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# Performance improvement of long-wave infrared InAs/GaSb strained-layer superlattice detectors through sulfur-based passivation

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ABSTRACT

We report on effective sulfur-based passivation treatments of type-II InAs/GaSb strained layer superlattice detectors (100% cut-off wavelength is 9.8 μm at 77 K). The electrical behavior of detectors passivated by electrochemical sulfur deposition (ECP) and thioacetamide (TAM) was evaluated for devices of various sizes. ECP passivated detectors with a perimeter-to-area ratio of 1600 $cm^{-1}$ exhibited superior performance with surface resistivity in excess of $10^4$ Ω cm, dark current density of $2.7 \times 10^{-3}$ A/$cm^2$, and specific detectivity improved by a factor of 5 compared to unpassivated devices ($V_{Bias} = -0.1$ V, 77 K).

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## 1. Introduction

The imaging of radiation in the long-wave infrared (LWIR, 8–14 μm) part of the electromagnetic spectrum is important for a variety of civil and military applications, such as monitoring of global atmospheric temperature profiles, astrophysical imaging, missile detection and tracking, and satellite based surveillance. The basic material properties of type-II InAs/GaSb strained layer superlattices (SLSs) provide a prospective benefit in the realization of high performance IR photodetectors with cut-off wavelengths in the LWIR range. In particular, InAs/GaSb SLS are characterized by suppressed Auger recombination relative to bulk mercury–cadmium–telluride (MCT) material leading to improved temperature limits of spectral detectivities [1–3]. Moreover, SLSs are less sensitive to the compositional non-uniformities in LWIR spectral band than the MCT alloys with the same band gap [4]. In addition, normal incidence absorption is permitted in type-II SLSs, contributing to high quantum efficiencies. Commercial availability of low defect density substrates as well as relatively easy material growth and fabrication of III–V materials compared to its II–VI counterpart also offers technological advantages for the InAs/GaSb SLS technology.

One of the expected characteristics of the third-generation IR systems is enhanced sensitivity (higher signal-to-noise ratio) that is achieved by increasing the number of individual array elements while decreasing their size. During the individual pixel isolation process, the periodic crystal structure is terminated abruptly resulting in the formation of unsatisfied (dangling) chemical bonds responsible for generation of surface states within the band gap and pinning of the Fermi level. Since smaller sized pixels have large surface/volume ratio their performance is strongly dependent on surface effects. The dark current component associated with surface states (further referred as surface leakage current) typically is the dominant source of noise for LWIR detectors.

Sulfur-based passivation has been known to be responsible for the reduction of surface states within the III–V semiconductor band gap by formation of covalently bonded sulfur layer with group-III and group-V atoms [5,6]. The most common sulfidization scheme of InAs/GaSb SLS detectors is ammonium sulfide passivation [7–9]. The $(NH_4)_2S$ treatment is easily integrated into the fabrication process since it is performed simply by immersion of the sample in $(NH_4)_2S$-based solutions. Moreover, no native oxide removal is required prior to passivation, since the Ga, In, As, and Sb-native oxides are etched by $(NH_4)OH$ formed in water solution of ammonium sulfide. However, the $(NH_4)_2S$ passivation may cause the degradation of device performance attributed to the secondary oxidation, since the hydrophobic surface generated by oxide removal repels the solution and leaves the surface exposed for $O_2$-re-adsorption.

Thioacetamide ($C_2H_5NS$ or TAM) has been proposed as an alternate sulfidizing agent for the passivation of GaSb and InAs surfaces [10] as well as GaInAsSb [11] and InAs/GaSb [12] LWIR photodiodes. Depending on the preparation method, the TAM solution may be acidic or basic, in contrast with always basic aqueous solution of $(NH_4)_2S$. As a result, a TAM treatment offers formation of more stable M–S bonds, where M is Ga, In, As or Sb, than ammonium sulfide treatment resulting in weaker M–O–S bonds.

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14. ABSTRACT

**We report on effective sulfur-based passivation treatments of type-II InAs/GaSb strained layer superlattice detectors (100% cut-off wavelength is 9.8 lm at 77 K). The electrical behavior of detectors passivated by electrochemical sulfur deposition (ECP) and thioacetamide (TAM) was evaluated for devices of various sizes. ECP passivated detectors with a perimeter-to-area ratio of 1600 cm 1 exhibited superior performance with surface resistivity in excess of 104 X cm, dark current density of 2.7 10 3 A/cm2, and specific detectivity improved by a factor of 5 compared to unpassivated devices (VBias = 0.1 V, 77 K).**

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Moreover, the TAM treatment does not produce elemental antimony on the semiconductor surface thus eliminating the conduction channel parallel to the semiconductor-atmosphere interface.

Electrochemical passivation involves the deposition of elemental sulfur in a controlled electro-chemical bath through the decomposition of $Na_2S$ in ethylene glycol. Successful application of electrochemical sulfur passivation (ECP) to MWIR InAs/GaSb SLS detectors has been already reported [13]. The electrochemical sulfidization provides a uniform sulfur coating with a high-density of S atoms, as was proven by scanning electron microscopy imaging and (obliquely) by good long-term stability of passivated surfaces, respectively. In this paper, we compare the effectiveness of the two alternative sulfur-based passivations, TAM and electrochemical sulfur deposition, on the performance of LWIR InAs/GaSb SLS detectors.

## 2. Experimental

The detector material used in this study was grown by solid source molecular beam epitaxy (MBE) on n-type (Te-doped) epi-ready (100) GaSb substrate at Intelligent Epitaxy Technology, Inc. (IntelliEPI). The detector heterostructure utilized the graded-band gap W-design SLS proposed by Vurgaftman et al. [14]. The band gap of such a *n*-on-*p* structure is increased in a series of steps from a lightly *p*-type narrow band gap IR-absorbing region to a *n*-type region with a band gap value typically 2–3 times larger, with the *p*–*n* junction occurring in the graded ("W") regions. The grading steps (W-SLS) were formed by a periodic InAs/GaInSb/InAs/AlGaInSb structure, with various barrier compositions and thicknesses for the electron and hole wells. The *p*-type GaSb contact layer ($p = 3 \times 10^{18}$ cm$^{-3}$) was grown next to the absorbing region formed by a *p*-type InGaSb/InAs SLS ($p = 4 \times 10^{15}$ cm$^{-3}$) with a total thickness of 4 μm. The *n*-type ($n = 4 \times 10^{17}$ cm$^{-3}$) InAs contact layer was deposited on the topmost *n*-doped wide band gap "W" region. Further design details were reported elsewhere [14].

The detector material was processed into a variable area diode array (VADA) of square and circular mesa diodes with the size of diode mesa sides (diameters) ranging from 25 to 400 μm using standard optical photolithography techniques. For radiometric characterization, the material was processed as single element detectors with 410 μm × 410 μm square mesas having circular apertures ranging in diameter from 25 to 300 μm. The processing was initiated by an inductively coupled plasma (ICP) etch to the middle of the bottom contact layer with a total etch depth of 4.9 μm. Next, Ti (500 Å)/Pt (500 Å)/Au (3000 Å) was deposited as the bottom and top contact metalization. Finally, detectors were passivated with different passivation schemes with details of each described below.

To perform TAM passivation the samples were immersed in a 0.18 M $CH_3CSNH_2$ solution for 40 min at 70 °C. The pH of the TAM solution was adjusted to be acidic (pH = 2.4) or basic (pH = 10.4) by adding an acetic acid (10%) or $NH_4OH$(30%), respectively. The electrochemical cell for the sulfur passivation consisted of the sample (anode), a platinum mesh electrode (cathode) and the electrolyte in a glass beaker at room temperature. The electrolyte was 0.1 M $Na_2S$ in ethylene glycol. A square-shaped 50% duty cycle current pulse with a magnitude of 33 μA was supplied from a programmable current source to the back of the sample for a limited amount of time (5 min). The samples were then rinsed with isopropanol and blow dried with $N_2$. Immediately before each passivation treatment the native oxides were removed by placing samples in a phosphoric acid based solution ($H_3PO_4$:$H_2O_2$:$H_2O$ = 1:2:20) for 30 s.

The cut-off wavelength of fabricated detectors was determined through spectral response measurements performed using a Nicolet 670 Fourier transform infrared (FT-IR) spectrometer with a glow-bar black body source. Passivation efficacy was evaluated by measuring current–voltage (*I*–*V*) dependence at 77 K for VADA detectors. All *I*–*V* measurements were conducted on variable-temperature Janis ST-500 micro manipulated probe station under zero field of view.

## 3. Results and discussion

Fig. 1 shows the representative normalized spectral response curves for various temperatures measured at −0.1 V of applied bias for unpassivated devices. The 100% cut-off wavelength of fabricated SLS detectors was equal to 9.8 μm at 77 K.

Fig. 2 shows a comparison between dark current densities of as-etched devices and devices treated by the different passivations schemes, each having perimeter-to-area ratio (P/A) of 1600 cm$^{-1}$. Under a typical operating bias of −0.1 V, the dark current density decreased from ∼0.8 A/cm$^2$ for unpassivated samples to ∼0.3 A/cm$^2$ and 0.04 A/cm$^2$ for acidic and basic solutions in the TAM treatments, respectively, and to ∼$2.7 \times 10^{-3}$ A/cm$^2$ for the ECP treatment.

Fig. 3 presents a plot of the inverse of the dynamic resistance area product ($R_dA$) versus the perimeter-to-area ratio (P/A) for the unpassivated SLS devices and devices passivated by various treatments SLS measured at 77 K under a typical operating bias of −0.1 V.

The surface dependence of ($R_dA$) can be approximated using Eq. (1):

$$\frac{1}{R_dA} = \frac{1}{R_dA_{Bulk}} + \frac{1}{r_{Surface}}\frac{P}{A} \quad (1)$$

where $(R_dA)_{bulk}$ is the bulk $R_dA$ contribution (Ω cm$^2$), $r_{Surface}$ is the surface resistivity (Ω cm), *P* is the diodes perimeter, and *A* is the diodes area. The slope of the function given by Eq. (1) is directly proportional to the surface-dependent leakage current of the diode. We found values of $r_{Surface}$ equal to $1.9 \times 10^2$, $3.5 \times 10^2$, $2.7 \times 10^3$, and $3.3 \times 10^4$ Ω cm for the unpassivated, TAM acidic, TAM basic, and ECP passivated detectors, respectively, revealing two orders of magnitude improvement of surface resistivity for ECP treated devices at 77 K under a given bias (−0.1 V).

The typical values of $r_{Surface}$ are ∼$10^4$ Ω cm, 204 Ω cm, and 196 Ω cm for polyimide [15], SU-8 [16], and SiN [17] passivations, respectively, applied to InAs/GaSb SLS detectors operating in the same spectral band (LWIR). Passivation of LWIR SLS detectors by other sulfidization schemes yields $r_{Surface}$ values of 29 Ω cm (ammonium sulfide-based passivation) [9] and $2.5 \times 10^3$ Ω cm (ZnS treatment) [12].

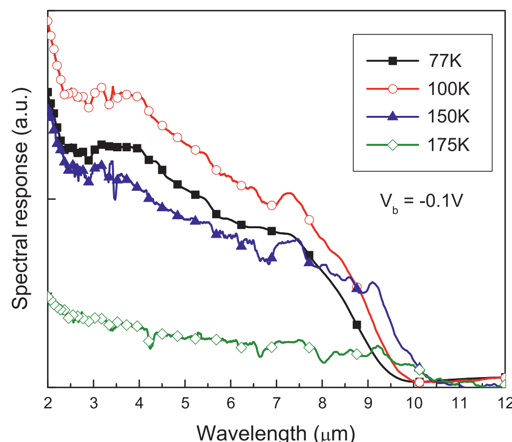


**Fig. 1.** Representative normalized spectral response curves measured at various temperatures at −0.1 V of applied bias.

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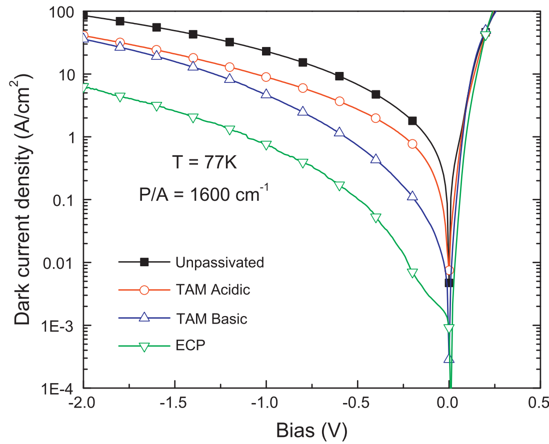


**Fig. 2.** Comparison between dark current densities of as-etched devices and devices treated by the different passivations schemes with perimeter-to-area ratio (P/A) of 1600 $cm^{-1}$ (mesa side size is 25 μm).

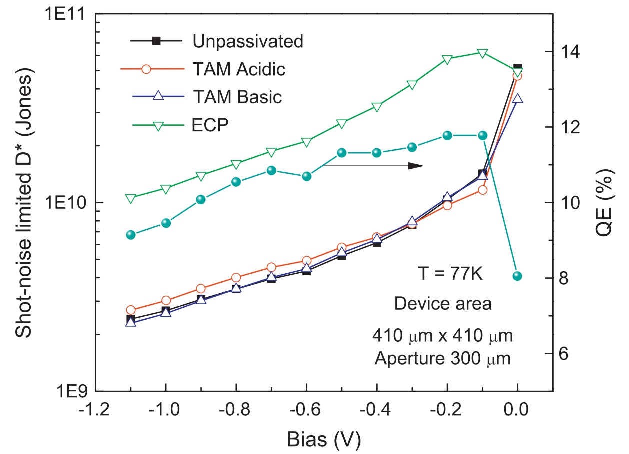


**Fig. 4.** The shot-noise limited $D^*$ as a function of applied bias for the as-fabricated detector and the detectors treated by the different passivation schemes evaluated at 77 K. The QE values evaluated at the same temperature are also shown.

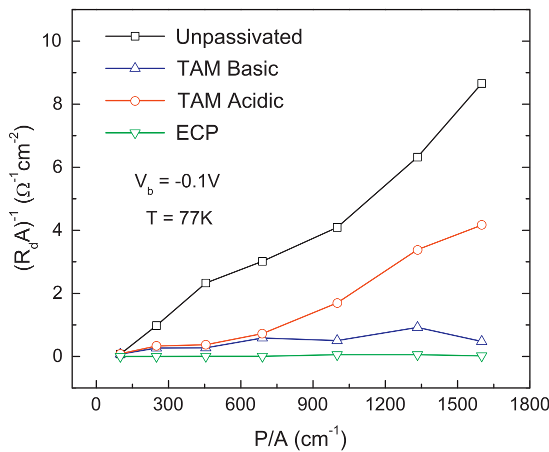


**Fig. 3.** Inverse of the dynamic resistance area product ($R_dA$) versus the perimeter-to-area ratio (P/A) for unpassivated and passivated SLS detectors measured at 77 K under −0.1 V of applied bias.

Moreover, the nearly linear dependence of $(R_dA)^{-1}$ vs (P/A) curve for the ECP treated sample indicates the negligible surface leakage currents. Contrary to previous observatoins of Salesse et al. [11] the basic TAM passivation demonstrated superior performance compared to the acidic TAM treatment. The reason for this phenomenon is currently under investigation.

The shot noise limited $D^*$ was estimated at 8 μm using Eq. 2:

$$D^* = \frac{R}{\sqrt{\left(\frac{4k_BT}{R_dA} + 2qJ\right)}} \quad (2)$$

where $R$ is responsivity, $k_B$ is the Boltzman constant, $T$ is temperature, $R_d$ is dynamic resistance, $A$ is diode area, $q$ is the electronic charge, and $J$ is the dark current density. The responsivity was measured with a calibrated blackbody source at 800 K for devices with 300 μm aperture. It should be noted that all the radiometric measurements have been carried out using a longwave bandpass filter (8.4–11.5 μm) in order to obtain the responsivity and detectivity in the LWIR range. Fig. 4 presents the estimated shot-noise limited $D^*$ as a function of applied bias for the detectors with the various passivations treatments and the control sample evaluated at 77 K. At an operating bias of −0.1 V, the ECP passivated device resulted in an improvement in the shot-limited D* by a factor of 5 compared to the unpassivated device. The quantum efficiency (QE) is equal ~12% at the same value of applied bias for the unpassivated and passivated samples.

## 4. Conclusion

In conclusion, we evaluated the electrical behavior of detectors passivated by two different sulfur-based treatments, TAM (acidic and basic) and ECP. ECP passivated detectors with perimeter-to-area ratio of 1600 $cm^{-1}$ exhibited superior performance with surface resistivity in excess of $10^4\,\Omega\,cm$, dark current density of $2.7 \times 10^{-3}$ A/$cm^2$, and specific detectivity improved by factor of 5 compared to unpassivated devices ($V_{bias} = -0.1$ V, 77 K).

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