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Sb-capping and decapping of MBE-grown GaSb(100)

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We present a study of GaSb(100) surfaces grown by molecular beam epitaxy, protected by an Sb cap during ambient storage, and annealed in ultra-high vacuum. The surface structure, composition and electronic transitions are investigated with low energy electron diffraction, Auger electron spectroscopy, and electron energy loss spectroscopy. Successful Sb-decapping is achieved by annealing at 300°C for 30 min. It leads to a (2×3)-c(2×6) reconstructed surface with less residual damage and higher Sb concentration than surfaces prepared by sputtering and annealing.

1. Introduction

Several studies have been devoted during the past few years to the protection of III–V compound semiconductor surfaces by capping layers for ambient transfer from growth to analysis or processing chambers [1–6]. Surfaces grown by molecular beam epitaxy (MBE) are being increasingly used for surface and interface research, and the need for transferring out of the growth chamber is becoming more frequent. The conservation of structural and electronic properties during transfer is an important issue which must therefore be investigated. So far, the bulk of the work has been done on As-capped GaAs surfaces [1–6] and has shown possibilities for efficiently preserving these surfaces in an ambient atmosphere for extended periods of time (days).

We present a study of the capping of MBE-grown GaSb with a thick Sb layer, and of the decapping in ultra-high vacuum (UHV). We find a critical decapping temperature of 300°C above which the GaSb surface degrades. In spite of some contamination of the resulting GaSb surface by carbon and oxygen, due to insufficient capping layer thickness, we find that the Sb can be used as an efficient and easily removed protective cap.

2. Experiment

The GaSb substrates (n-doped, $(2\text{–}4)\times10^{17}$ cm^{-3}) were etched in a $1:10^4$ solution of bromine : methanol before insertion in the MBE chamber (base pressure 10^{-10} Torr). The substrate oxide was removed by annealing at 540°C under a 4×10^{-9} Torr pressure of Sb. This produced a well defined ring-like reflection high energy electron diffraction (RHEED) pattern. The GaSb(100) layers were grown at 520°C at a growth rate of ~0.75 μm/h measured with RHEED oscillations. During growth, a sharp (1×3) RHEED pattern was observed. At the end of the growth, the Ga flux was interrupted and the sample cooled down to room temperature under Sb flux. The deposition of the capping layer lasted ~20 min for a nominal Sb thickness

of 2–3000 Å. The samples were removed from the MBE system and left in a dessicator for about a month. They were then introduced in an analysis chamber equipped with a double-pass cylindrical mirror analyzer for Auger and electron energy loss spectroscopy (AES, EELS) and a four-grid low energy electron diffraction (LEED) optics. The AES and EELS spectra were taken with incident electron energies of 3 keV and 120 eV, respectively. The LEED patterns were recorded at low temperature (120 K) to decrease thermal atomic vibrations on the GaSb surface.

The Sb cap was removed by annealing the sample at various temperatures ranging between 200 and 350°C. The samples were heated by passing current through the Mo foil in which they were held. The temperature was raised either in steps or rapidly, and kept at its maximum value for different amounts of time (30–220 min). The temperature was measured with an infrared pyrometer pre-calibrated with a thermocouple. A scanning electron microscope (SEM) study of the surface morphology before and after annealing was also performed.

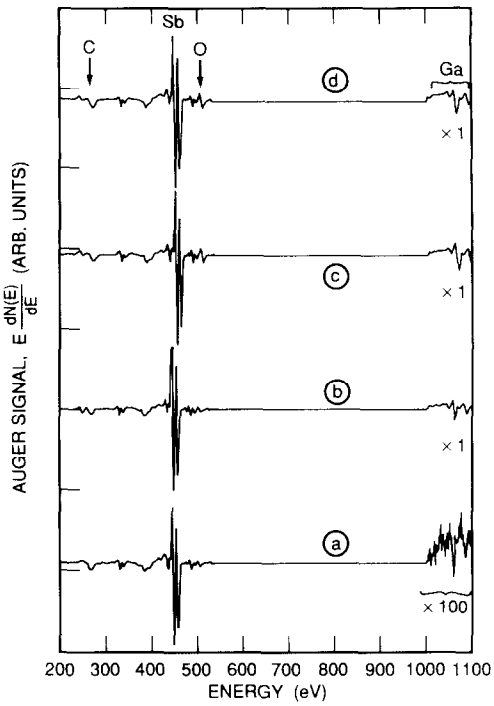

Fig. 1. High energy AES spectra of (a) the Sb capping layer, and (b), (c), and (d) after a 300°C annealing for 30, 160 and 225 min, respectively.

3. Results and discussion

3.1. Capped surface

The high energy AES spectrum (fig. 1a) shows a continuous Sb layer with surface contamination by carbon and oxygen. The amount of Sb oxide is small, indicating that the capping layer did not degrade significantly during storage. Yet, in spite of a targeted Sb thickness of 2–3000 Å, a very small high energy $L_3M_{4,5}M_{4,5}$ Ga peak (1070 eV, escape depth 15–20 Å) remains visible. We can rule out interface reaction and Ga segregation on top of Sb, as well as partial desorption of the Sb cap during the room temperature storage. Thus, areas of the deposited Sb cap might be as thin as 100 Å (~ 5 times the escape depth). The low energy AES spectrum (fig. 2a) only shows the Sb $N_{4,5}O_{2,3}O_{2,3}$ transition at 20.5 eV. Although optical inspection of the Sb layer shows a mirror-like surface, the SEM micrograph (fig. 3a) points out features which could correspond to thickness inhomogeneities and columnar growth in the Sb layer. This might explain the presence of the high energy AES Ga peak. No LEED pattern is obtained from the thick Sb layer. Finally, the energy loss spectrum (fig. 4a) shows a transition from the spin–orbit split Sb 4d level to empty states (~ 34 eV), and the Sb bulk plasmon at 16.1 eV. The 10.9 eV peak and the low energy structure (4.9–6.9 eV) correspond to the surface plasmon and to transitions between the Sb valence band and empty states, respectively. The 7 eV peak corresponds to the 2p level of the oxygen present on the Sb surface.

3.2. Decapped surface

The decapping was performed with two different procedures: at low temperature (~ 200°C) for extended periods of time; and at higher temperatures (up to 350°C). The former produces poor diffraction patterns and heavily contaminated

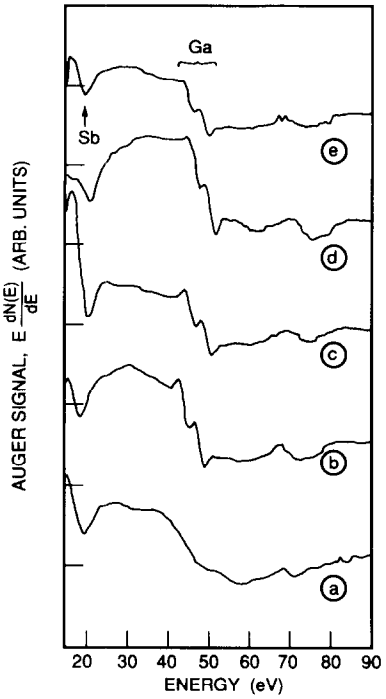

Fig. 2. Low energy AES spectra of (a) the Sb capping layer, and (b), (c), (d) and (e) after a 300°C annealing for 30, 90, 160 and 225 min, respectively.

surfaces. The best results are obtained by rapidly ramping the temperature up to 300°C and annealing time up to ~30 min. The temperature range is in good agreement with that found for the desorption of a thick layer of Sb from GaAs [7]. Annealing up to 330–350°C leads to a rapid degradation of the surface characterized by Sb loss and Ga clustering. The main criterion for the quality of the resulting surface is the LEED pattern. Fig. 5 shows the (2×3)-c(2×6) reconstruction obtained at 300°C. The sharpness of the spots and the low background indicate a well ordered surface. A similar reconstruction is observed on (100) surfaces observed directly following MBE growth [8], or prepared by sputtering and annealing [9]. The quality of the pattern, however, is clearly superior to what is generally obtained by sputtering and annealing. When surfaces must be transferred under non-UHV conditions, preparation by decapping is therefore preferable, in particular for surfaces of compounds like GaSb which cannot be heated to high temperature to anneal out all the damage created during sputtering. The SEM micrograph taken after removal of the Sb cap shows a very smooth surface morphology (fig. 3b).

Figs. 1 and 2 show the high and low energy AES spectra for increasing annealing times at 300°C. The line shape of the peaks and the Sb(454 eV)/Ga(1070 eV) ratios do not evolve significantly beyond the first 30 min anneal. However, one observes a reduction in the amplitude of the low energy Ga peak with annealing times up to 225 min, indicating a degradation of the surface. The Sb(454 eV)/Ga(1070 eV) ratio, after correction for sensitivity factors, is 1.32 following the 30 min anneal. As expected from the surface prepa-

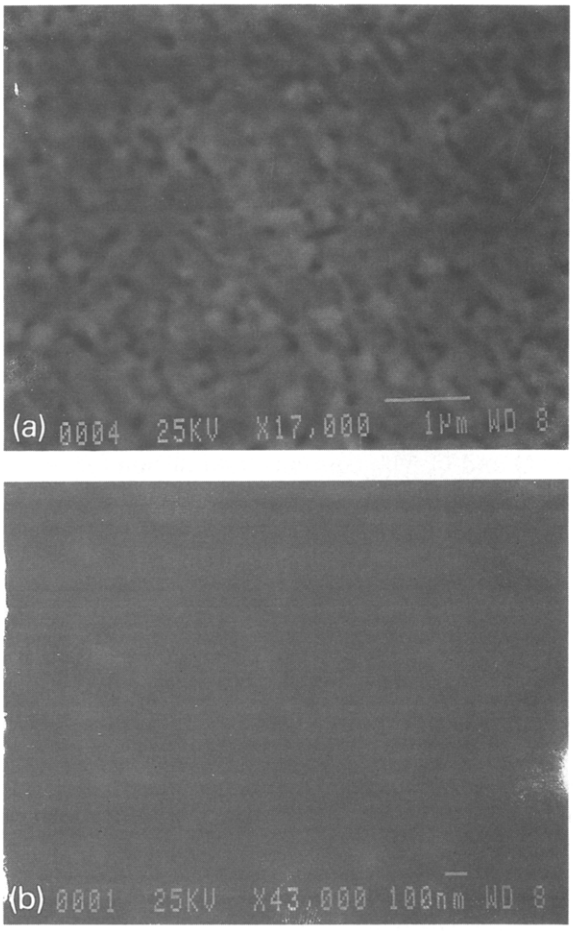

Fig. 3. SEM micrographs of (a) the Sb-capped GaSb(100) surface and (b) after a 225 min annealing at 300°C.

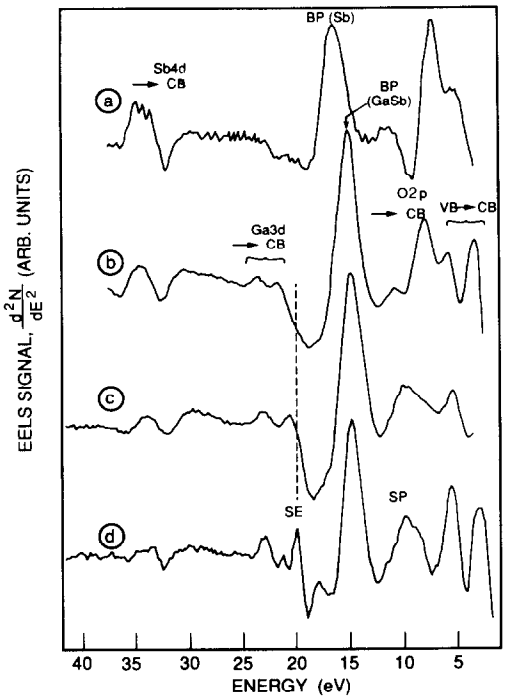

Fig. 4. EELS spectra (a) from the Sb-capped surface; (b) from the same surface after a 30 min annealing at 300°C; (c) from a sputtered and annealed (100) surface; and (d) from a cleaved (110) surface.

ration technique, this ratio reflects a higher Sb concentration than that obtained by sputtering and annealing (ratio = 1.19) [8]. The AES spectra also reveal a significant amount of contamination by O and C. The concentration of both elements is of the order of 0.1 ML. We believe that contamination occurred during the month of ambient storage rather than during MBE growth or Sb-decapping. Yet, this does not suggest a failure of the principle of Sb-capping. As discussed in section 3.1, the capping layer was thinner than expected or exhibited inhomogeneities, leading to contamination over time of the underlying surface. The quality of the LEED pattern, however, is a clear indication that the Sb layers can efficiently protect the surface and that sufficiently thick protective caps should eliminate any contamination.

The EELS spectrum taken after 30 min at 300°C (fig. 4b) shows the usual energy loss features observed on GaSb: bulk plasmon at 15 eV (BP), transitions between the Sb 4d and Ga 3d core levels and empty states of the conduction band at 34 eV (Sb 4d → CB) and 21–23 eV (Ga 3d → CB), respectively, and valence band to conduction band transitions at 3 and 5.6 eV (VB → CB). The small peak at 10.6 eV is attributed to a surface-like plasmon. The 7 eV peak corre-

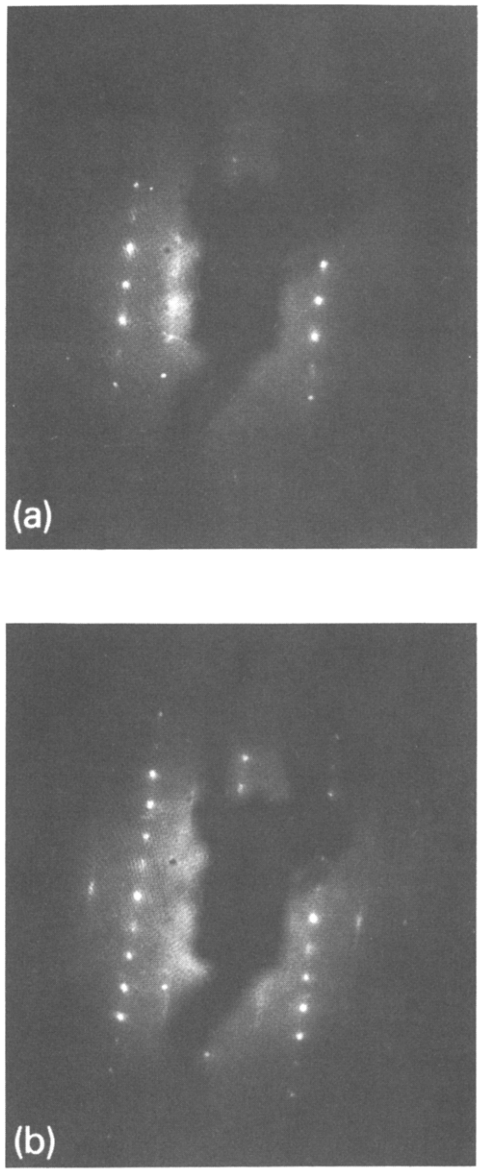

Fig. 5. GaSb(100) LEED patterns recorded at 120 K following a 30 min, 300°C annealing showing the (2×3)-c(2×6) reconstruction (a) 84 eV; (b) 99 eV.

sponds to the excitation of the 2p electrons to empty states of the oxygen contaminant adsorbed on the surface. The resolution obtained on the various peaks compares favorably with that obtained from cleaved (110) surfaces (fig. 4d) or from the sputtered and annealed (100) surfaces (fig. 4c). The 20 eV surface exciton peak (SE) [10,11] is characteristic of a transition between the Ga 3d core level and the empty Ga dangling bond surface state in the conduction band of the (110) surface (fig. 4d). As such, it is a highly sensitive measure of the quality of the surface. Although the (b) and (c) spectra show a broadening at 20 eV, the SE peak is not resolved (it is usually resolved on as-grown (100) MBE surfaces [8]). The O and C contamination in (b) and damage caused by sputtering in (c) are likely reasons for the small magnitude of this surface state sensitive transition.

4. Conclusions

In spite of surface contamination due to insufficient Sb thickness, we find that effective protection of GaSb can be achieved with an Sb capping layer. The layer is easily deposited following MBE growth and is removed at fairly low temperature in UHV. We show that atomic order, superior to that obtained by sputtering and annealing, is preserved at the GaSb surface. With increased Sb thickness and transfer or storage under conditions similar to those used for As-capped GaAs MBE layers (N_2 atmosphere or low vacuum), the properties of the GaSb layer should be adequately protected.

Acknowledgements

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