

# Passivation of type II InAs/GaSb superlattice photodetectors with atomic layer deposited Al<sub>2</sub>O<sub>3</sub>

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## ABSTRACT

We have achieved significant improvement in the electrical performance of the InAs/GaSb midwave infrared photodetector (MWIR) by using atomic layer deposited (ALD) aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) as a passivation layer. Plasma free and low operation temperature with uniform coating of ALD technique leads to a conformal and defect free coverage on the side walls. This conformal coverage of rough surfaces also satisfies dangling bonds more efficiently while eliminating metal oxides in a self cleaning process of the Al<sub>2</sub>O<sub>3</sub> layer. Al<sub>2</sub>O<sub>3</sub> passivated and unpassivated diodes were compared for their electrical and optical performances. For passivated diodes the dark current density was improved by an order of magnitude at 77 K. The zero bias responsivity and detectivity was 1.33 A/W and 1.9 x 10<sup>13</sup> Jones, respectively at 4 μm and 77 K. Quantum efficiency (QE) was determined as %41 for these detectors.

**Keywords:** Superlattice, Photodetector, InAs/GaSb, Al<sub>2</sub>O<sub>3</sub>, ALD, Passivation

## 1. INTRODUCTION

Type-II super lattice (T2SL) InAs/GaSb photodetectors have recently received great interest in the development of midwave and long wave infrared detectors due to advantages like band gap engineering [1], suppression of Auger recombination [2], and interband tunneling [3]. Type-II super lattice technology is a very promising alternative to MCT and QWIP in focal plane array (FPA) applications where, low dark current below 77 K is required. As the confinement of current requires the fabrication of a mesa structure, one of the challenges of T2SL system is the large number of surface states generated due to the abrupt termination of the crystal structure on the mesa side walls. Dangling bonds, inversion layer and interfacial traps are possible sources of surface leakage currents. Small pixel size photodetectors suffer from surface leakage more than large pixel photodetectors due to high perimeter to area ratio. Especially for the FPA applications and long wavelength operations, passivation becomes a vital issue. In order to overcome surface leakage currents of small sized photodetectors, various passivation methods such sulfide [4, 5], silicon dioxide layers [6], polymeric layer [7] and even overgrowth with wide bandgap materials [8] were proposed. Passivation is expected to suppress oxidation of the side walls and saturate dangling bonds to prevent surface states. In sulfur passivation, oxygen is replaced with sulfur at the mesa side walls saturating dangling bonds [5, 9]. It is a very effective passivation method and relatively easy to apply nonetheless the effect of passivation is not permanent. Also some reports claim that sulfur passivation damages the surface of the photodetector [9]. Despite the fact that silicon dioxide has been shown to be an effective technique, the high temperature or high RF power requirements carries potential for damage. Relatively high growth temperatures (400 °C), may damage SL surfaces and high density energetic ions in a plasma can cause damage on SL surfaces.

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In this work, we report on the study of  $\text{Al}_2\text{O}_3$  as a passivation layer for InAs/GaSb SL photodetectors. We choose to use atomic layer deposition (ALD) to apply the  $\text{Al}_2\text{O}_3$ . With sequential gas phase reactions, ALD is a self limiting process. The growth of  $\text{Al}_2\text{O}_3$  with ALD uses two gasses that are introduced to the chamber one at a time and which react with the gas on the surface adsorbed during the previous sequence. ALD deposited  $\text{Al}_2\text{O}_3$  has many advantages as a passivation layer such as the control of thickness at the molecular level since in the ALD process, thickness depends on the number of reaction cycles. This leads to precise thickness control as well as perfect conformal coverage even at sharp edges, large area thickness uniformity, very low process temperatures and plasma free operation. Furthermore  $\text{Al}_2\text{O}_3$  is a very good dielectric over a very large frequency range. Due to very thin multiple InAs/GaSb pairs in T2SL photodetectors, mesa etching leads to uneven etching of the side walls where conformal coverage at the atomic level is very beneficial. Oxidation of the freshly etched surfaces is typically very rapid and a thin layer of oxides forms almost immediately prior to passivation. A successful passivation technique must be eliminate the native oxides formed between mesa etching and passivation steps. Thus a self cleaning procedure eliminating the already formed thin oxide layer would be most welcome. Studies on the surface and interface chemistry of III-V surfaces passivated with atomic layer deposited  $\text{Al}_2\text{O}_3$  has shown that it is possible to reduce the native oxides during deposition. This is due to the fact that formation of  $\text{Al}_2\text{O}_3$  is energetically preferred due to lower Gibbs free energy of  $\text{Al}_2\text{O}_3$  (-377.9 kcal/mol) [10]. The Gibbs free energies of  $\text{Ga}_2\text{O}$ ,  $\text{Ga}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$ ,  $\text{As}_2\text{O}_3$ ,  $\text{As}_2\text{O}_5$  and  $\text{Sb}_2\text{O}_3$  which are -75.3 kcal/mol, -238.6 kcal/mol, -198.6 kcal/mol, -137.7 kcal/mol, -187.0 kcal/mol and -151.5 kcal/mol, respectively [11, 12] which are all higher than  $\text{Al}_2\text{O}_3$ . X-ray photoelectron spectroscopy (XPS) by Hinkle et al. has shown that deposition of  $\text{Al}_2\text{O}_3$  on etched GaAs strongly reduces Ga and As oxides [13]. ALD  $\text{Al}_2\text{O}_3$  on InAs has also shown strong reduction of In and As oxides [14]. MOS capacitors fabricated on GaSb has demonstrated strong suppression of  $\text{Sb}_2\text{O}_3$  due to  $\text{Al}_2\text{O}_3$  deposition [15]. These properties of ALD grown  $\text{Al}_2\text{O}_3$  makes it a perfect candidate for passivation of InAs/GaSb super lattice FPA photodetectors. No use of  $\text{Al}_2\text{O}_3$  as a passivation layer has been made so far for InAs/GaSb super lattice system.

## 2. EXPERIMENTAL

The SL structure was designed for MWIR operation and was grown commercially (IQE Inc. USA) with molecular beam epitaxy on a GaSb substrate. The photodetector is designed as p-i-n photodetector with design cutoff wavelength of 5  $\mu\text{m}$ . Figure 1a. shows periodic structure of the p-i-n design superlattice crystal with corresponding thicknesses and doping concentrations.

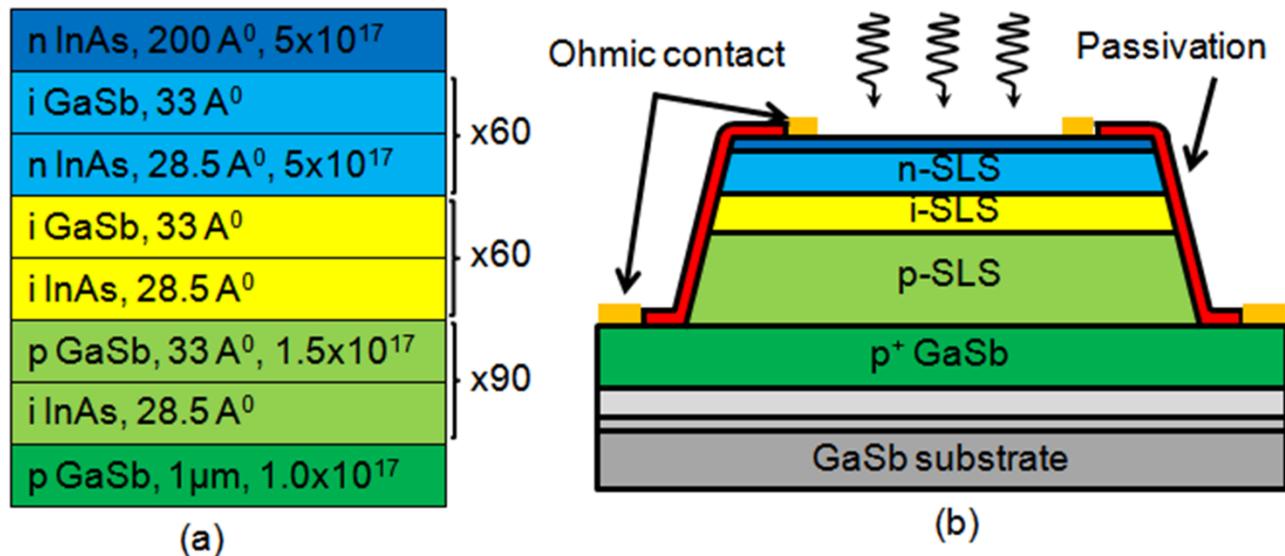


Figure 1. (a) Superslattice periodic structure. (b) Structure of the single pixel photodetector.

It starts with 100 nm thick GaSb buffer layer and 20 nm  $\text{Al}_x\text{GaAs}_y\text{Sb}$  as an insulator and etch stop layer, followed by 1000 nm GaSb:Be ( $p=1.0 \times 10^{17} \text{ cm}^{-3}$ ) p contact layer. Pin part of the design consist of 90 periods 8 monolayers InAs/8 MLs GaSb:Be ( $p=1.5 \times 10^{17} \text{ cm}^{-3}$ ), 60 periods 8 monolayers InAs / 8 MLs GaSb, 60 periods 8 monolayers InAs:Te ( $n: 5 \times 10^{17} \text{ cm}^{-3}$ )/8 MLs GaSb:Be and structure terminated by 20 nm InAs:Te ( $n: 5 \times 10^{17} \text{ cm}^{-3}$ ) cap layer to assure good ohmic contact. Appropriate shutter sequences were applied to compensate the tensile strain caused by lattice mismatch between InAs and GaSb layers.

Single pixel photodetectors were fabricated with mesa sizes between  $200 \times 200$  and  $600 \times 600 \mu\text{m}$  by standard lithography and wet etch solution. For wet chemical etching, orthophosphoric acid (85%), citric acid (100.0%), hydrogen peroxide (30%) solutions and deionized water are used. Mesa-isolated photodiodes are defined at room temperature, using the chemical solution based on  $\text{H}_3\text{PO}_4/\text{C}_6\text{H}_8\text{O}_7/\text{H}_2\text{O}_2/\text{H}_2\text{O}$  with 200 nm per minute etch rate. The etch process has been stopped when etch depth reached the bottom contact layer. The etch depth was about 1.5  $\mu\text{m}$ . Figure 1b shows device structure of the p-i-n photodiode. 200 cycles  $\text{Al}_2\text{O}_3$  passivation layer deposition carried out in atomic layer deposition system (Cambridge Nanotech Savannah 100) with 150  $^\circ\text{C}$  as the substrate holder temperature. Growth of  $\text{Al}_2\text{O}_3$  has been done by delivering 0.015 s water vapor ( $\text{H}_2\text{O}$ ) and 0.015 s trimethylaluminum (TMA) pulses into the chamber in a sequential manner under constant 20 sccm  $\text{N}_2$  gas flow. A wait time of 20 s was added after each pulse to ensure surface reactions to take place. Both trimethylaluminum and water were unheated. The thickness of the film grown in this manner was determined as 20 nm by subsequent etching and measurement of the  $\text{Al}_2\text{O}_3$  film. For comparison purpose, same etch procedure was used to fabricate photodetectors with  $\text{SiO}_x$  passivation layer.  $\text{SiO}_x$  passivation layer deposition carried out in plasma enhanced chemical vapor deposition (PECVD) system at 160  $^\circ\text{C}$  and the process was carried out under the pressure of 0.5 Torr and RF power of 9 W. Flow rates were 180 sccm for  $\text{SiH}_4$  (9% in  $\text{N}_2$ ) and 225 sccm for  $\text{N}_2\text{O}$ . Final thickness of the  $\text{SiO}_2$  film was about 300 nm. Exact same procedures were applied to another sample without passivation layer to act as a reference detector. 5 nm Titanium (Ti) and 200 nm Gold (Au) on the bottom and top contact layers of the detectors were evaporated for ohmic contacts.

### 3. RESULTS AND DISCUSSIONS

The effect of  $\text{Al}_2\text{O}_3$  passivation was studied on samples which were mounted on a liquid nitrogen cooled cold finger. Dark current measurements were performed at 77 K by using a HP41420A source-measure unit. Figure 2a shows the measured dark current density vs applied bias voltage characteristics of the unpassivated,  $\text{SiO}_x$  and  $\text{Al}_2\text{O}_3$  passivated  $400 \times 400 \mu\text{m}$  single pixel test diodes at 77 K.  $\text{Al}_2\text{O}_3$  passivated detectors show reduction in dark current density by two orders of magnitude compared with unpassivated detectors and an order of magnitude reduction when compared with  $\text{SiO}_x$  passivated photodetectors. At -0.1 V bias voltage, dark current densities are measured as  $6.5 \times 10^{-5} \text{ A/cm}^2$ ,  $4.1 \times 10^{-6} \text{ A/cm}^2$  and  $6.6 \times 10^{-7} \text{ A/cm}^2$  for the unpassivated,  $\text{SiO}_x$  passivated and  $\text{Al}_2\text{O}_3$  passivated diodes, respectively. These measurements yielded  $R_0A$  product values of  $1.4 \times 10^3 \Omega \cdot \text{cm}^2$ ,  $4.0 \times 10^4 \Omega \cdot \text{cm}^2$  and  $3.7 \times 10^5 \Omega \cdot \text{cm}^2$  for the unpassivated,  $\text{SiO}_x$  passivated and  $\text{Al}_2\text{O}_3$  passivated samples, respectively.  $\text{SiO}_x$  passivation is an industry standard for FPA fabrication. Our electrical measurements showed that  $\text{Al}_2\text{O}_3$  is a better alternative for  $\text{SiO}_x$  passivation. The significant reduction in dark current and increase in dynamic resistance due to ALD deposited  $\text{Al}_2\text{O}_3$  passivation is very encouraging for use in FPA applications [9, 16, 17]. The inverse of the dynamic resistance area product at zero bias as a function of the perimeter to area ratio at 77K for passivated and unpassivated detectors are shown in Fig. 2b. The surface part of the resistance-area product can be calculated from the slope of the graph [9]. Calculated surface resistivity ( $r_{\text{surface}}$ ) values at zero bias are  $6.9 \times 10^4 \Omega \cdot \text{cm}$ ,  $2.9 \times 10^5 \Omega \cdot \text{cm}$  and  $1.3 \times 10^7 \Omega \cdot \text{cm}$  for unpassivated,  $\text{SiO}_x$  passivated and  $\text{Al}_2\text{O}_3$  passivated photodiodes, respectively. The results reveal that  $\text{Al}_2\text{O}_3$  passivated diodes show improved surface resistance ( $r_{\text{surface}}$ ) of a factor of 200 and 50 when it is compared with unpassivated and  $\text{SiO}_x$  passivated diodes, respectively at 77K. This clearly shows that  $\text{Al}_2\text{O}_3$  passivation suppresses the surface related current more efficiently than  $\text{SiO}_2$  passivation.

To understand nature of the dark current, temperature dependent measurements of the dark current has been done. Figure 3a shows dark current density vs applied bias voltage for temperatures between 40 K and 250 K. For temperatures lower than 60K, dark current becomes too small for our measurement system and leads to noise around zero bias point. This noise is amplified when dynamic resistance is calculated. We, therefore, prefer to use the dark current vs  $1000/T$  graph to analyze surface leakage currents. Relationship between the dark current densities and inverse temperatures at -0.1V bias are shown in Figure 3b. The current voltage (I-V) curve is dominated by diffusion current at high temperatures and generation-recombination current at mid temperatures. For the lower temperatures surface currents become dominant.

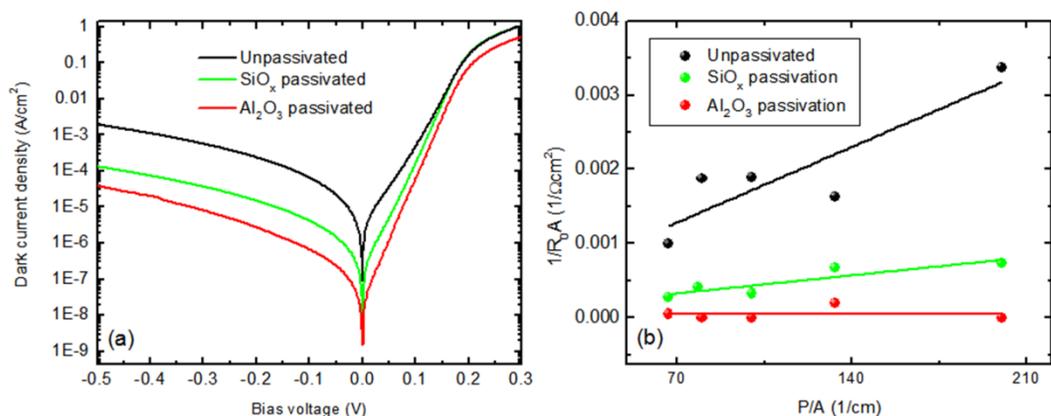


Figure 2. (a) Dark current density vs. applied bias of unpassivated, SiO<sub>x</sub> passivated and Al<sub>2</sub>O<sub>3</sub> passivated single pixel square diodes measured at 77K. (b) Dependence of dynamic resistance-area product at zero bias vs. perimeter to area ratio for unpassivated and passivated devices at 77K. Slope is directly proportional to the surface related leakage current of the diode.

The diodes with Al<sub>2</sub>O<sub>3</sub> passivation show lower dark currents than unpassivated photodetectors at low temperatures. This indicates that the Al<sub>2</sub>O<sub>3</sub> passivation satisfies surface states and prevents current flow through the surface channel. Al<sub>2</sub>O<sub>3</sub> passivated photodetectors show Arrhenius type behavior above 100 K, characterizing the dominant bulk diffusion current. The activation energy has been calculated as 0.233 eV which is close to the band gap of the device. For lower temperatures, current starts to divert from the Arrhenius type of behavior. Generation recombination (G-R) current becomes dominant for mid temperatures. At 40 K, dark current density shows tendency to decrease, indicating that surface leakage starts to become important in this range [18]. For the unpassivated detector, dark current density deviate from the Arrhenius type of behavior at the temperatures lower than 140 K indicating surface related currents start to become dominant at this range.

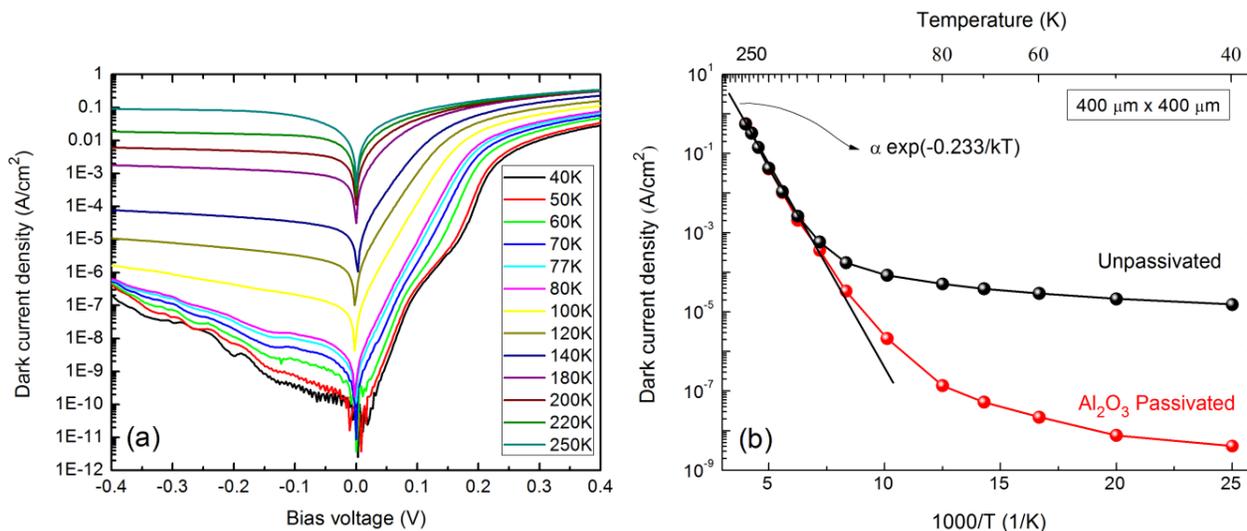


Figure 3. (a) Dark current density vs. applied bias of Al<sub>2</sub>O<sub>3</sub> passivated 400 μm single pixel square diodes measured at different temperatures. (b) Temperature dependent dark current measurements of Al<sub>2</sub>O<sub>3</sub> passivated and unpassivated photodetectors at -0.1 V bias.

Fourier transform infrared spectroscopy (Bruker Equinox 55) and a liquid nitrogen cooled cold finger system was used to measure spectral response of the photodetectors. Figure 4 shows responsivity vs wavelength graphs of the unpassivated and Al<sub>2</sub>O<sub>3</sub> passivated photodetectors measured under single pass and front side illumination conditions. For both Al<sub>2</sub>O<sub>3</sub> passivated and unpassivated photodetectors, the cut-off wavelength is determined to be 5.1 μm.

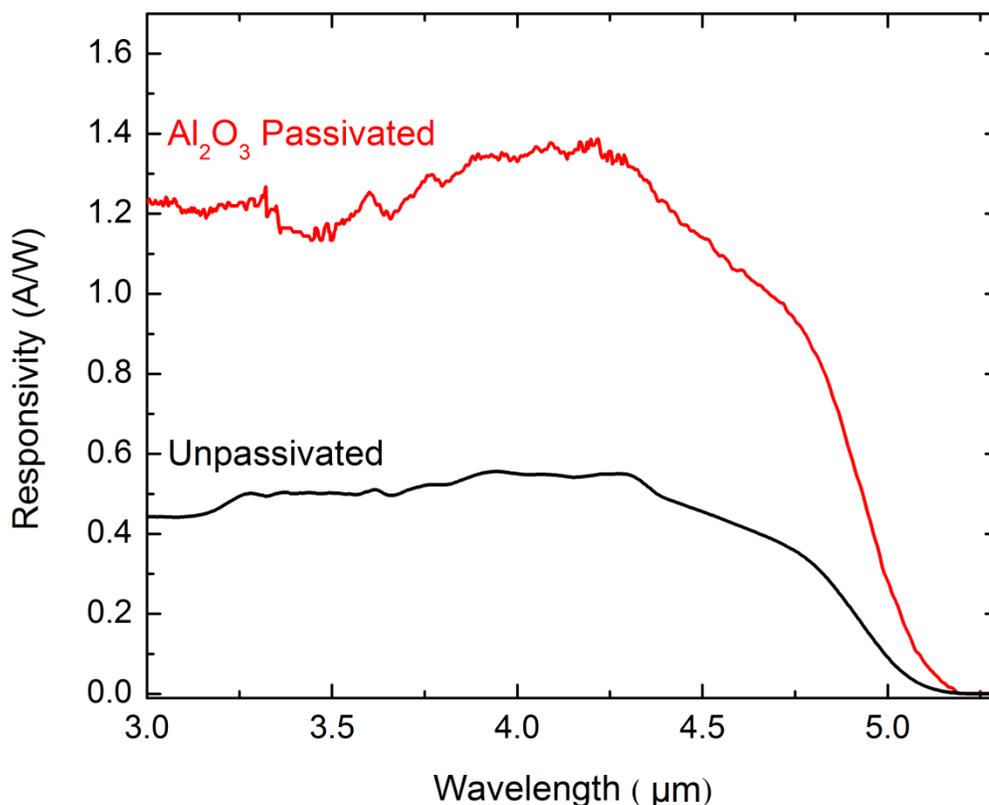


Figure 4. Spectral responsivity of the unpassivated and Al<sub>2</sub>O<sub>3</sub> passivated photodetectors at 77K. The cut-off wavelength of the Al<sub>2</sub>O<sub>3</sub> passivated and unpassivated photodetectors is ~5.1 μm.

A calibrated blackbody source at 800 °C (Newport, Oriel 67000), lock-in amplifier (SRS, SR830 DSP) and mechanical chopper (SRS, SR540) system was used to measure the responsivity of the photodetectors at 77 K. The detectors were illuminated with a 300 K background with a 2π field-of-view. A 3-5 μm blackbody filter has been used to eliminate unwanted illumination. Quantum efficiency (QE) and Johnson-noise limited detectivity (D\*) versus applied bias voltage for Al<sub>2</sub>O<sub>3</sub> passivated photodetector is shown in Figure 3. The zero bias responsivity was equal to 1.33 A/W at 4 μm and 77K for Al<sub>2</sub>O<sub>3</sub> passivated photodetectors. The peak D\*, was equal to 1.9 x 10<sup>13</sup> Jones for the Al<sub>2</sub>O<sub>3</sub> passivated single pixel photodetector at 4 μm and 77 K. Under single pass front illumination conditions quantum efficiency (QE) of the passivated photodetector was determined as % 41. A comparison of our results with recent data [9, 16-20], shows that ALD grown Al<sub>2</sub>O<sub>3</sub> passivated T2SL photodetectors are very promising.

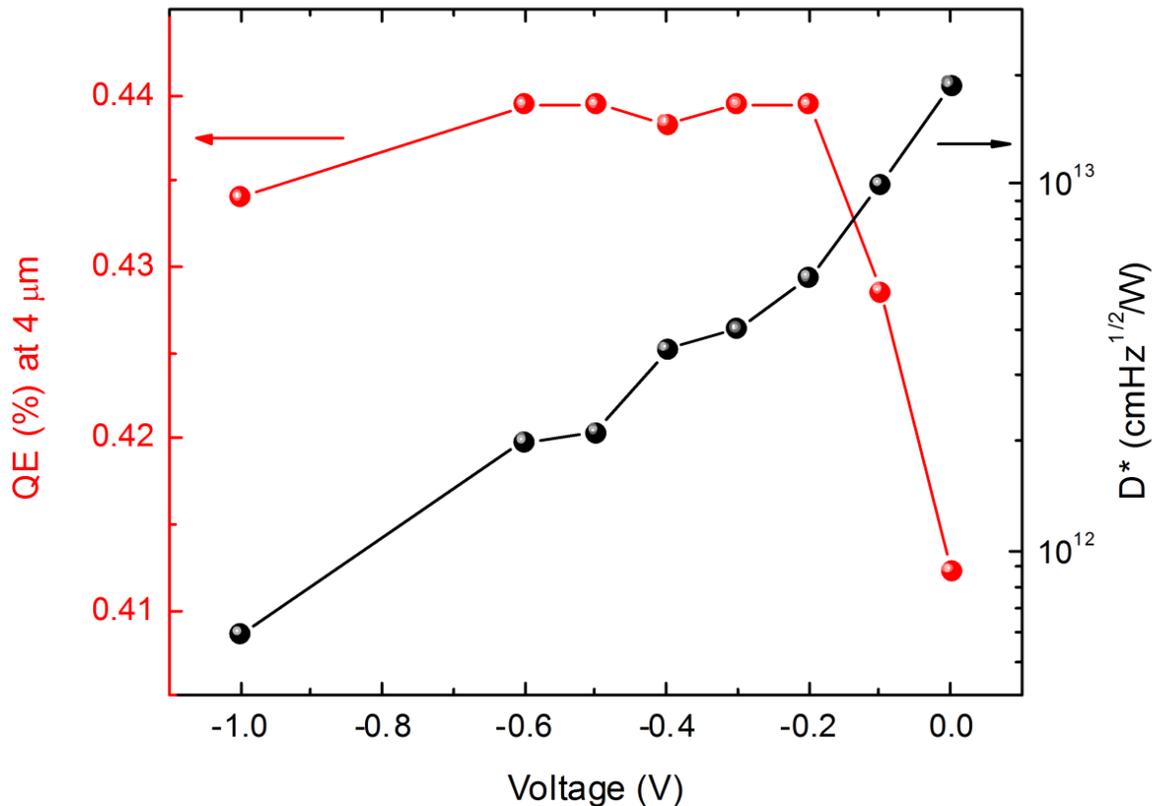


Figure 5. Quantum efficiency and detectivity of Al<sub>2</sub>O<sub>3</sub> passivated, 400x400 μm single pixel test detectors at 77K and 4 μm. The zero bias QE and the peak value of detectivity, D\* of Al<sub>2</sub>O<sub>3</sub> passivated photodetector was equal to %41 and 1.9 x 10<sup>13</sup> Jones, respectively.

Oxide layers of few nanometers thick native oxide layers form very quickly on freshly etched surface of the superlattice since they are very reactive [21]. Oxygen reacts with surface metals to form oxides like; Sb<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub> and As<sub>2</sub>O<sub>3</sub>. Conductive surface channel can form and cause large surface dark current due to these native oxides. Due to favorable Gibbs free energies, Al<sub>2</sub>O<sub>3</sub> formation is energetically preferred to native oxide of InAs and GaSb. Alternatively, As atoms that form As<sub>2</sub>O<sub>3</sub> or In atoms in an In<sub>2</sub>O<sub>3</sub> molecule are replaced by Al<sup>3+</sup> atoms in the TMA molecule [22]. Similar reaction pathways with oxides of other metal atoms are also possible. These are so called interfacial self cleaning reactions of surface oxides [10].

#### 4. CONCLUSION

In conclusion, suppression of dark current and increase in optical response of the InAs/GaSb superlattice photodetectors with cutoff wavelength at 5.1 μm (MWIR) was demonstrated. ALD deposited Al<sub>2</sub>O<sub>3</sub> passivation layer was used on InAs/GaSb p-i-n design superlattice photodetectors. Conformal coating of atomic layer deposition creates perfect protective layer against environmental effects especially against oxidation. This conformal coverage of rough surfaces also satisfies dangling bonds more efficiently while eliminating metal oxides in a self cleaning process. Single pixel Al<sub>2</sub>O<sub>3</sub> passivated detectors show two orders of magnitude reduction on dark current density compared with unpassivated detectors and an order of magnitude reduction compared with SiO<sub>x</sub> passivated photodetectors. These measurements yielded R<sub>0</sub>A product values of 1.4 x 10<sup>3</sup> Ω·cm<sup>2</sup>, 4.0 x 10<sup>4</sup> Ω·cm<sup>2</sup> and 3.7 x 10<sup>5</sup> Ω·cm<sup>2</sup> for the unpassivated, SiO<sub>x</sub> passivated and Al<sub>2</sub>O<sub>3</sub> passivated samples, respectively. Dependence of dynamic resistance-area product at zero bias

vs. perimeter to area ratio measurements revealed that Al<sub>2</sub>O<sub>3</sub> passivated diodes improve surface resistance ( $r_{\text{surface}}$ ) of a factor of 200 and 50 when it is compared with unpassivated and SiO<sub>x</sub> passivated diodes, respectively at 77K. Responsivity and detectivity ( $D^*$ ) are determined as 1.33 A/W and  $1.9 \times 10^{13}$  Jones, respectively for the Al<sub>2</sub>O<sub>3</sub> passivated photodetector at 4  $\mu\text{m}$  and 77K at zero bias. Quantum efficiency (QE) of the passivated photodetector has been determined as % 41 for single pass front illumination condition. Dark current measurements as a function of temperature revealed that passivated devices show Arrhenius type of behavior at higher temperatures. This is an indication that dominant current is bulk diffusion current. The calculated activation energy was found to be close to the design band gap as 0.233 eV. ALD coating of p-i-n InAs/GaSb superlattice photodetectors with Al<sub>2</sub>O<sub>3</sub> is a efficient passivation technique.

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