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Atomic hydrogen cleaning of GaSb(001) surfaces

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We show that the (001) surface of GaSb can be cleaned efficiently by exposure to atomic hydrogen at substrate temperatures in the range 400–470 °C. This treatment removes carbon and oxygen contamination, leaving a clean, ordered surface with a symmetric (1×3) reconstruction after a total H_2 dose of approximately 150 kL. An ordered but partially oxidized surface is generated during cleaning, and the removal of this residual oxide is the most difficult part of the process. Auger electron spectroscopy and low energy electron diffraction were used to monitor the chemical cleanliness and the ordering of the surface during the cleaning process, whereas high resolution electron energy loss spectroscopy was used to probe the electronic structure in the near-surface region. The results obtained indicates that this cleaning procedure leaves no residual electronic damage in the near-surface region of the Te-doped ($n \sim 5 \times 10^{17}$ cm^{-3}) samples of GaSb(001) studied. © *1996 American Institute of Physics.* [S0003-6951(96)03744-8]

The surface cleaning of III–V materials by annealing under a flux of atomic hydrogen has been widely studied in recent years.[1–4] The advantages of this method arise from the high cleaning efficiency that can be achieved at relatively low substrate temperatures, resulting in very little surface roughening and residual damage. Additionally, an atomic hydrogen source can easily be incorporated into a standard molecular beam epitaxy (MBE) system, and can be used for purposes other than surface cleaning. For example, atomic hydrogen has recently been shown to act as a surfactant in heteroepitaxial semiconductor growth.[5,6] Studies of atomic hydrogen cleaning of III–V semiconductor materials have thus far focused on the InP(001) (Refs. 1 and 3) and GaAs(001) (Refs. 1, 2, and 4) surfaces, both of which can be successfully cleaned using moderate annealing temperatures. However, with increasing interest in alternative III–V materials such as the antimonides, from both fundamental and technological standpoints, it is useful to broaden the range of materials studied.

The pseudomorphic growth of ternary compounds such as $Ga_{1-x}In_xSb$ and $InAs_{1-x}Sb_x$ lattice matched to GaSb substrates has attracted much attention of late.[7,8] These materials are of particular interest for application as midinfrared lasers[9] and as detectors used in atmospheric monitoring of gases such as CO, HCl, CO_2, and O_3, which all have strong absorption lines in the 2.0–5.0 μm band.[10] Several surface preparation techniques have been applied in order to produce clean GaSb(001) substrates. Although thermal desorption of the native oxide layer can be achieved in ultrahigh vacuum by annealing to 600 °C under a Sb_4 overpressure, this process results in significant surface roughening.[11] Several cycles of low energy argon ion bombardment and annealing have also been shown to produce clean, ordered (1×3) surfaces.[12,13] However, in related III–V materials, this latter treatment results in a high degree of residual electronic damage that cannot be repaired by annealing. For example, in n-type GaAs a high concentration of acceptorlike defects remains, resulting in strong carrier depletion near the surface.[14] By contrast, in both n- and p-type InSb, the residual defects are donorlike in character and a layer of enhanced electron concentration is formed below the surface.[15] We have investigated surface cleaning procedures on several other III–V materials, including InAs(001) and InSb(001),[16] and in this letter we report on the cleaning of the GaSb(001) surface using atomic hydrogen.

We have used GaSb(001) wafers doped with Te to a level of $n \sim 5 \times 10^{17}$ cm^{-3}. The samples were mechanically polished and chemically etched by the manufacturer (MCP Electronic Materials, Ltd., UK) and loaded directly into ultrahigh vacuum (UHV) without further treatment. High resolution electron energy loss spectroscopy (HREELS), low energy electron diffraction (LEED), and Auger electron spectroscopy (AES) were all used to study the cleaning process. A commercially built atomic hydrogen source was used (EPI Ltd., UK) consisting of a tungsten cracking filament surrounded by a water-cooled jacket into which hydrogen gas was admitted via a leak valve. The filament was operated at a temperature of 2100 °C giving an overall H_2 cracking efficiency of approximately 6%, as estimated from the manufacturer's calibration measurements.[17] The chamber pressure during hydrogen cleaning was typically 3×10^{-5} Torr, with the total duration of hydrogen exposure not exceeding 2 h, in order to produce a clean sample. Hydrogen doses were measured in terms of molecular hydrogen exposure, in units of kL (1 kL)= 10^{-3} Torr s). The temperature was measured by a Cromel–Alumel thermocouple in direct contact with the samples, which were heated radiatively.

Prior to any hydrogen cleaning treatment, AES indicated heavy contamination of the samples with carbon and oxygen. Figure 1 indicates the surface composition of the samples as determined by AES peak height intensity ratios, modified by the relative sensitivity factors of the Auger transitions.[18] For the as-loaded samples, the signal was dominated by C contamination and the sample exhibited no ordered LEED pattern. In HREELS the specular elastic peak was very weak and broad, with an angular spread of 15° full width at half-maximum (FWHM). A specular HREEL spectrum from the as-loaded sample is shown in Fig. 2, with an electron beam

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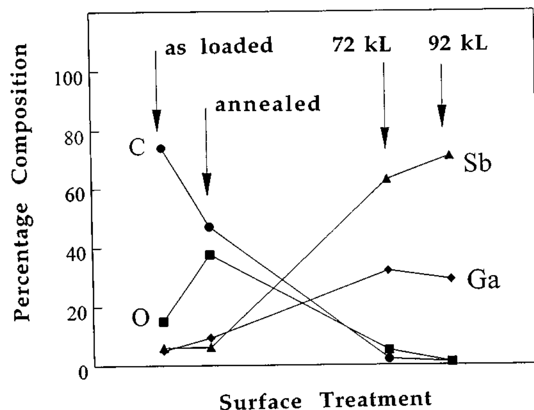

FIG. 1. GaSb(001) surface composition determined by AES as a function of cleaning treatment (annealing at 400 °C for 30 min, followed by hydrogen cleaning at 400 °C with an H_2 dose of 72 kL, followed by a further 20 kL).

energy of 30 eV. Broad and very intense loss features extend out to approximately 150 meV; there is also a strong C–H stretching mode at 363 meV (not shown). After annealing in vacuum to 400 °C for 30 min, the C contamination was significantly reduced (see Fig. 1), but the O signal remained very strong. The intensity of the C–H mode in HREELS was reduced, but the broad feature at <150 meV were not significantly affected. We assign this intense loss structure to a combination of Sb–O (Ref. 15) and Ga–O (Ref. 19) vibrations in the oxide layer.

After hydrogen cleaning at 400 °C, with an H_2 dose of between 50 and 100 kL, the HREELS spectrum changed dramatically (Fig. 2). The relative intensity of the loss features dropped sharply, while the specular elastic peak became more intense and narrower (5° FWHM), indicating a significant improvement of the surface ordering. A distinct loss peak was observed at 125 meV, superimposed on a steeply declining background about the elastic peak. We confirmed that this loss feature was due to a surface vibrational excitation rather than a collective mode such as a plasmon, by varying the electron energy in the range 7–60 eV. The loss peak intensity relative to the elastic peak decreased rapidly with increasing beam energy, ruling out the possibility of a plasmon excitation. We assign this loss feature to an oxide vibration of the partly cleaned surface. Figure 1 shows

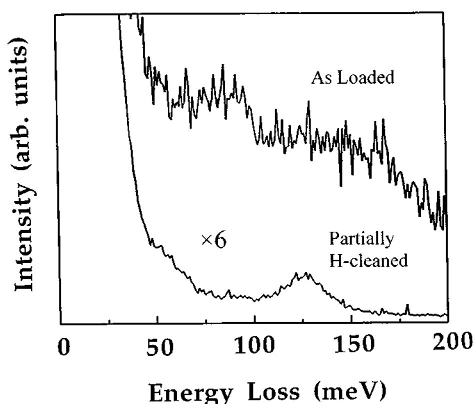

FIG. 2. Specular HREEL spectra (at 30 eV) from an as-loaded (upper curve) and partially cleaned GaSb(001) sample. The H_2 dose was 50 kL at a sample temperature of 400 °C for the lower curve (enlarged by a factor of 6).

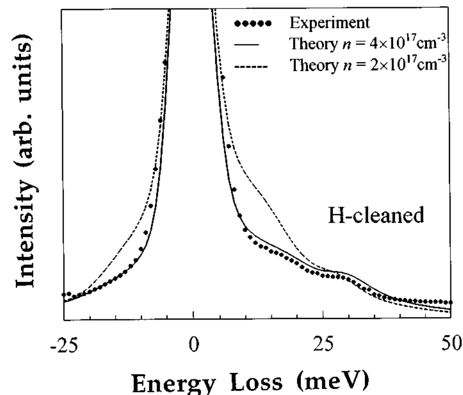

FIG. 3. Specular HREEL spectrum (at 30 eV) from fully cleaned GaSb(001) together with simulated spectra based on dielectric theory. The experimental spectrum (solid circles) was obtained after an additional H_2 dose of 50 kL at a sample temperature of 470 °C. The simulated spectra assume bulk carrier concentrations of 4×10^{17} cm^{-3} (solid curve) and 2×10^{17} cm^{-3} (dashed curve).

a sharp drop of both C and O AES signals following hydrogen cleaning at 400 °C with a H_2 dose of 72 kL. Oxygen was barely detectable after this cleaning cycle, but an additional 20 kL was sufficient to reduce the O signal to below the detection limit of AES (approximately 1% of a monolayer). However, the oxide mode at 125 meV in HREELS persisted after H_2 doses of more than 100 kL at 400 °C. In order to remove this residual surface oxide, it was necessary to dose further with atomic hydrogen at an increased substrate temperature. The partly cleaned sample showed weak (1×1) features in the LEED pattern, with a high background and faint fractional order features in the (1×3) positions. This indicates that the surface was reasonably well ordered despite the presence of the residual surface oxide.

With a final dose of 50 kL H_2 at 470 °C, the loss peak at 125 meV disappeared completely and the specular elastic peak improved further in both intensity and reduced angular spread (2° FWHM). A sharp symmetric (1×3) LEED pattern accompanied this improvement. A specular HREEL spectrum from this fully cleaned surface is shown in Fig. 3, obtained with an incidence energy of 30 eV and an instrumental broadening of 7 meV FWHM. The spectrum is featureless at higher loss energies, but a strong ''double shoulder'' can be seen below 40 meV in loss energy (Fig. 3, solid circles). This is assigned to the coupled plasmon–phonon (''plasmaron'') excitations propagating in the near-surface region of the material. The transverse optical phonon energy of GaSb is 28.5 meV,[20] and the plasmon energy for a carrier concentration of 5×10^{17} cm^{-3} is 31 meV. These energies are sufficiently close to cause strong mode coupling, producing plasmaron excitations of mixed character.[21] We performed dielectric theory simulations[22] in order to model the experimental spectra, and two simulated curves are shown in Fig. 3 (solid and dashed curves). We have used a two-layer charge profile, assuming carrier depletion within 50 Å of the surface, and described the plasma response by using the Drude model. The HREELS measurements are sensitive to the plasma response well below the surface[15] allowing us to probe the electron gas up to 1500 Å into the bulk. The shape of the double shoulder is a sensitive function of the bulk

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plasma frequency from which we can derive the carrier concentration in the subsurface region. A simulation assuming a bulk carrier concentration of 4×10^{17} cm^{-3} produced the solid curve shown in Fig. 3, which represents the best fit to the experimental data. Setting the bulk carrier concentration to 2×10^{17} cm^{-3} produced a very poor fit, shown as the dashed curve in Fig. 3, due to excessive intensity in the lower energy plasmaron mode. The carrier concentration deduced from the HREELS measurements is consistent with the bulk doping level, bearing in mind the high density of acceptorlike defects normally found in GaSb that prevent accurate Te doping to levels of less than 3×10^{17} cm^{-3}.[10] We can therefore rule out any significant change of carrier concentration in the region probed by the HREELS measurements as a result of the cleaning process. In particular, the active donor concentration is not reduced due to the indiffusion of atomic hydrogen, which has previously been observed to reduce the subsurface carrier concentration in heavily doped GaAs after room temperature exposure.[23]

In conclusion, we have demonstrated that GaSb(001) surfaces may be efficiently cleaned by exposure to atomic hydrogen at 400–470 °C with molecular hydrogen doses of 100–150 kL. After 100 kL at 400 °C the surfaces are free of contamination, as determined by AES. However, these surfaces exhibit poor LEED patterns and an oxide vibrational mode is still observed in HREELS. The removal of this loss feature requires exposure to a further 50 kL at 470 °C and results in the appearance of a sharp symmetric (1×3) LEED pattern. The intensities of the plasmaron modes that appear in the HREEL spectra indicate that the carrier concentration in the near-surface region of the material is unaffected by the atomic hydrogen cleaning process.

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