy, $\text{Ga}_{1-y}\text{In}_y\text{N}_x\text{As}_{1-x}$, as it can be lattice matched to GaAs with an emission wavelength in the 1.3–1.55 μm range that is important for optical communications technology.² In contrast, there have been relatively few investigations of dilute nitride alloys of the narrow gap III-Vs, which have the potential to compete with HgCdTe in far-infrared applications, such as thermal imaging and detection of environmentally important gases.³ Alloying nitrogen with InSb can extend the cut-off wavelength from 7 μm at 300 K into the 8–12 μm atmospheric transition band where gases such as SO_2 , NH_3 , O_3 , and CO_2 all have absorption lines.⁴ Indeed, time-resolved optical measurements have been used to observe an absorption edge of 11 μm at 290 K in an alloy with a nominal composition of $\text{InN}_{0.965}\text{Sb}_{0.035}$.⁵ However, a persistent difficulty with the $\text{InN}_x\text{Sb}_{1-x}$ material grown to date is the variation of the fraction of nitrogen atoms in the alloy that substitute onto Sb lattice sites.^{3–6} The location of the remaining proportion of the nitrogen atoms detected by secondary ion mass spectrometry (SIMS) has yet to be determined. The presence of nitrogen at locations other than on the group V lattice site has also hindered attempts to use x-ray diffraction to quantify the effective alloy composition. While nitrogen incorporation on Sb sites has the effect of reducing the lattice constant towards that of InN, the non-substitutional nitrogen tends to cause dilation of the lattice.

The results of an x-ray photoelectron spectroscopy (XPS) investigation of the bonding configurations of the nitrogen in $\text{InN}_x\text{Sb}_{1-x}$ epilayers are presented in this letter. Additionally, high-resolution electron-energy-loss spectroscopy (HREELS) of the conduction band electron plasmon excitations has been performed to determine the effects of

annealing on the electronic properties of the epilayers.

The $\text{InN}_x\text{Sb}_{1-x}$ samples were grown by molecular beam epitaxy (MBE) using standard Knudsen effusion cells for the indium and antimony sources, while nitrogen was provided by an Astex AX4300 electron cyclotron resonance (ECR) plasma source. Hydrogen was additionally introduced to the ECR source to enable the plasma to be sustained at low nitrogen pressures. Details of the sample growth have been presented elsewhere.³ XPS analysis of the In 3d, Sb 3d, and N 1s photoelectron spectra was performed using a Scienta ESCA300 spectrometer with a monochromated Al K α x-ray source ($h\nu=1486.6$ eV) at the National Center for Electron Spectroscopy and Surface Analysis, Darebury Laboratories, UK. The total spectrometer resolution was set to the relatively low value of 1.2 eV to obtain greater count rates in the N 1s core level region because of the small atomic sensitivity factor of the N 1s photoelectrons and the small atomic percentages of nitrogen in the dilute $\text{InN}_x\text{Sb}_{1-x}$ alloys. The HREELS experiments were performed using a specular scattering geometry with an incident and scattered polar angle of 45°. The resolution of the HREEL spectrometer determined from the full width at half maximum of the elastic peak was 12 meV. The surfaces of the $\text{InN}_x\text{Sb}_{1-x}$ epilayers were prepared *in situ* for the XPS and HREELS analysis by a two-stage atomic hydrogen cleaning process consisting of a 5 kL dose of H_2 at room temperature followed by a 5 kL dose at a sample temperature of 300 °C. Each 5 kL dose took 20 min using a hydrogen gas pressure of 5×10^{-6} mbar. The molecular hydrogen was thermally cracked with ~50% efficiency using a TC-50 atomic hydrogen source (Oxford Applied Research Ltd., UK). The samples were radiatively annealed at 300 °C using a tungsten filament mounted behind.

The N 1s XPS spectra from one of the samples, with a nominal composition from SIMS of $\text{InN}_{0.01}\text{Sb}_{0.99}$, are shown in Fig. 1. All of the spectra have been fitted with a Shirley background and a series of Voigt functions each with a full

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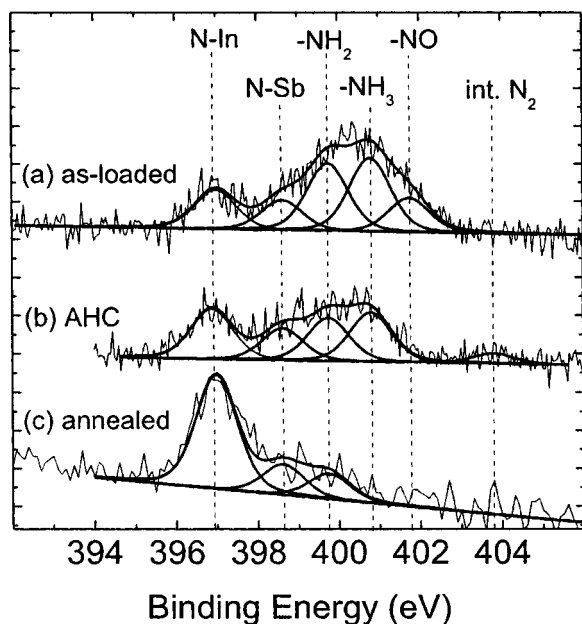


FIG. 1. X-ray photoelectron spectra of the N 1s core level recorded from $\text{InN}_x\text{Sb}_{1-x}$ grown by MBE (a) as-loaded, (b) atomic hydrogen cleaned, and (c) annealed for 8 h at 300 °C.

width at half maximum of 1.2 eV, consisting of 20% Lorentzian and 80% Gaussian line shapes. Spectrum 1(a) was recorded from the as-loaded $\text{InN}_x\text{Sb}_{1-x}$ surface. The peak at 396.9 eV is due to N–In bonding;⁷ that is, N located substitutionally on group V sites, which causes the band gap reduction in dilute III–N–V materials. By analogy with the binding energies of N bonded to P in InP ,⁷ the peak at 398.6 eV is assigned to N–Sb bonding. The peaks at 399.7 and 400.7 eV are due to $-\text{NH}_2$ and $-\text{NH}_3$ complexes, respectively.^{8,9} The remaining contribution to the N 1s region at 401.8 eV is ascribed to N–O bonding associated with the atmospheric contamination on the surface prior to cleaning.¹⁰ At this stage, there was intensity in the C 1s region associated with hydrocarbon contamination. Moreover, the In 3d and Sb 3d regions were dominated by In–oxide and Sb–oxide components. The O 1s peak was obscured by the oxide component of the Sb 3d_{5/2} peak.

After atomic hydrogen cleaning (AHC), there was no observable intensity in the C 1s region, no oxide components apparent in the In 3d or Sb 3d region, and no O 1s peak was visible, indicative of complete removal of the native oxides and the hydrocarbon contamination. As shown in Fig. 1(b), the N–O bonding component of the N 1s spectrum was no longer present after AHC. The N–In and N–Sb components were unchanged. The intensity of the $-\text{NH}_2$ and $-\text{NH}_3$ components of the N 1s peak decreased with respect to those recorded before cleaning. A small additional peak is just discernible at 403.8 eV and is attributed to interstitial N_2 molecules.⁷ Finally, the total area of the N 1s peaks decreased as a result of AHC. These changes to the N 1s spectrum are evidence of the complete removal of N–O and partial removal of N–H species, with some of the liberated N desorbing from the sample and some combining to form interstitial N_2 molecules. It is not possible to discern whether these changes to the N 1s spectrum were due to the AHC process as a whole or a result of the 20 min anneal at 300 °C

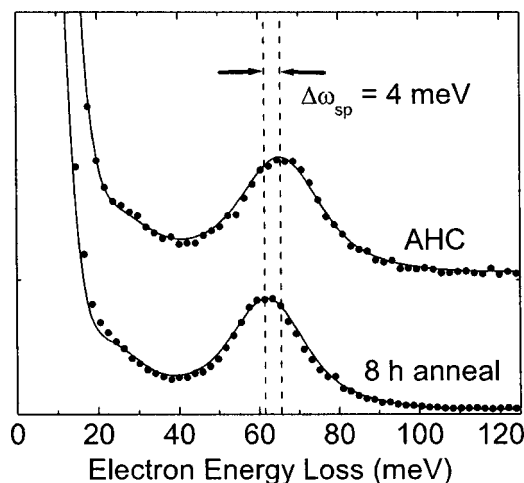


FIG. 2. Experimental specular HREEL spectra (dotted lines) recorded using 30 eV electrons from $\text{InN}_x\text{Sb}_{1-x}$ grown by MBE after (a) atomic hydrogen cleaning, and (b) AHC and annealing at 300 °C for 8 h. Semiclassical dielectric theory simulations of the spectra are also shown (solid lines).

required to remove the oxide and hydrocarbon contamination.

The N 1s spectrum after a much longer anneal (8 h at 300 °C) is shown in Fig. 1(c). The interstitial N_2 peak is no longer present, presumably as a result of N_2 diffusing to the surface and desorbing into the vacuum. The $-\text{NH}_3$ peak has also disappeared and the $-\text{NH}_2$ peak intensity has decreased. The N–Sb peak has remained unchanged, and the N–In peak has increased in intensity. These changes suggest that the annealing process has removed hydrogen from the N–H complexes and increased the degree of anion substitution. Apart from the removal of the interstitial N_2 , the total area of the N 1s peaks remained constant, indicating that no other nitrogen was removed by annealing.

Specular HREEL spectra recorded using an incident electron energy of 30 eV from $\text{InN}_x\text{Sb}_{1-x}$ are shown in Fig. 2 following AHC and after an 8 h anneal. The two features of these spectra are a shoulder on the elastic peak at 23 meV due to Fuchs–Kliwer surface phonon excitations, and the peak at higher loss energy (60–70 meV) due to conduction band electron plasmon excitations. The plasmon peak position decreased from 65.5 meV for the AHC $\text{InN}_x\text{Sb}_{1-x}$ epilayer to 61.5 meV after the 8 h anneal. HREEL spectra recorded over an incident electron energy range of 7–60 eV were simulated using semiclassical dielectric theory.¹¹ A two layer model was used consisting of a 70-Å-thick plasma-free depletion layer and a semi-infinite bulk layer, where each layer has its own hydrodynamic dielectric function.¹² The bulk plasma frequencies used in the simulation of the spectra from the $\text{InN}_x\text{Sb}_{1-x}$ epilayer recorded after AHC and 8 h anneal were 68.5 and 65.5 meV, respectively. The observed plasmon peaks in the HREEL spectra occur at loss energies lower than the bulk plasma frequency because of the effect of the depletion layer. The plasmon lifetime used to simulate the 60 eV spectrum decreased from 0.064 ps for the AHC $\text{InN}_x\text{Sb}_{1-x}$ alloy to 0.048 ps after annealing for 8 h.

These annealing-induced changes in the electronic properties can be explained in terms of the observed changes in nitrogen bonding configurations induced by annealing. The reduction of the plasma frequency is due to either an increase

in the effective mass, a reduction of the carrier density, or a combination of both. The reduced plasmon lifetime suggests an increase in the ionized impurity scattering. The XPS results demonstrate that annealing removes hydrogen from N–H complexes, leaving more N bonded to In. Both experimental and theoretical studies have shown that N is an isoelectronic acceptor in GaNP, GaNAs, and GaInNAs^{13,14} and that N–H complexes are electrically inactive.^{13,15} Our results suggest that H and N have the same effect in InNSb. Upon annealing, H is removed from neutral N–H complexes and diffuses out of the material. This leaves a greater concentration of N acceptors (electron traps) which results in a decreased conduction electron density and reduced plasma frequency. The additional acceptors also cause enhanced ionized impurity scattering, reducing the plasmon lifetime. An increase in the electron effective mass may also occur upon annealing, but this would not, on its own, account for both the reduction in plasma frequency and the decreased plasmon lifetime. The XPS results suggest that annealing results in additional N–In bonding, increasing the x value in the alloy composition $\text{InN}_x\text{Sb}_{1-x}$. However, an increased x value does not necessarily increase the effective mass at the Fermi level.¹⁶

Nitrogen in the dilute $\text{InN}_x\text{Sb}_{1-x}$ alloys grown using a mixed nitrogen and hydrogen plasma has been found to be bonded to both In and Sb and is also located in N–H complexes. Annealing for 8 h at 300 °C partially removes hydrogen from N–H complexes and increases the amount of N bonded to In. Electrical measurements indicate that annealing decreases the conduction electron concentration and increases the ionized impurity scattering. Both of these electronic effects are the result of the removal of H from neutral

N–H complexes, leaving a greater concentration of isoelectronic N acceptors.

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