

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 solution ($[(\text{NH}_4)_2\text{S}/(\text{NH}_4)_2\text{SO}_4] + \text{S}$) is reported for stabilizing the very reactive surface of bulk Te doped n -GaSb (100). Scanning electron microscopy shows a significant improvement in morphology due to an etching effect while the photoluminescence is enhanced three-fold. The surface state density, calculated from the forward I - V characteristics of a Au/ n -GaSb Schottky, is $\sim 10^{14} \text{ cm}^{-2}$ and concentrated around the middle of the band gap. Notably, a three-fold reduction in the surface state density is observed following treatment. Treatment also seems to unpin the Fermi level as is evidenced by an increase in the barrier height. Importantly, the reverse leakage current also reduces.

1. Introduction

GaSb is a versatile III-V semiconductor material and heterojunctions of GaSb show great promise as near infra-red (IR) lasers, light emitting diodes (LEDs), pollutant gas detectors, thermophotovoltaic devices and photo-detectors in the wavelength regions 2-5 and 8-14 μm [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 composition of ternary semiconductors, the lattice constant and band gap can be tailored for specific applications. Undesirably however, 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 that may act as either traps or nonradiative recombination centres that will impede the development of GaSb based photonic devices.

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 to this, Dutta *et al.* [5] and Liu *et al.* [6, 7] also studied the effect of sulphur passivation on predominantly the electrical properties of this material. The purpose of this study was to investigate the effect of an alternative sulphur blended $[(\text{NH}_4)_2\text{SO}_4/(\text{NH}_4)_2\text{S}]$ solution (from hereon called $[(\text{NH}_4)_2\text{S}/(\text{NH}_4)_2\text{SO}_4] + \text{S}$) on the surface, optical and electrical properties of bulk n -GaSb. Current-voltage (I - V) characteristics of Au/ n -GaSb Schottky barrier diodes (SBDs) were used to study the effect of sulphurization on the surface state density (N_{ss}).

2. Experimental

Bulk Te-doped n -GaSb (supplied by Semiconductor Waver, Inc., $n \sim 2 \times 10^{17} \text{ cm}^{-3}$) was sulphurized in an aqueous solution of $[(\text{NH}_4)_2\text{S}/(\text{NH}_4)_2\text{SO}_4] + \text{S}$ in an attempt to reduce the surface state density. The material was degreased by successively ($\times 3$) boiling it in trichloroethylene, acetone and methanol, followed by a quick rinse in de-ionized (DI) water ($\rho = 18.2 \text{ M}\Omega\text{cm}$). The samples were then blown dry with nitrogen. Two samples 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 $[(\text{NH}_4)_2\text{S}/(\text{NH}_4)_2\text{SO}_4] + \text{S}$ at 60°C for 30 min. The solution was prepared by dissolving 0.2 g of sulphur in 15 ml of a 10% aqueous $(\text{NH}_4)_2\text{S}$ solution. According to the supplier, each litre of $(\text{NH}_4)_2\text{S}$ contained 4.7g of $(\text{NH}_4)_2\text{SO}_4$, 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 possible etching by the sulphur treatment, half of a sample was masked using wax followed by sulphur treatment. The surfaces were subsequently de-waxed, rinsed (DI H₂O) and dried where-after the surface was profiled using a Dektak 150 Surface Profiler.

For photoluminescence (PL) measurements, samples were loaded in a closed-cycle liquid helium cryostat. Spectra were recorded at 11 K using the 514.5 nm line of an Ar⁺ laser (set at 7 mW) as the excitation source. The PL signal was detected by a liquid nitrogen cooled Ge photo-detector. For (*I-V*) measurements, Au Schottky barrier diodes were fabricated on both the reference and the $[(\text{NH}_4)_2\text{S}/(\text{NH}_4)_2\text{SO}_4] + \text{S}$ treated *n*-GaSb samples. After degreasing but prior to sulphur treatment, ohmic contacts were fabricated on one side of the sample by resistively depositing a 100 nm AuGe (88:12) layer 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 N₂ prior to loading into a vacuum system with a base pressure of 2×10^{-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 SBDs.

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 $[(\text{NH}_4)_2\text{S}/(\text{NH}_4)_2\text{SO}_4] + \text{S}$ (*sample B*), however, appear smooth suggesting either uniform etching or covering of the surface features by a sulphur treatment related deposit.

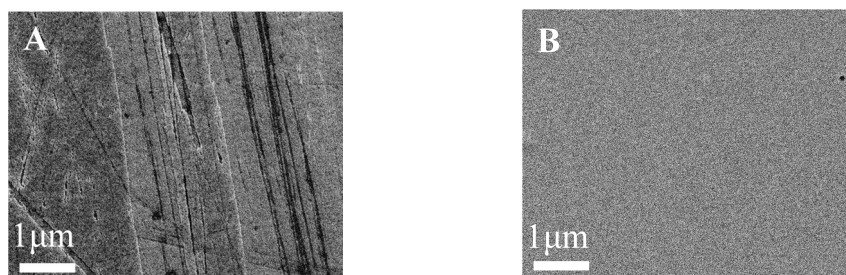


Figure 1, SEM micrographs of (A) the reference and (B) the $[(\text{NH}_4)_2\text{S}/(\text{NH}_4)_2\text{SO}_4] + \text{S}$ treated samples.

Figure 2 depicts Dektak step measurements of the GaSb surface after exposing it to $[(\text{NH}_4)_2\text{S}/(\text{NH}_4)_2\text{SO}_4] + \text{S}$ for predetermined time intervals. A non-linear time dependent etching effect is clearly evident. Treatment for a period of 30 minutes resulted in an etch step of approximately 6 μm across the sulphur exposed surface. It is instructive to note that the etch rate is temperature dependent as it deviated considerably ($\pm 20\%$) for repeat experiments due to fluctuations in the bath temperature.

Figure 3 shows PL spectra obtained from *samples A* and *B*. Both spectra exhibit a broad range of transitions as is 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 (0.777 eV) and the other towards the lower energy (0.733 eV) side are clearly distinguishable. Undoped GaSb is intrinsically *p*-type due to gallium vacancies (V_{Ga}) and gallium antisite defects (Ga_{Sb}), acting as acceptors. These acceptors are reported to induce a luminescence band, called the A band, centred around 777 meV [8].

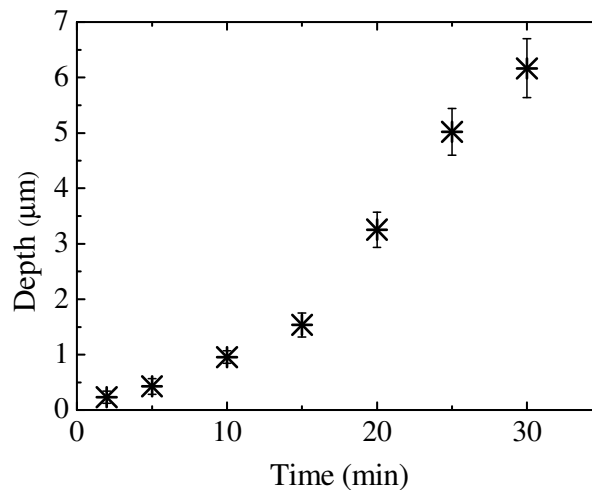


Figure 2, The etch rate of bulk n-GaSb treated with the aqueous $[(\text{NH}_4)_2\text{S}/(\text{NH}_4)_2\text{SO}_4] + \text{S}$ solution for predetermined times.

There are clear differences in the PL intensity and line width for these samples. The intensity of spectrum B is approximately 3 times of that of spectrum A suggesting that sulphur treatment improves the quantum efficiency in the near surface region of the material.

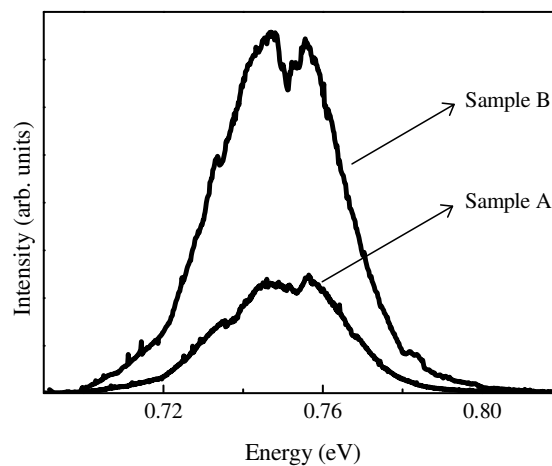


Figure 3, PL spectra obtained from the reference and the sulphur treated GaSb surfaces.

Diode characteristics extracted from I - V curves measured at room temperature revealed an ideality factor of 3.1 and a barrier height of 0.43 eV for *sample A*. Additionally, the reverse leakage current for *sample A* was significantly higher than for *sample B*. A rectification ratio of 5, determined at ± 0.2 V was obtained for *sample A*. For samples treated with $[(\text{NH}_4)_2\text{S}/(\text{NH}_4)_2\text{SO}_4] + \text{S}$ 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 surface states responsible for tunnelling and surface recombination currents, had been reduced. 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 also that the “high” free carrier concentration of these samples will result in a narrow depletion favouring quantum mechanical tunnelling. Apart from being detrimental to general device operation, large reverse leakage currents also 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 linearly proportional to the applied bias only if the series resistance (R_s) is negligible. Surface states will contribute to the series resistance of the device and will cause the logarithm of the current to deviate from linearity (bend downward) for increasing forward biases. When surface states are present, the capture and release of charge

from them will dominate the current through the device consequently affecting the effective barrier height [10]. This bias dependence of ideality factor (and barrier height) therefore enables the quantification of the surface state density (N_{ss}) and its distribution within the band-gap of the semiconductor.

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

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

where $n(V)$ is the voltage dependent ideality factor, W is the space charge width, ϵ_s and ϵ_i , are the permittivity of the semiconductor and the interfacial layer respectively. δ is the thickness of the interfacial layer [12, 13, 14] which has been estimated from XPS depth profiles. Figure 4 depicts the energy distribution of the interface states with respect to the bottom of the conduction band ($E_c - E_{ss}$).

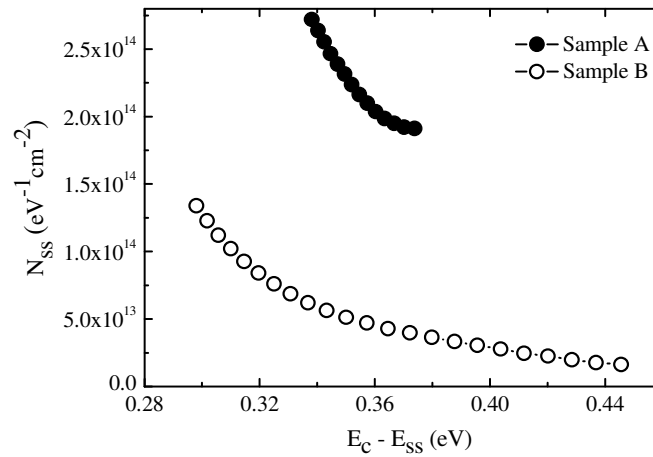


Figure 4, Density of the interface states (N_{ss}) as a function of position in the band gap ($E_c - E_{ss}$) for the diodes fabricated on sample A and sample B respectively.

An exponential increase in the surface state density is apparent for both samples ranging from mid-gap towards the bottom of the conduction band, similar to observations reported by Hudait et al. and Karatas et al. [12, 13] respectively. Clearly the surface state density is higher in *sample A* compared to *sample B*, suggesting that sulphurization reconstructs/“passivates” the GaSb surface, consequently reducing the surface state density. This reduction may account for the lowering in the ideality factor and reverse leakage via trap assisted tunnelling.

4. Conclusions

The sulphur blended $[(NH_4)_2S/(NH_4)_2SO_4]$ solution etches the bulk n -GaSb surface 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 lower ideality factor for *sample B* compared to *sample A*. Quantification of the interface state density shows that it is significantly reduced by sulphur treatment.

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