Effect of ruthenium passivation on the optical and electrical properties of gallium antimonide

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Improvements in optical and electrical properties were observed after ruthenium passivation of gallium antimonide surfaces. On passivation, luminescence efficiency increased up to 50 times and surface state density reduced by two orders of magnitude. Also, the reverse leakage current was found to decrease by a factor of 30–40 times. Increase in carrier mobility as a result of grain boundary passivation in polycrystalline GaSb was observed. © 1995 American Institute of Physics.

Amongst III-V compound semiconductors, gallium antimonide (GaSb) has recently gained renewed interest both for fundamental studies as well as device applications.

For device fabrication, surface passivation has been found to be an important step due to its beneficial effects on the optical and electrical properties of semiconductors.

In the past, the development of GaSb-based devices has been hindered due to the high leakage currents usually encountered and the fast degradation of the bare surface exposed to ambient. This makes surface passivation an essential step in GaSb device technology. Very little work has been done in this direction.

In a previous report, we had demonstrated excellent improvements in optical and electrical properties of GaSb by sulphur passivation. In this communication, we present the optical and electrical properties of GaSb after ruthenium passivation. In particular, we observe an enhancement of PL intensity as high as 50 times was observed by Ru treatment. Furthermore, if the Ru treatment was carried out on a sample etched by HCl: H2O, an enhancement of PL intensity as high as 50 times was observed. Ruthenium being highly reactive to oxygen, first removes the oxide layer and then deposits a protective layer on the surface. Even after a few weeks, there was no degradation in the PL intensity of the Ru treated samples indicating the stable nature of the passivated surface. The PL spectrum of untreated GaSb showed residual acceptor (777 meV) and acceptor bound exciton (792 meV) features, whereas for Ru-treated GaSb, free exciton (810 meV) and acceptor bound excitons (797 meV) were also observed.

The influence of various etchants before surface passivation was previously investigated by us in detail. The highest PL intensity was observed for the samples etched in HCl:H2O followed by Ru treatment at 40–50 °C for 10 min and dried in air. The PL spectra of the undoped p-type and Te-doped n-type samples are shown in Figs. 1(a) and 1(b), respectively, before and after Ru treatment. The spectra labelled (1) refer to the GaSb samples exposed to air for a few days. These samples were simply degreased prior to recording the PL spectra. As can be seen from the figure, for both the samples, a broad peak around 1.6 eV, which is above the band gap, appears. Also, the native acceptor level at 777 meV and the tellurium related peak at 746 meV appear for the p-type and the n-type GaSb, respectively. The broad peak is attributed to the thick native oxide layer present on the sample surface. The PL spectra of the samples etched in HCl:H2O (1:1) did not exhibit the broad peak (spectra 2). The broad peak was also absent in the Ru treated air exposed samples. The strength of the PL signal as a function of surface treatment is also indicated in the figure. Increase in PL intensity by 3–4 times was observed just by removing the oxide layer by HCl: H2O from the air exposed surface. However, increase in PL intensity by 35–40 times was observed by Ru treatment. Furthermore, if the Ru treatment was carried out on a sample etched by HCl: H2O, an enhancement of PL intensity as high as 50 times was observed. Ruthenium being highly reactive to oxygen, first removes the oxide layer and then deposits a protective layer on the surface. Even after a few weeks, there was no degradation in the PL intensity of the Ru treated samples indicating the stable nature of the passivated surface. The PL spectrum of untreated GaSb showed residual acceptor (777 meV) and acceptor bound exciton (792 meV), whereas for Ru-treated GaSb, free exciton (810 meV) and acceptor bound excitons (797 meV) were also observed. This indicates that the dangling bonds at the surface are terminated by Ru, which leads to the reduction of recombination centers of excitons. The highly resolved spectral features seen in the passivated sample are likely to be due to the reduction in non-radiative surface recombination centers.

Figure 2 shows the forward current-voltage (I-V) characteristics of Au/n-GaSb Schottky diode fabricated on the unpassivated and the passivated samples at 90 and 250 K, respectively. For the unpassivated sample at 90 K (curve 1), we observed two distinct exponential regions with ideality factors of 1.8 and 1.3 at low and high bias, respectively. An ideality factor between 1 and 2 indicates that the electron diffusion current and surface recombination current are comparable in magnitude. It is also clear from the figure that at higher bias voltages, the diffusion current begins to dominate. Moreover, as can be seen from Fig. 2(b), the surface recombination component becomes less at higher temperatures. If we eliminate the effects of surface recombina-
tion by subtracting the low voltage portion of the measured diode characteristics, the dotted line with ideality factor close to 1 is obtained. The passivated diodes exhibit I-V characteristics with no surface recombination component as shown in the figure by curve (2). The decrease in ideality factor after passivation is mainly due to the reduction in surface recombination current. The reverse leakage current in Schottky diodes decreased by a factor of 30–40 times as a result of surface treatment. This may be due to the decrease in the surface channel conductivity.

Metal-oxide-semiconductor (MOS) structures were fabricated on n-GaSb to evaluate the surface properties after passivation. The oxidation was carried out by wet oxygen annealing at 400 °C for 200 min. The thickness of the oxide film was approximately 1000 Å. The resistivity was found to be approximately $1.5 \times 10^{10}$ Ω cm and the breakdown field strength was $1.7 \times 10^{6}$ V/cm. After Ru treatment, the oxide resistivity increased to $5 \times 10^{10}$ Ω cm and the breakdown field strength to $4 \times 10^{6}$ V/cm. The capacitance-voltage (C-V) characteristics of the unpassivated and passivated Al/oxide/n-GaSb MOS at 1 MHz are shown in Fig. 3. A small injection-type hysteresis loop is seen in both the cases. The width of the hysteresis loop is around 0.6 V for the unpassivated sample and 0.2 V for the passivated one. The decrease in loop width after passivation confirms the reduction in the interface state density at the oxide-semiconductor junction. Moreover, the passivated sample exhibited more ideal C-V characteristics than the unpassivated one. The interface density as determined by Terman's method$^{10}$ was found to be $2 \times 10^{12}$ and $3 \times 10^{10}$/cm$^2$ eV for the unpassivated and the passivated samples, respectively.

The improved surface property after passivation in our case is due to the adsorption of the Ru$^{3+}$ ions followed by partial removal of the surface states from the band gap due to the electrostatic interaction. Similar effects have been observed in the case of other surfaces.

![Figure 1](image1.png)

**FIG. 1.** Relative PL intensities at 4.2 K for (a) p-GaSb and (b) n-GaSb as a function of surface treatment. (1): air exposed sample, (2): air exposed sample after etching in HCl:H$_2$O (1:1), (3): air exposed sample after Ru treatment.

![Figure 2](image2.png)

**FIG. 2.** Forward I-V characteristics of untreated (1) and Ru treated (2) n-GaSb samples at (a) 90 K and (b) 250 K.

![Figure 3](image3.png)

**FIG. 3.** C-V characteristics of the MOS structures. Solid curve is for the untreated sample and the dotted curve is for the treated sample.
served by Parkinson et al. in GaAs. The fact that the PL intensities increase with surface treatment for both the n-type and p-type samples indicates that the surface Fermi level is unpinned and there is an increase in band bending. This shows the amphoteric nature of Ru on GaSb surfaces depending on the conductivity type, i.e., positively charged on p-GaSb and negatively charged on n-GaSb. However, C-V measurements on Schottky diodes fabricated by thermal evaporation of various metals on the untreated and the treated samples indicate the barrier heights to be independent of metal work function. The fact that surface pinning is observed after Schottky barrier formation is due to the reaction of the metals with GaSb which causes repinning.

Apart from surface passivation, Ru has also been used for grain boundary passivation in solar cell grade polycrystalline semiconductors. Our investigations on polycrystalline p-type and n-type GaSb also showed an increase in the mobility of the passivated samples due to grain boundary passivation. Increase in room temperature mobility from 460 to 670 cm$^2$/V s for the p-type and 1200 to 1560 cm$^2$/V s for the n-type samples were observed as a result of passivation. Moreover, the dark current density in the Au/n-GaSb Schottky diodes decreased by an order of magnitude after passivation and the ideality factor decreased from 3.7 to 1.5 indicating the reduction in leakage currents in the diodes.

For technological applications, it is essential to produce a passivating surface which not only reduces the density of surface states but also remains chemically stable under atmospheric conditions for long periods. In our case, there was no degradation in PL intensity even after exposing the passivated samples to air for a few weeks. To check the thermal stability of the passivating film, heat treatment at 200–450 °C in N$_2$ atmosphere for 10–80 min was performed. It was found that the passivating effect remained even after such a treatment. The beneficial effect of the treatment should be quite general and similar improvements in performance could be obtained on other GaSb-based devices. Moreover, the passivating film has been found to be robust and does not hinder the long-term device performance.

In conclusion, we have investigated the effects of ruthenium trichloride treatment on optical and electrical properties of GaSb. Enhancement in PL intensity and reduction both in surface state density and diode leakage current were observed as a result of passivation. Increase in carrier mobility due to grain boundary passivation in polycrystalline GaSb was also observed. The stability of the modified surface after heat treatment and exposure to atmospheric conditions have been evaluated. These results indicate that on such an interface it is possible to fabricate devices with improved characteristics and long term stability.

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