Modification of the near surface optical and electrical properties of bulk GaSb (100) resulting from a sulphur-based chemical treatment

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Abstract. An alternative sulphur blended $[(NH_4)_2S/(NH_4)_2SO_4]$ solution is reported for stabilizing the bulk GaSb (100) surface. Scanning electron microscopy of treated surfaces shows a significant improvement in morphology over untreated surfaces. Dektak step profiling reveals that sulphurization causes a non-linear time dependent etching effect accompanied by smoothening of the surface while the photoluminescence is enhanced three-fold after a 30 minute treatment. The surface state density (N_{ss}) distributions were calculated from forward IV characteristics of Au/*n*-GaSb Schottky structures. Surface state densities of ~10^{14}cm^{-2}, at midgap, were calculated, with treated surfaces showing about 3 times less than untreated. Treatment apparently unpins the Fermi level in Au/*n*-GaSb Schottky structures as evidenced by a larger barrier height. Additionally, treatment also reduces the reverse leakage current. The reverse current however does not saturate with applied reverse bias. This may be attributed to either quantum mechanical tunnelling or near surface recombination via surface states not completely passivated (or removed) by the sulphurization.

1. Introduction

GaSb is a versatile III-V semiconductor material and heterojunctions of GaSb and other III-V semiconductors show great promise as near infra-red (IR) lasers, light emitting diodes (LEDs), pollutant gas detectors, thermo-photovoltaic devices and photo-detectors in the wavelength regions 2-5 and 8-14μm [1, 2]. Additionally, its matching lattice parameter renders it an excellent substrate for the epitaxial growth of ternary and quaternary III-V compound semiconductors and strained layer superlattices such as (AlGaIn)(AsSb). By varying the ternary and binary composition, the lattice constant and bandgap may be tailored. The GaSb surface is highly reactive, resulting in the spontaneous formation of a native oxide (Ga-O and Sb-O) layer. This, together with an interfacial Sb layer contributes substantially to the presence of surface and interface states on this material that may act as either traps or nonradiative recombination centres. The development of GaSb based devices is consequently impeded.

Passivation of the GaSb surface has been demonstrated as an important step in the development of GaSb based devices. Dutta *et al.* [3], studied ruthenium passivation of the GaSb surface while Hearn *et al*. [4], studied the passivation of GaSb by ZnS. In addition, Dutta *et al.* [5] and Liu *et al.* [6, 7] also studied sulphur passivation of this material.The purpose of this study was to investigate the effect of an alternative sulphur blended $[(NH_4)_2S/(NH_4)_2SO_4]$ solution on the surface optical and electrical properties of bulk GaSb. Current-voltage (*I-V*) characteristics of Au/*n*-GaSb Schottky structures were used to quantify the surface state density (Nss) distributions of the treated material.

2. Experimental

Bulk Te-doped *n*-GaSb (supplied by Semiconductor Waver, Inc., n~2x10^{17} cm^{-3}) was sulphurized in an aqueous solution of $[(NH_4)_2S/(NH_4)_2SO_4$ + S] in an attempt to reduce the surface state density.The material was first degreased by successively (x3) boiling it in trichloroethylene, acetone and methanol, followed by a quick rinse in de-ionized (DI) water (ρ = 18.2 MΩ.cm).

The samples were then blown dry with nitrogen. Two sample surface treatments were subsequently investigated:

i) *Sample A:* no further treatment after degreasing (referred to as reference or as-received).
ii) *Sample B:* etched in 18.5 % HCl, rinsed in DI water then immersed in ([$(NH_4)_2S$/$(NH_4)_2SO_4$] + S) at 60°C for 30 min. The solution was prepared by dissolving 0.2 g of sulphur in 15 ml of a 10% aqueous $(NH_4)_2S$ solution. According to the supplier, each litre of $(NH_4)_2S$ contained 4.7g of $(NH_4)_2SO_4$, resulting in a pH of 8.2.

Following treatment, the samples were again rinsed in DI water, blown dry and promptly loaded into a Jeol JSM-700 1F Field Emission Scanning Electron Microscope (FESEM) for surface morphology assessment.

In order to investigate the effect that the sulphur treatment may have on the surface half the sample was masked using wax followed by sulphur treatment. The surfaces were subsequently profiled using a Dektak 150 Surface Profiler.

In the case of photoluminescence (PL) measurements, samples were loaded in a closed-cycle helium cryostat. Spectra were recorded at a temperature of 11 K using the 514.5 nm line of an Ar^+ laser as the excitation source. The PL signal was detected by a liquid nitrogen cooled Ge photodetector and a laser power of 7 mW used was.

For (*I-V*) measurements, Au Schottky barrier diodes were fabricated on both the reference and the ([$(NH_4)_2S$/$(NH_4)_2SO_4$] + S) treated *n*-GaSb samples. After degreasing but prior to sulphur treatment, ohmic contacts were fabricated on one side of the sample by resistively depositing 100 nm AuGe (88:12) followed by a 50 nm Ni layer, capped with a 50 nm Au layer. The contact resistance was minimized by annealing samples in Ar at 300 °C for five minutes. The samples were again degreased, sulphurized and then blown dry with pure nitrogen gas prior to loading into a vacuum system with a base pressure of $2 \times 10^{-5}\ torr$. Circular Au Schottky contacts ($\phi = 0.50\ mm$), 100 nm thick, were subsequently resistively evaporated through a metal shadow mask. Room temperature *I-V* measurements were performed to assess the electrical response of the Schottky barrier diodes (SBD) following sulphur treatment.

3. Results and Discussion

Figure 1, (A) and (B) depicts typical SEM micrographs of the as-received and sulphurized GaSb surfaces. The surface of the reference *sample A* is rather irregular and contains a multitude of, what appears to be, supplier related polishing scratches. Samples treated with ([$(NH_4)_2S$/$(NH_4)_2SO_4$] + S) *B*, however, appear smoother with hardly any visible scratches, suggesting more or less uniform etching of the surface features previously seen on the reference sample. The scratches observed on the reference appear to be relatively shallow they disappear following treatment.

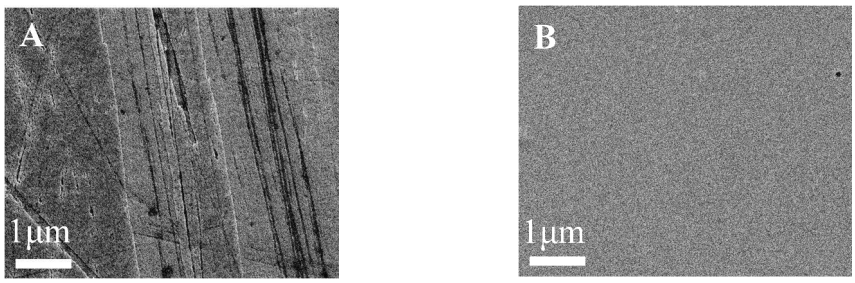

Figure 1, SEM micrographs of (A) the reference and (B) the ([$(NH_4)_2S$/$(NH_4)_2SO_4$] + S treated samples.

Step profiling shows a non-linear time dependent etching effect accompanied by smoothening of the GaSb surface. Measurements reveal that treatment for 30 minutes results in a uniform step size across the surface of approximately 6µm (It is instructive to

note that the etch rate seems to be fairly temperature dependent as the step size for repeat experiments deviated considerably (21%), a deviation attributed to fluctuations in the bath temperature). Figure 2 depicts the step size versus treatment time for a particular sample.

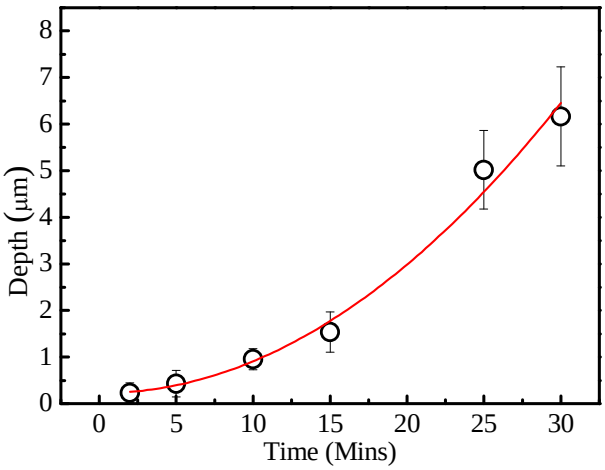

Figure 2, The etch rate of the ($[(NH_4)_2S/(NH_4)_2SO_4]$ + S) aqueous solution.

Figure 3, shows PL spectra obtained from *samples A and B*. Both spectra exhibit a broad range of transitions expected for bulk material. Two main peaks at 0.755 eV and 0.754 eV respectively are clearly visible. Two "shoulders", one towards the higher energy side (0.777 eV) and the other other towards the lower energy side (0.733 eV) are also distinguishable. Undoped GaSb is intrinsically *p*-type due to gallium vacancies (V_{Ga}) and gallium antisites (Ga_{Sb}) acting as acceptors. These acceptors induce a luminescence band at 777 meV usually called band A [8]. There are clear differences in the PL intensity and linewidth for these samples. The intensity of the spectrum *A* is at least 1/3 that of spectrum *B* showing that sulphur treatment improves the quantum efficiency of the GaSb surface.

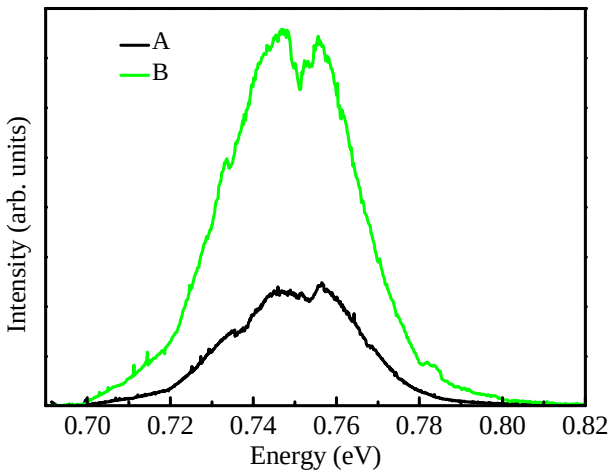

Figure 3, PL spectra obtained from the reference (A) and the sulphur treated (B) GaSb surfaces.

Diode characteristics extracted from room temperature *I-V* behaviour of Schottky barrier diodes fabricated on *samples A and B* respectively showed that diodes on *A* had a significantly higher reverse leakage current accompanied by a modest rectification ratio of 5 determined at ±0.2 V.

For samples treated with ([$(NH_4)_2S$/$(NH_4)_2SO_4$] + S) the ideality factor reduced from 2.73 to 1.17 while the barrier height increased from 0.44 eV to 0.54 eV [9]. The rectification ratio increased 10 fold suggesting that tunnelling and surface recombination currents, instead of thermionic emission, are the dominant current transport mechanisms especially in *A*. The reverse leakage currents for both *samples A and B* do not saturate, possibly suggesting that surface states responsible for recombination have only been partially "passivated" by sulphurization. It is instructive to note too that the "high" free carrier concentration (n~$2x10^{17}$ cm^{-3}) will prevent the formation of a sufficiently large depletion width to avoid quantum mechanical tunnelling. Large reverse leakage currents pose a challenge for the analysis of electrically active defects in materials by Deep Level Transient Spectroscopy (DLTS).

In Schottky structures the logarithm of the current is non-linearly proportional to the applied bias at larger applied biases. Here the capture or release of charge from the surface states dominates the current transport behaviour affecting the effective barrier height [10]. Consequently the bias dependent ideality factor and barrier height in the non-linear region of the *I-V* curve enable the quantification of the surface state density *(N_{ss})* distribution within the band-gap of the semiconductor.

According to Card and Rhodherick [11] the surface state density *(N_{ss})* for a Schottky diode in equilibrium with the semiconductor is given by:

$$n(V) = 1 + \frac{\delta}{\varepsilon_i}\left[\frac{\varepsilon_s}{W} + qN_{ss}\right], \qquad (1)$$

where *n(V)* is the voltage dependent ideality factor, W is the space charge width, ε_s and ε_i, are the permittivities of the semiconductor and the interfacial layer respectively and δ is the thickness of the interfacial layer. Figure 4, depicts the energy distribution of the interface states with respect to the bottom of the conduction band ($E_c - E_{ss}$), obtained from the forward *I-V* characteristics for *samples A and B* respectively.

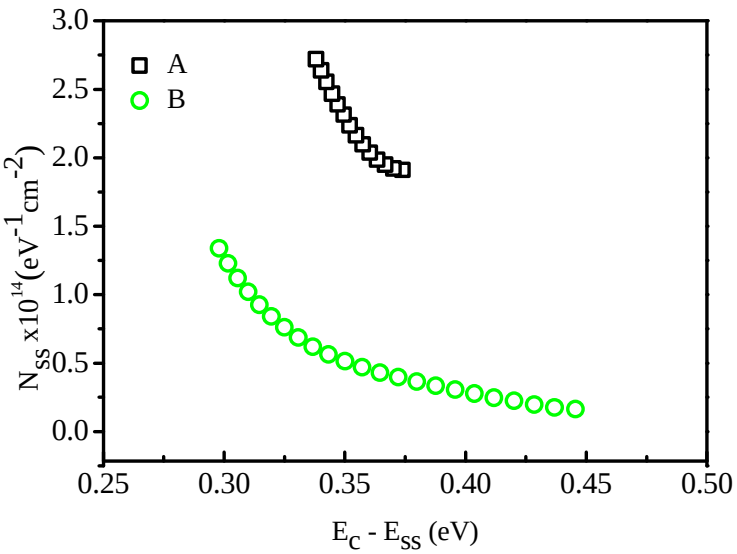

Figure 4, Density of interface states (N_{ss}) as a function of position in the bandgap ($E_c - E_{ss}$) for the diodes fabricated on Samples A and B respectively.

An exponential increase in the surface state density is apparent for both samples ranging from mid-gap towards the bottom of the conduction band [12, 13]. Clearly the surface state density is higher in s*ample A* compared to *sample B,* suggesting that sulphurization reconstructs/ "passivates" the surface the GaSb surface consequently reducing the surface state density.

This reduction may account for the lowering in ideality factor and reverse leakage via trap assisted tunnelling.

4. Conclusions

The sulphur blended ($[(NH_4)_2S/(NH_4)_2SO_4]$ + S) solution has a non-linear time dependent etching effect on GaSb resulting in improved morphological, optical and electrical properties. Treatment enhances the observed photoluminescence, an indication of partial passivation of nonradiative recombination centres. Passivation also improves the electrical properties of Au/*n*-GaSb Schottky structures as evidenced by a lower reverse leakage current, a larger barrier height and ideality factor closer to unity for *sample B* compared to *sample A*. Quantification of the interface state density shows that it is significantly reduced by sulphur treatment.

Acknowledgements

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