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Improved characteristics for Au/n-GaSb Schottky contacts through the use of a nonaqueous sulfide-based passivation

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The influence of nonaqueous sulfide passivation (using Na_2S in the inert solvent benzene) on Au/*n*-GaSb Schottky junction behavior was studied. The junction parameters, Schottky barrier height and ideality factor, were derived and compared with those of as-received GaSb surfaces as well as surfaces treated with aqueous sulfide solutions. The Schottky junction made on as-received GaSb is highly nonideal, while S-based passivation treatment of the GaSb surface before contact formation improves the rectifying behavior, and markedly reduces the reverse current. A benzene-based nonaqueous sulfide treatment results in GaSb surfaces with lower oxide and elemental antimony content than does the aqueous sulfide treatment. The produced Schottky barrier height increases to 0.61 eV and the Au/*n*-GaSb contact is close to an ideal Schottky junction.
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GaSb is an important III–V compound semiconductor for high-speed and optoelectronic devices operating in the infrared and near-infrared region.[1] Due to its small band gap, there is often difficulty in achieving a high-quality metal–GaSb Schottky contact with near-ideal current–voltage ($I-V$) characteristics. Surface and interface properties are critical in determining metal–semiconductor contact behavior, and the existence of an interfacial layer, or a high density of defect states at the metal and semiconductor interface, can lead to highly nonideal characteristics. Air oxidation of GaSb at room temperature results in a thick overlayer of native oxide and a high concentration of elemental antimony at the oxide–GaSb interface.[2–4] The presence of elemental Sb at the surface can lead to device degradation. Due to its metallic nature, Sb can increase the surface leakage current and lead to the generation of gap-region surface states, reducing the minority carrier lifetime and limiting device performance. Surface passivation using sulfide-based solutions can effectively remove the native oxide and improve the surface electronic and electrical properties.[5–7] Previous studies of the sulfur-based passivation using a $(NH_4)_2S$–water solution have shown improved Schottky characteristics with a Au–GaSb barrier of 0.52–0.57 eV being reported.[8,9] The use of an aqueous process however, with and without S passivation, leads to a variety of results in the formation of a Au–GaSb Schottky diode with a wide range of the barrier height values being reported, even exceeding the band-gap energy.[10] Further improvements in the reproducibility and stability of the Au–GaSb diodes require a thorough removal of surface oxides and elemental Sb which entails a nonaqueous environment. Nonaqueous passivation using an inert solvent, such as benzene, as the sulfidization medium results in a GaSb surface with decreased amounts of oxide residue and elemental Sb content compared to that generated by aqueous sulfide treatment.[7] In this work, the impact of a nonaqueous S-based passivation treatment on the Au/*n*-GaSb Schottky junction behavior was studied. In particular, a nonaqueous sulfide passivation process was applied before metalization, and compared with the aqueous sulfide treatment in terms of improving GaSb-based Schottky device performance.

Te-doped *n*-GaSb with a carrier concentration of about 10^{17} cm^{-3} was used in this study. All wafers were chemically degreased, and then blown dry with nitrogen. The back side ohmic contacts were made by electron-beam (e-beam) evaporation of Au–Ge/Ni/Au and then alloyed at 300 °C for 4 min. Before the deposition of Au contact on the topside, the GaSb surface was prepared in several ways, including chemical degreasing, immersion in concentrated HCl, or sulfide treatment in aqueous or nonaqueous Na_2S-saturated solutions. The nonaqueous passivation solution consists of Na_2S in the inert solvent benzene, with the addition of a macrocyclic polyether (15-crown-5) to solubilize Na_2S, and an organic oxidizing agent (anthraquinone) to facilitate electron flow into the solution. The details of this process were described previously.[7] The performed surface treatments before Au deposition are summarized below:

(a) Without further treatment after chemical degreasing;
(b) Dipping in concentrated HCl for 5 min, then rinsing with 2-propanol;
(c) Dipping in concentrated HCl for 5 min, rinsing with 2-propanol, then immersing in a saturated Na_2S aqueous solution for 1 h, then rising with water; and rinse;
(d) Dipping in concentrated in HCl for 5 min, rinsing with 2-propanol, then immersing in a benzene-based Na_2S solution for 1 h, then rinsing with 2-propanol.

The topside contacts were then fabricated by the e-beam deposition of Au onto the chemically treated room-temperature GaSb sample surfaces. The contact area was defined by a shadow mask, and the diameter of the circular diode, Φ, was 130 μm. Between four and ten diodes were measured for each surface treatment. Representative $I-V$ characteristics under forward and reverse biases were then recorded at room temperature and are shown in Fig. 1. At room temperature, the Au/*n*-GaSb contact exhibits Schottky junction behavior. The current transport between metal and semiconductor is governed by thermionic emission for the

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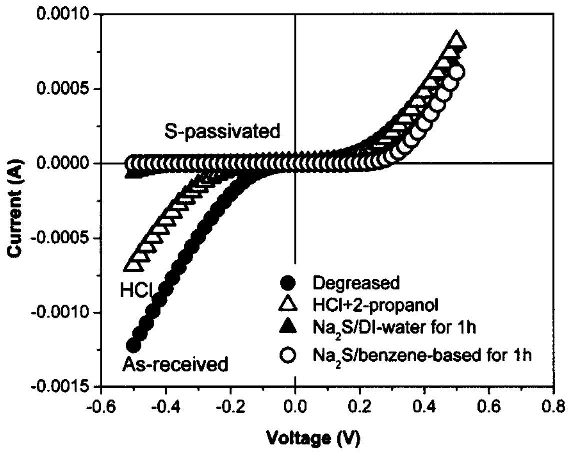

FIG. 1. I–V curves of Au/n-GaSb Schottky contacts under forward and reverse biases. The diodes were fabricated on n-GaSb surfaces prepared by the processes (a) through (d).

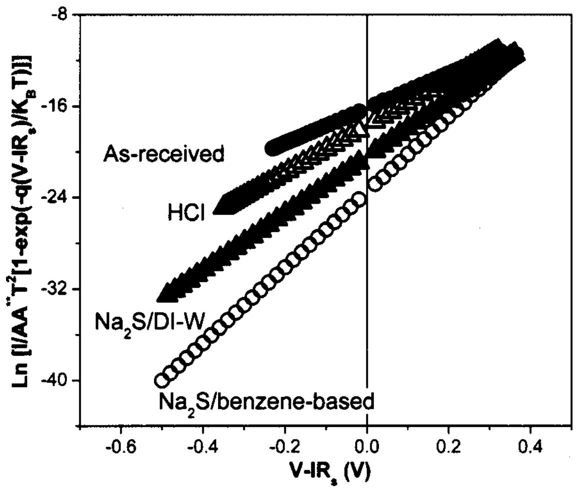

FIG. 2. I–V curves corrected for the series resistance and plotted on a semilog scale.

moderately doped semiconductors. For an ideal Schottky junction, the electrical current due to the thermionic emission over the Schottky barrier is given by:[11,12]

$$I = AA^{**}T^2 \exp\left[-\frac{q}{k_BT}(\phi_B)\right]\left[\exp\left(\frac{qV}{k_BT}\right) - 1\right], \tag{1}$$

where A is the metal contact area, and A^{**} is the modified Richardson constant, which is 5.16 A cm^{-2} K^{-2} taking into account the effective mass of electrons in the Γ valley of the GaSb conduction band. ϕ_B is the Schottky barrier height, and V is the applied bias voltage.

In practice, Schottky diodes usually exhibit nonideal characteristics. The departure from an ideal junction may result from a thick interfacial layer between the semiconductor and metal, or parallel current transport mechanisms, such as generation and recombination in the depletion region and quantum-mechanical tunneling. The nonideality of a real contact is characterized by the ideality factor, n. Also, the presence of series resistance, R_s, from the bulk semiconductor below the depletion region and back side ohmic contact resistance, will decrease the practical potential drop across the metal–semiconductor contact. Using Norde's method,[13] the series resistance is determined to be $200 \pm 30\ \Omega$. The modified I–V characteristic with the inclusion of series resistance is then given by:[14,15]

$$I = AA^{**}T^2 \exp\left[-\frac{q}{k_BT}\phi_e\right]\exp\left[\frac{q(V-IR_s)}{nk_BT}\right] \times\left\{1 - \exp\left[-\frac{q(V-IR_s)}{k_BT}\right]\right\}. \tag{2}$$

The plot of $\ln\{I/AA^{**}T^2/1-\exp[-q(V-IR_s)/k_BT]\}$ versus $(V-IR_s)$ yields a straight line at low bias voltage, as seen in Fig. 2. From the slope and the y-axis interception point, corresponding to (q/nk_BT) and $(-q\phi_e/k_BT)$, respectively, the Schottky diode parameters, ideality factor, and barrier height, were determined. The results are listed in Table I.

The Schottky diode made on the as-received GaSb surface exhibits a small barrier height (0.42 eV), and a highly nonideal junction ($n > 2$). The reverse current does not saturate as in an ideal Schottky junction. S-based treatments of the GaSb surface before contact fabrication improve Au/n-GaSb rectifying characteristics, as evidenced by the increased effective barrier height and reduced ideality factor. Na_2S aqueous treatment increases the barrier height to 0.53 eV. If the GaSb surface is passivated using a benzene-based sulfide solution prior to metallization, the Schottky barrier height is further increased to 0.61 eV, and the ideality factor is reduced to near unity.

The as-received GaSb surface is characterized by a thick oxide overlayer of 3–5 nm. This native oxide consists of gallium and antimony oxides, as well as elemental antimony, all in the atomic ratio of 1:0.58:0.23.[4] The highly nonideal rectifying behavior of the as-received GaSb surface is attributed, in part, to the thick oxide layer between the metal and the GaSb surface. A surface dielectric layer, such as an oxide, can impact the current transport in several regards. Ideally, a surface dielectric serves as a series capacitance to the depletion region capacitance, allowing for a smaller built-in voltage. Depending on the thickness of the dielectric layer, this can alter the current and the deduced barrier height. More commonly, the poor electrical quality of these native or chemically formed oxides leads to trap states within and at the interface of the dielectric–semiconductor interface. These trap states provide conduction pathways in parallel with thermionic emission over the barrier, allowing for a high n value and a low calculated value of the barrier height. As a result, the reverse current does not saturate as an ideal Schottky diode.[7] In addition, the elemental Sb increases the surface leakage current and also contributes to the high reverse current.

Techniques which reduce the thickness of any interfacial oxide layer, the gap region surface state density, and the elemental antimony content on the surface, generally im-

TABLE I. Device parameters: Ideality factor, n, and barrier height, ϕ_e, of a Au/n-GaSb Schottky diode resulting from various surface treatments performed prior to Au contact fabrication. The reported errors are derived from measurements of four to ten separate diodes for each surface treatment.

Surface treatment	Ideality factor n	Effective barrier height ϕ_e (eV)
(a) Degreased	2.54 ± 0.06	0.42 ± 0.04
(b) HCl+2-propanol	1.89 ± 0.05	0.46 ± 0.02
(c) Na_2S/deionized water	1.55 ± 0.02	0.53 ± 0.01
(d) Na_2S/benzene-based	1.17 ± 0.03	0.61 ± 0.02

prove the GaSb-based Schottky junction behavior. Preparation of the GaSb surface by dipping in concentrated HCl and rinsing with 2-propanol reduces the thickness of the oxide overlayer from 3–5 to 1–2 nm based on x-ray photoemission spectroscopy (XPS) measurements.[4] The Schottky diode fabricated on a GaSb surface after such HCl treatment exhibits both an increased zero-bias barrier height (0.46 eV) and a decreased ideality factor (1.89). This is associated with the reduction in thickness of the native oxide.

Sulfur-based as well as other GaSb surface passivation treatments modify the surface electronic structure and improve the Schottky junction characteristics. In particular, the nonaqueous sulfide treatment results in a reproducible high Schottky barrier height (0.61 eV) and an ideality factor close to unity. This treatment removes or reduces the surface oxide layer thickness with the subsequent chemisorption of sulfur. Sulfur chemisorption reduces the gap-region surface state density,[16] decreasing the surface band bending. The photoluminescence (PL) intensity, mainly due to electron and hole recombination in the charge neutral region, can be correlated to the thickness of the depletion region[17] and, therefore, to the surface band bending. It was found that aqueous sulfidization resulted in a three-fold increase in PL intensity compared to the as-received GaSb sample, while up to a seven-fold enhancement in PL intensity was observed from *n*-GaSb samples sulfidized using benzene-based nonaqueous Na_2S solutions,[7] indicating a further improvement of surface electronic properties. Surface chemical analysis by XPS indicates that both aqueous and benzene-based sulfide treatments reduce the amount of surface oxide significantly. The nonaqueous sulfide treatments resulted in decreased amounts of surface oxides and a higher concentration of gallium sulfides on the surface than do the aqueous treatments. Additionally, the concentration of elemental antimony on the surface after the nonaqueous sulfide treatment is approximately one-half of that resulting from the aqueous treatment. The sulfur-based treatment therefore limits the oxidation, removes potential trap-mediated current paths, and provides a robust chemical surface passivation allowing for the e-beam deposition of Au onto the wafer surface.

In conclusion, the Au Schottky junction made on the as-received GaSb surface exhibits a small barrier height and highly nonideal electrical behavior. Sulfur-based treatments of the GaSb surface before contact fabrication increases the Schottky barrier height and improves the contact rectifying characteristics. In particular, benzene-based nonaqueous sulfidization prior to metallization increases the Au/*n*-GaSb barrier height to 0.61 eV and reduces the ideality factor to close to unity. Nonaqueous processing of GaSb effectively passivates the GaSb surface, enabling the formation of stable and reproducible Schottky contacts despite its small band gap.

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