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## Surface passivation of GaInAsSb photodiodes with thioacetamide

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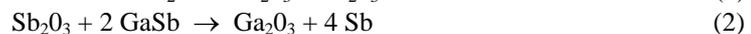
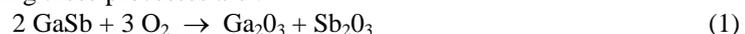
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AlGaAsSb/GaInAsSb heterojunction mesa photodiodes having 2.2µm cutoff wavelength, grown by MBE on (p) GaSb substrates, have been passivated using thioacetamide CH<sub>3</sub>CSNH<sub>2</sub> and ammonium sulphide (NH<sub>4</sub>)<sub>2</sub>S. Superior characteristics were obtained from devices processed with thioacetamide in acid medium (pH = 2.4). At room temperature the surface leakage currents were suppressed, and the photodiodes showed R<sub>0</sub>A product as high as 15 Ωcm<sup>2</sup> and detectivity D\*(2µm, 0V) ~ 10<sup>10</sup> cm Hz<sup>1/2</sup> W<sup>-1</sup>. A model explaining improvement with thioacetamide is proposed.

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### 1 Introduction

The GaInAsSb/GaSb system is a well-known candidate for the fabrication of mid-infrared photodetectors operating at high temperature above 2µm [1-3], for applications such as thermo-photovoltaic generators, high resolution infrared imaging, pollution monitoring, and free space communications. But the as-grown GaSb-based structures exhibit undesirable surface leakage currents, which drastically limit the device performance. Leakage currents mainly are due to the presence at the semiconductor surface of elemental antimony Sb. Indeed when a GaSb surface is exposed to air, it gives rise to Sb<sub>2</sub>O<sub>3</sub> and Ga<sub>2</sub>O<sub>3</sub> native oxide layers. Then some Sb<sub>2</sub>O<sub>3</sub> reacts with GaSb to produce Ga<sub>2</sub>O<sub>3</sub> and a conductive layer of free Sb [4,5]. The basis reactions illustrating these processes are :



In order to suppress this degradation mechanism chalcogenide passivation, by sulfur or selenium atoms, is currently employed [6]. Ammonium sulphide (NH<sub>4</sub>)<sub>2</sub>S is widely used with relative success for antimony-based compounds [7-12]. A new wet passivation method with thioacetamide CH<sub>3</sub>CSNH<sub>2</sub> (TAM) was proposed as an alternative to standard (NH<sub>4</sub>)<sub>2</sub>S for sulfur passivation of GaAs [13,14] and InAs [15]. In this article we compare the effects on device characteristics of TAM and (NH<sub>4</sub>)<sub>2</sub>S passivation treatments of the surface of mesa photodetectors. The devices are AlGaAsSb/GaInAsSb photodiodes grown by molecular beam epitaxy on GaSb substrates. TAM passivation, realized in acid medium, was found superior to (NH<sub>4</sub>)<sub>2</sub>S treatment. A simplified model of sulfuration is proposed to explain this improvement.

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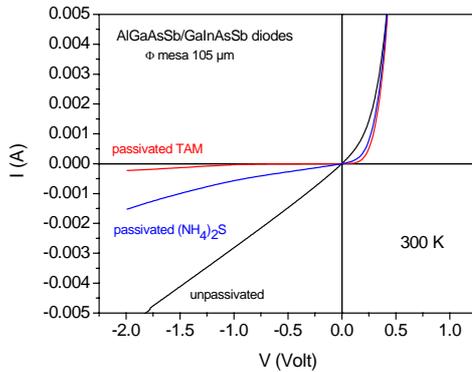
## 2 Experimental

The device structure was grown by molecular beam epitaxy on Zn-doped (100)-oriented GaSb substrates. At first undoped P-type  $\text{Ga}_{0.85}\text{In}_{0.15}\text{As}_{0.13}\text{Sb}_{0.87}$  absorbing layer was grown. The thickness is  $1.5\mu\text{m}$  and the residual carrier concentration is  $P \sim 5\text{-}8 \times 10^{16} \text{ cm}^{-3}$ . Then a thin layer (50nm) of P-type  $\text{Al}_{0.4}\text{Ga}_{0.6}\text{As}_{0.03}\text{Sb}_{0.97}$  was epitaxied, followed by a N-type 50nm-thick layer of the same material. Finally a  $0.2\mu\text{m}$ -thick Te-doped ( $N = 2.10^{18} \text{ cm}^{-3}$ ) GaSb contact layer was grown at the top. The whole structure is lattice-matched to the substrate. Its cutoff wavelength is  $2.2\mu\text{m}$ . The AlGaAsSb wide band gap (1.2 eV) P-N junction inserted at the P-GaInAsSb/N-GaSb interface partially reduces the dark current, which is mainly controlled by carrier diffusion in the GaInAsSb layer, and increases the breakdown voltage of the diode.

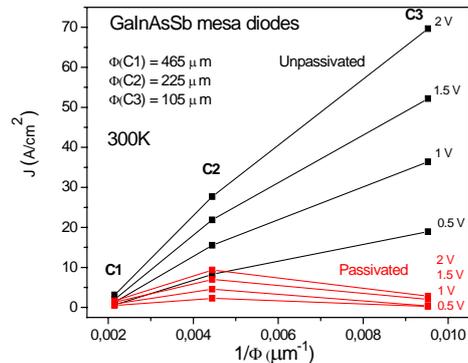
Circular mesas were obtained using standard photolithography with a mask set containing various test diodes of different sizes and geometry. Metallizations were ensured by AuZn sputtering on the P-GaSb substrate and AuGeNi sputtering on the N-GaSb top layer, followed by contact alloying at  $275^\circ\text{C}$  for 60s. Mesa etching was realized with  $\text{CH}_3\text{COOH}:\text{HF}(40\%):\text{HNO}_3(50\%)$  in proportions 30ml:1ml:19ml. The addition of tensioactive product in the solution was found making easier the production of regular sides and smooth bottom.

All the mesa structures were initially degreased by sequential immersion in trichloroethylene, acetone and methanol, and dried with nitrogen. The samples were then cleaned by concentrated HCl for 1 min to remove a part of the surface oxides, and rinsed in deionized water. After that the samples were soaked for TAM passivation in  $\text{H}_2\text{O}:\text{CH}_3\text{CSNH}_2$  (0.2 mole/litre) solution at  $70^\circ\text{C}$  for 40 minutes, and for ammonium sulfide passivation in  $\text{H}_2\text{O}:(\text{NH}_4)_2\text{S}$  (4:1) solution at  $50^\circ\text{C}$  for 40 min. The pH of the TAM solution was adjusted to 2.4 by adding acetic acid (10%). The ammonium sulfide solution was basic, with a pH close to 10.6. After this process the samples were thoroughly rinsed in deionized water and blown dry with nitrogen. After passivation the devices were packaged in TO-5 supports, and inserted into a liquid nitrogen cryostat possessing infrared optical window.

## 3 Results and discussion



**Fig. 1** Typical current-voltage characteristics at room temperature of as-etched,  $(\text{NH}_4)_2\text{S}$  passivated, and TAM passivated detectors.

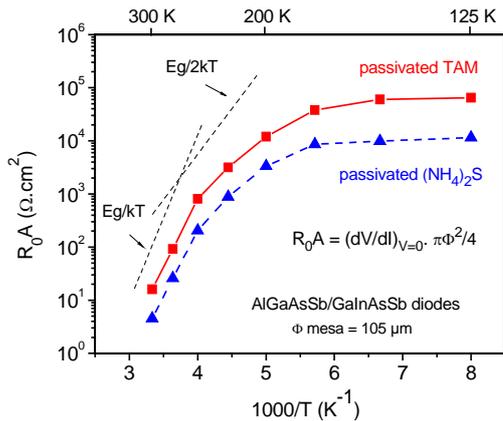


**Fig. 2** Dark current density of TAM passivated diodes versus the inverse of mesa diameter for different reverse bias.

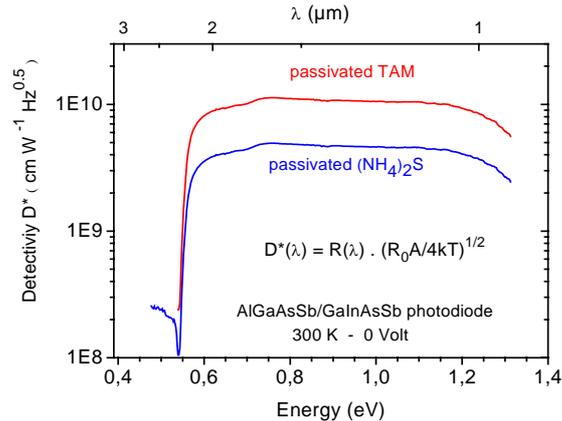
Figure 1 shows a comparison between as-etched and passivated detectors. The dark current density under  $-0.5\text{V}$  bias typically decreases from  $\sim 10 \text{ A/cm}^2$  for unpassivated samples, to  $\sim 1 \text{ A/cm}^2$  for the ammonium sulfide solution treatment and to less than  $10^{-2} \text{ A/cm}^2$  for the acidic TAM solution treatment, respectively. Best result was obtained with TAM treatment, which induced a reduction of dark current by more than 1000 fold. On the other hand for passivated samples an elbow clearly appears in the I-V char-

acteristics at small current, without an increase of the series resistance This indicates that leakage currents were reduced, without modifying the bulk characteristics, so that one can affirm that the sulfur passivation was effective.

Figure 2 shows the dependence with the mesa diameter of the dark current density, measured at different reverse bias, for as-etched diodes and TAM passivated diodes taken from the same chip. The step increase of the  $J_{\text{dark}}(1/\Phi)$  curves for unpassivated samples indicates large surface leakage currents. At the reverse the flat behavior of TAM passivated devices show that leakage currents are negligible.



**Fig. 3** Variation of  $R_0A$  product with temperature for two devices passivated by TAM and by ammonium sulphide respectively.

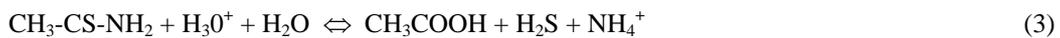


**Fig. 4** Evolution of the detectivity  $D^*(300K, 0V)$  with photon energy for the two devices of Fig.3.

An important parameter for photodetectors is the  $R_0A$  product where  $R_0$  is the differential impedance at a bias voltage of 0 V and  $A$  is the area of the diode. The temperature dependence of  $R_0A$  product is shown in Fig.3 for two typical passivated detectors, the first by TAM, the other by ammonium sulphide. At room temperature, the  $R_0A$  values are  $16 \Omega\text{cm}^2$  and  $4.5 \Omega\text{cm}^2$  respectively. They are among the best published values for antimony based detectors operating at more than  $2 \mu\text{m}$ . The  $R_0A$  increases when the temperature is lowered, with at first a variation law roughly proportional to  $\exp(E_g/kT)$  where  $E_g$  is the energy gap of the GaInAsSb absorbing layer (0,58 eV). This indicates that the dark current is diffusion controlled at relatively high temperatures [16]. At low temperatures, the  $R_0A$  product slowly changes with  $T$ , suggesting the dark current is then controlled by tunneling mechanisms or surface leakage [16].

In order to evaluate the detectivity  $D^*$  of the passivated devices we measured their photoresponse  $R(\lambda)$  at room temperature by a Nicolet-870 Nexus Fourier transform infrared (FTIR) spectrometer.  $D^*$  is proportional to  $R(\lambda)$  and to the square root of  $R_0A$  :  $D^*(\lambda) = R(\lambda) [R_0A/4kT]^{1/2}$ . The responsivities of TAM and  $(\text{NH}_4)_2\text{S}$  passivated detectors were found similar, close to 0.35 A/W in photovoltaic regime ( $V = 0$  Volt). The corresponding external quantum efficiency is 21%. The calculated evolution of  $D^*$  with the photon energy is shown in Fig.4 for the two passivated devices of Fig.3. At zero bias, for a  $2\mu\text{m}$  incident wavelength, the detectivity  $D^*$  is  $1.05 \times 10^{10} \text{ cm Hz}^{1/2} \text{ W}^{-1}$  for the TAM passivated photodetector and  $4.6 \times 10^9 \text{ cm Hz}^{1/2} \text{ W}^{-1}$  for the detector passivated with ammonium sulphide treatment.

Why the thioacetamide  $\text{CH}_3\text{CSNH}_2$  seems more efficient for passivating semiconductor devices than standard  $(\text{NH}_4)_2\text{S}$  ? In aqueous solution TAM dissolution gives rise to the following chemical reactions :

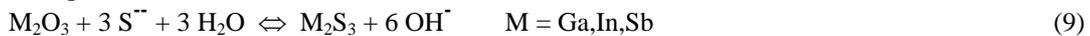


For (Ga, In, Sb, S)  $\rightarrow$  H<sub>2</sub>O systems, (we neglect Al and As elements for the lack of simplicity) the predominant soluble species, determined from the Pourbaix chemical potential diagrams [17] are function of the pH of the solution. In *acidic medium*, for small pH (pH = 2.4), the predominant soluble species are : H<sub>2</sub>S, In<sup>+++</sup>, Ga<sup>+++</sup>, and SbO<sup>+</sup>, and the native oxides present at the semiconductor surface are dissolved in the liquid solution. A first consequence is there is no etching of the semiconductor surface. Another important consequence is the impossibility for reaction (2) to occur, due to the vanishing by dissolution of Sb<sub>2</sub>O<sub>3</sub>. The expected sulfuration reactions are :



All the free energies of the reactions (6) to (8) are negative, what means that the sulphides are stable.

In the case of (NH<sub>4</sub>)<sub>2</sub>S treatment, the *solution is always basic*, so that the predominant soluble species, given by the Pourbaix diagram, are : S<sup>---</sup>, Ga<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub> and Sb<sub>2</sub>O<sub>3</sub>. The probable reactions of sulfuration can be simplified as :



Sulfur can react directly with M by creating M-S bonds, but it can also react via oxygen by creating M-O-S bonds. Sulfuration is effective, but in the last case the M-O-S bonds are weaker. Besides the presence of unreacted Sb<sub>2</sub>O<sub>3</sub> in the solution does not prevent the reaction (2) which produces free Sb.

So thioacetamide sulfuration in acid medium offers a priori higher chemical stability than ammonium sulphide treatment, and does not product elemental antimony at the semiconductor surface. This explain the success of our passivation experiments of GaIn(As)Sb mesa detectors with TAM.

## References

- [1] I.A. Andreev, M.A. Afrailov, A.N. Baranov, V.G. Danil'chenko, M.A. Mirsagatov, M.P. Mikhailova, Yu.P. Yakovlev, Sov. Tech. Phys. Lett. **12**, 542 (1986).
- [2] E. Tournié, J.L. Lazzari, E. Villemain, A. Joullié, L. Gousskov, M. Karim, I. Salesse, Electron. Lett. **27**, 1237 (1991).
- [3] M.P. Mikhailova, N.D. Stoyanov, O.V. Andreychuk, K.D. Moiseev, I.A. Andreev, Y.P. Yakovlev and M.A. Afrailov, IEEE Proc. Optoelectron. **149**, 41 (2002).
- [4] Z. Lu, Y. Jiang, W.I. Wang, M.C. Teich, and R.M. Osgood Jr., J. Vac. Sci. Technol. **B10**, 1856 (1992).
- [5] K.M. Schirm, P. Soukiassian, P.S. Mangat, Z. Hurych, L. Soonckindt, and J.J. Bonnet, J. Vac. Sci. Technol. **B10**, 1867 (1992).
- [6] V.N. Bessolov, M.V. Lebedev, Semiconductors, **32**, 1141 (1998).
- [7] M. Perotin, P. Coudray, L. Gousskov, H. Luquet, C. Llinares, J.J. Bonnet, L. Soonckindt, B. Lambert, J. Electron. Mater. **23**, 7 (1994).
- [8] I.A. Andreev, E.V. Kunitsyna, V.M. Lantratov, T.V. L'vova, M.P. Mikhailova, Yu.P. Yakovlev, Semiconductors **31**, 556 (1997).
- [9] B. Wu, G. Xia, Z. Li, J. Zhou, Appl. Phys. Lett. **80**, 1303 (2002).
- [10] Zhihuai Li, Guanqun Xia, Binhe Wu, Wenkui Huang, and Zongquan Cheng, J. Appl. Phys. **94**, 1295 (2003).
- [11] X. Zhang, A.Z. Li, C. Lin, Y.L. Zheng, G.Y. Xu, M. Qi, Y.G. Zhang, J. Crystal. Growth **251**, 782 (2003).
- [12] A. Gin, Y. Wei, A. Hood, A. Bajowala, V. Yazdanpanah, M. Razeghi, M. Tidrow, Appl. Phys. Lett. **84**, 2037 (2004).
- [13] D. Lu, F.P. Zhang, S.H. Xu, et al., Appl. Phys. Lett. **69**, 2282 (1996).
- [14] F.Q. Xu, E.D. Lu, H.B. Pan, C.K. Xie, P.S. Xu, and X.Y. Zhang, Surface Review and Letters **8**, 19 (2001).
- [15] D.Y. Petrovykh, J.P. Long, and L.J. Whitman, Appl. Phys. Lett. **86**, 242105 (2005).
- [16] B. Reine, A.K. Sood, and T.J. Tredwell, *Photovoltaic Infrared Detectors*, in Semiconductors and Semimetals, Vol.18, ed. R.K. Willardson and A.C. Beer ( Academic Press, New York, 1981).
- [17] M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, NACE , ISBN 1-915567-98-9 (1974).