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Author: Ewa Papis-Polakowska, Janusz Kaniewski, Jarosław Jureńczyk, Agata Jasik, Krzysztof Czuba, A. E. Walkiewicz, Jacek Szade

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Surface passivation of (100) GaSb using self-assembled monolayers of long-chain octadecanethiol

E. Papis-Polakowska,^{1,a} J. Kaniewski,¹ J. Jureńczyk,¹ A. Jasik,¹ K. Czuba,¹
A. E. Walkiewicz,² and J. Szade³

¹Institute of Electron Technology, Al. Lotnikow 32/46, 02-668 Warsaw, Poland

²University of Warsaw, Biological and Chemical Research Centre, Al. Zwirki i Wigury 101, 02-089 Warsaw, Poland

³A. Chełkowski Institute of Physics, University of Silesia, ul. Uniwersytecka 4, 40-007 Katowice, Poland

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The passivation of (100) GaSb surface was investigated by means of the long-chain octadecanethiol (ODT) self-assembled monolayer (SAM). The properties of ODT SAM on (100) GaSb were characterized by the atomic force microscopy using Kelvin probe force microscopy mode and X-ray photoelectron spectroscopy. The chemical treatment of 10mM ODT-C₂H₅OH has been applied to the passivation of a type-II superlattice InAs/GaSb photodetector. The electrical measurements indicate that the current density was reduced by one order of magnitude as compared to an unpassivated photodetector. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4949754>]

GaSb and related materials are well recognized for their application in modern infrared photonic devices. In particular, type-II InAs/GaSb superlattice (T2SL) is attractive for the third generation of infrared photodetectors as an alternative material system to HgCdTe alloy for improved stability, reduced Auger recombination and unwanted tunneling currents.^{1,2} It is well known that GaSb exhibits the chemically active surface, therefore, Sb-based devices suffer from the rapid oxidation of the surface in the air inducing high surface-leakage currents. Additionally, an elemental Sb may occur at the oxide/GaSb interface, giving rise to the conduction path parallel to the interface.³

Thus, in order to eliminate these problems and improve the overall device performance, the surface passivation is necessary. Generally, efficient passivation must both minimize the surface states density (electronic passivation) and protect the surface prior to the oxidation (chemical passivation). On the other hand, the passivation process should not induce additional stress and not destroy the complex thin layered superlattice structure. Various passivation methods have been reported in the literature, including the deposition of the dielectric coatings, the overgrowth of a wide band-gap semiconductor layer, polyimide capping and the modification of atomic structure. The results of our previous work show that the modification of the atomic structure using the (NH₄)₂S-based treatment improves the electrical properties of T2SL InAs/GaSb photodetector, however, it can disrupt the stability of the surface/interface due to the mesa etching and leave unwanted sulfur residues.⁴ From the chemical point of view, the deposition of organic self-assembled monolayers (SAMs) may offer the several practical benefits compared to the traditional treatment, based on an inorganic sulfides. In particular, the sulfur containing long-chain thiol can reduce the superficial native oxide layer and protect the surface without any etching. Generally, SAMs are defined as “a molecular assemblies that are formed spontaneously by the immersion of an appropriate substrate into a solution of an active surfactant in an organic solvent”.⁵ The long-chain thiol is a perfect type of such a surfactant because it consists of a surface-active sulfur group that binds to the semiconductor surface, a hydrocarbon chain of various lengths that defines the packing of the monolayer, and the functional group

^aCorresponding author: papis@ite.waw.pl (E. Papis-Polakowska)

at the end determines the functional properties of the thiol. Particularly, the alkanethiol SAMs on GaAs surfaces can be used for bio- and chemical sensing, molecular electronics, nanolithography and surface passivation. SAMs are created from a solution of the desired thiol in alcohol, allowing to obtain chemical resistant long-term stable passivated layers. The low dielectric constants of alcohol affect the formation of stronger, in comparison with an aqueous solution, covalent bonds between sulfur and semiconductor atoms. This phenomenon is known as the solvent effect.⁶

While a number of investigations have been performed in order to perform SAM thiol-based treatment of GaAs, InP and InAs surface,⁷⁻⁹ there is no information about the thiol reaction of GaSb and related materials. Although, Salihoglu *et al.* report the effects of an octadecanethiol (ODT) monolayer on type-II InAs/GaSb photodetector, however, they do not explain the mechanism of passivation.¹⁰ Furthermore, they show the improve of the dark current density only at 77 K temperature. From the practical point of view, the higher temperatures of the detector operation are desired. In particular, the temperature of 225 K obtained by means of 4-stage thermoelectric Peltier cooler is important.

In this work, we present the novel study of ODT SAM on the (100) GaSb surface. The properties of (100) GaSb surface covered with ODT monolayers were investigated by atomic force microscopy (AFM) using Kelvin probe force microscopy (KPFM) mode and X-ray photoelectron spectroscopy (XPS). We propose to use ODT SAM, as an alternative to the $(\text{NH}_4)_2\text{S}$ -based treatment, for the passivation of T2SL InAs/GaSb photodetector. The passivation efficiency has been determined by the current-voltage (I-V) characteristic measurement.

(100) GaSb substrates, tellurium doped to the concentration of $n = 5 \times 10^{17} \text{ cm}^{-3}$ were used in the experiments. Prior to the passivation treatments, the samples were cleaned sequentially with hot acetone, hot and cold isopropanol for 5 min each. The GaSb samples were then etched in 5% HCl for 1 min in order to remove surface oxides followed by direct rinsing in degassed ethanol. The small amount of dissolved oxygen in ethanol was removed by bubbling with dried nitrogen gas for 30 min. After drying in nitrogen flow, one sample was immersed in 10 mM ODT- $\text{C}_2\text{H}_5\text{OH}$ solution at RT for 72 h and rinsed in degassed ethanol for 3 min and dried in a nitrogen stream, while the second sample was immersed in 21% $(\text{NH}_4)_2\text{S}$ at RT for 30 min and rinsed in deionized water for 1 min and dried with a nitrogen flow.

The both of $(\text{NH}_4)_2\text{S}$ and ODT compounds were obtained from Aldrich in 99.9% and 98.9% purity, respectively.

The surface topography and the surface potential were examined by the Agilent/ Keysight 5500 AFM system which was equipped with the standard 90 μm scanner and the triple-lock in the MAC III controller. In contact mode of imaging, the tip usually lightly touches the surface and is moved up and down with the topographical features of the sample. With increased force the probe can interact strongly with the sample and remove soft matter from its surface. This approach is useful in the nanografting technique used for the thin and soft layers characterization methods.¹¹ The KPFM is an extension of AFM that provides the ability to map the surface potential in addition to imaging of the surface topography. The surface potential is determined by eliminating the electrostatic interactions between the tip and sample and by applying a Direct Current (DC) bias which is tuned by a feedback loop that monitors mechanical oscillations induced in the tip due to an Alternating Current (AC) voltage ($U_{\text{AC}} = 1 \text{ V}$). The KPFM images were recorded using lift mode (also known as a hover mode) operation. The surface potential images were recorded registered in air using Nanoworld NCH cantilevers with JPK Nanowizard II AFM in a hover mode KPFM.

The chemistry of (100) GaSb surface was analyzed by XPS using a Physical Electronics PHI 5700 spectrometer with monochromatized Al K_{α} ($E = 1486.6 \text{ eV}$) radiation system. The XPS database from Physical Electronics Handbook of Photoelectron Spectroscopy¹² and National Institute of Standards and Technology¹³ database were utilized to identify the chemical states of elements. The MULTIPAK software of Physical Electronics was used to deconvolute the XPS spectra and calculate atomic concentrations. The detector structure consisting of a p-doped GaSb contact layer ($p \sim 10^{18} \text{ cm}^{-3}$), 300 period pairs of undoped 10 monolayer (ML) InAs /10 ML GaSb and the 20 nm thick n-doped InAs cap layer, was grown on undoped (100) GaSb substrate by means of molecular beam epitaxy (MBE). Detectors with an active area from $50 \times 50 \mu\text{m}$ to $400 \times 400 \mu\text{m}$ were performed by use of the photolithography and a dry BCl_3/Ar plasma etching techniques. Then, the ohmic

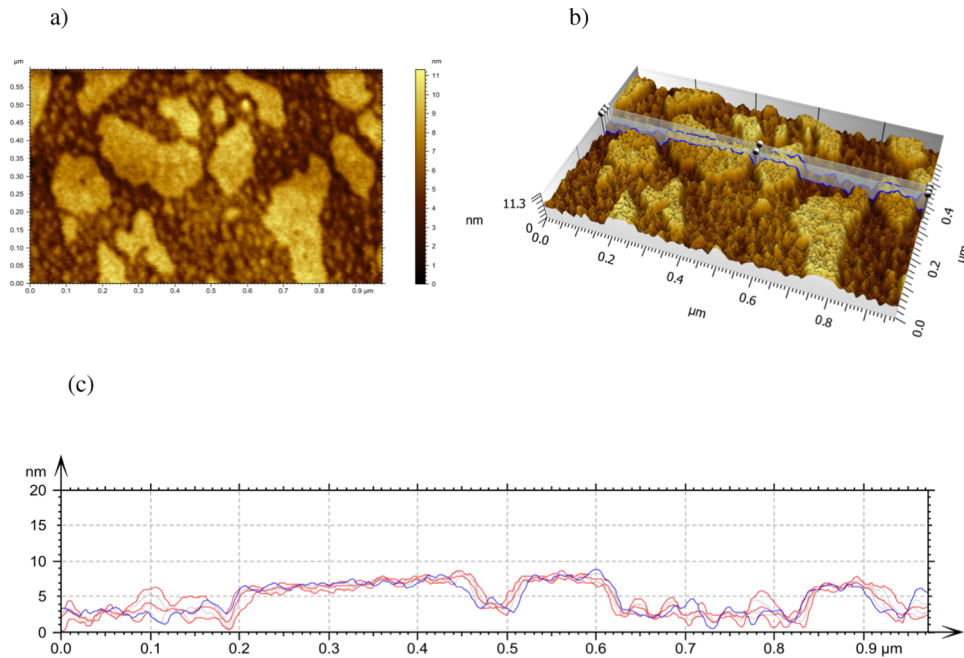


FIG. 1. (a) AFM image of GaSb surface topography after passivation in 10mM ODT- C_2H_5OH , (b) 3D projection of surface topography with profiles extraction indicator, (c) the height profile along lines in (b).

contact was defined by evaporating of Ti (500 Å)/Pt (500 Å)/Au (3000 Å) on the top contact layer. Current-voltage characteristics in both forward and reverse-bias mode were measured at different temperatures (75 K-300 K). The values of leakage current density were applied to determine the passivation effectiveness at the temperature of 200 K.

The AFM topography image and height profile on the (100) GaSb surface after treatment in 10mM ODT- C_2H_5OH shown in Fig. 1, reveals the presence of islands on the top of the substrate, typical for the thiols monolayers deposition.^{14,15} The height of islands is uniform and it is about 5 nm – Fig. 1(b) indicating that the area of the islands can be even a bilayers of GaSb surface. The similar results were obtained for the GaAs substrate.¹⁶ This is the effect of the interdigitation phenomenon.¹⁷ According to the literature research, our work is a pioneer study in the subject, for the first time the results of study of the GaSb surface using SAMs are presented. This is the reason why there is no reference on this subject. Furthermore, our existing experience indicates that even longer period of rinsing in ethanol does not allow to remove the excess of particles. This applies to both the n- and p- type GaSb substrate.

The fundamental question in these experiments was if we obtained a homogeneous layer outside the islands. To answer that, a nanolithography was performed to create a special pattern over the surface of ODT on the (100) GaSb surface by using an AFM probe. The scratch test was needed not only to check the ODT layer thickness but primarily look into the surface potential difference between the ODT layers and the GaSb surface. It is well known that water contact angle measurement is a powerful method to check the quality of SAMs and we have to plan perform it for n- and p-type of GaSb substrates. Due to the fact that we wanted to investigate not only for the surface quality but also for other properties we decided that for this pioneer study the scratch test provides conditions allowing us to draw several conclusions from one simple test.

Figures 2 and 3 present the AFM topography image with the height profile and a corresponding surface potential. The height of this pattern changes from 10 nm to 20 nm - Fig. 2(b). The Fig. 3(a) exhibits a pronounced difference ($U = 100mV$) in the surface potential on the border of the pattern – see cross-section plot, Fig. 3(b). The difference in the surface potential suggests that the surface outside the pattern is uniform as a result of the puncture of the thiol layer to the semiconductor surface.

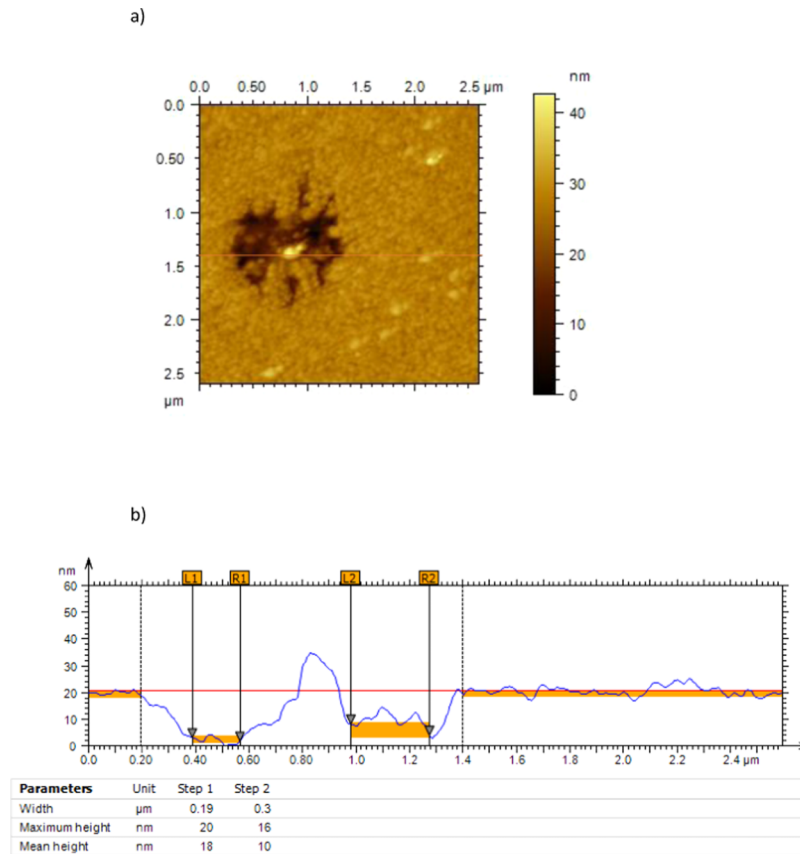


FIG. 2. (a) AFM topography of ODT thiol pattern on (100) GaSb surface, (b) the height profile along line in (a).

Figures 4 and 5 show the results of fit of the XPS spectra which contain contribution from Ga 3s and S 2p levels. The spectra were obtained within the period of 2 months (Fig. 5) shows the spectrum obtained later. Both spectra were acquired using the same spectrometer and with the same parameters. The studied area had the diameter of 0.8 mm. The tested region of the sample was situated in the same central part of the sample but we cannot prove that exactly the same part was measured. The sample was stored in air between two measurements. There is a clear difference between two sets of spectra. First, the ratio S/Ga derived from the intensities of the fitted lines of S 2p and Ga 3s changed from 0.37 to 0.56. Second, the position of the S 2p line changed while the energy and line width of the Ga 3s line was roughly unchanged. The variation of the S 2p photoemission binding energy (BE) can be discussed in relation with bonding between the sulfur atom in the ODT molecule and GaSb substrate. According to the literature data binding energy of the S 2p_{3/2} line in pure ODT is 163.5 eV.¹⁸ It is close to the energy we observed for the sample stored in air. The lower BE can indicate the bonding of the sulfur atom to the GaSb substrate. The energy for the bonding of the sulfur atom to GaAs is reported as about 162 eV.^{18,19} It is worth to mention that BE of about 162 eV is common for sulfides.¹³ The position of the S 2p_{3/2} line which was observed for the sample measured immediately after passivation, indicates the formation of bonding between thiol groups and GaSb substrate. The AFM observations indicate a possible formation of excessive islands residing on the ODT monolayer. The position of the sulfur line originating from the interface between double layers would be then rather close to that found in pure ODT. Thus, the S 2p photoemission doublet line observed in Fig. 4 for the as prepared sample would be a composition of the lines ascribed to the bonding with the GaSb substrate (visible as lines at 163.2 eV and 164.4 eV) and the one coming from the second ODT layer (163.7 eV and 164.9 eV). The bonding to the substrate appears to be relatively weak and due to the contact with air it is probably broken after 2 months. The ODT molecules are then situated on the surface of GaSb

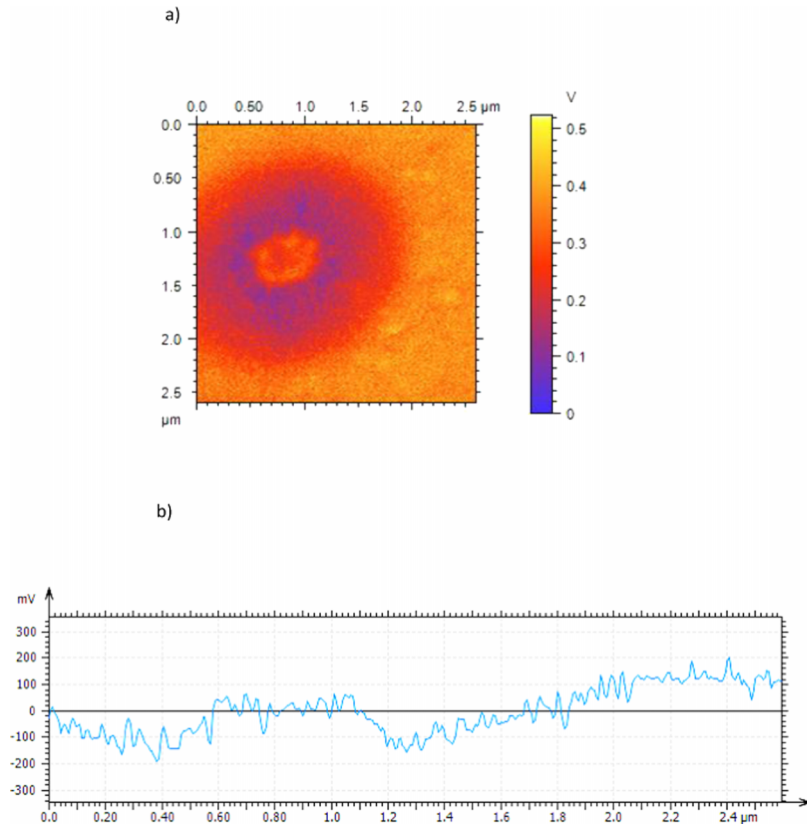


FIG. 3. The surface potential (a) and profile (b) of ODT thiol pattern on (100) GaSb surface.

where additional oxides of Ga and Sb are formed. This causes a relative increase of sulfur content with respect to gallium which means that passivation process requires the second step in order to protect the surface against the air.

The surface passivation efficiency has been monitored by current-voltage characteristics. The electrical characteristics at 225 K, obtained for T2SL InAs/GaSb photodetectors, unpassivated and

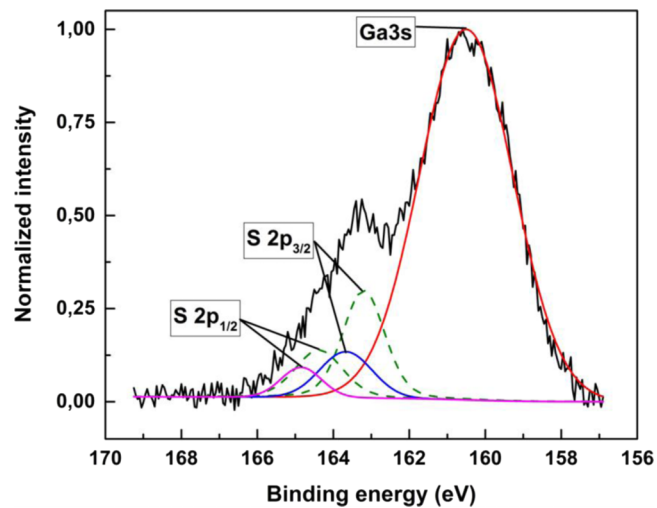


FIG. 4. XPS spectra of Ga 3S and S 2p levels for the (100) GaSb surface after passivation in 10 mM ODT-C₂H₅OH. Deconvolution results are shown in the same figure. The green dashed line corresponds to the S bonded with the GaSb substrate, blue and pink lines are coming from the ODT layer.

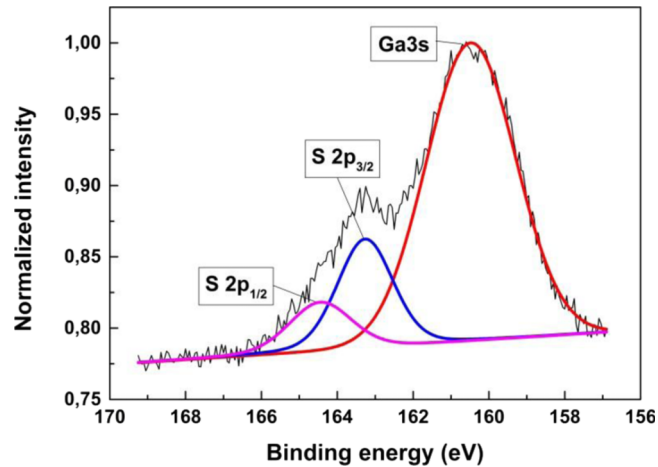


FIG. 5. XPS spectra of Ga 3S and S 2p levels for (100) GaSb surface after passivation in 10 mM ODT-C₂H₅OH. The measurement was performed 2 months after the passivation. Deconvolution results are shown in the same figure. The blue and pink lines are coming from the ODT layer.

passivated by means of two different methods, are shown in Fig. 6. Before passivation the dark current in the reverse bias regime saturates relatively fast and for the voltages greater than about $U = -60$ mV the current starts to increase more slowly than for the near zero biases. After passivation in 21% (NH₄)₂S the dark current decreases a little in the whole range of biases. The greatest decrease, about 2 times, is observed for the bias voltages up to $U = -0.5$ V. After passivation in 10mM ODT-C₂H₅OH a greater improvement in the dark current occurs, especially in the low reverse bias voltage regime. For the near zero voltages the dark current is reduced by one order of magnitude. The effect of the improvement only for low voltages is correlated with the size of the structure and bulk current mechanisms which starts to dominate at this temperature.

In conclusion, the passivation of (100) GaSb surface was investigated with self-assembled monolayers of the long-chain octadecanethiol. The AFM and KPFM techniques were used to characterize the pattern of the ODT layer on (100) GaSb surface, in terms of topography and surface potential. Such an innovative approach of the surface examination has been allowed to show the homogenous surface with the nano islands having a thickness of $d = 5$ nm. The XPS results indicate the formation of the bonding between thiol groups and GaSb substrate. This bonding appears to be

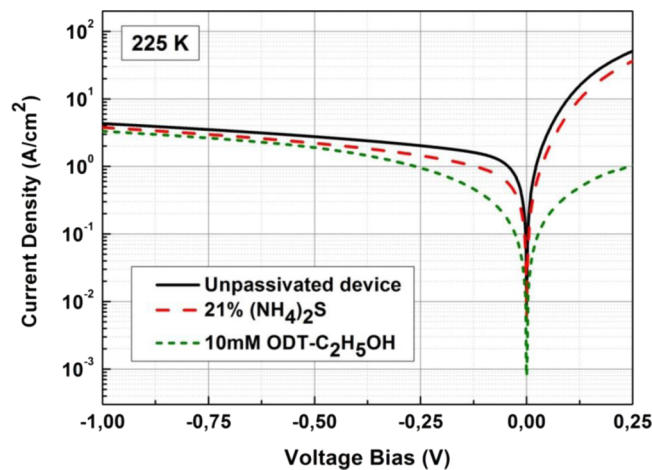


FIG. 6. Current-voltage characteristics at 225 K for T2SL InAs/GaSb photodetectors: unpassivated and passivated in 21% (NH₄)₂S and 10mM ODT-C₂H₅OH.

relatively weak and due to the contact with the air, it is probably broken. The ODT-based treatment is promising for the passivation of a T2SL InAs/GaSb photodetectors. The dark current was reduced at least by one order of magnitude for T2SL InAs/GaSb detector passivated in 10mM ODT-C₂H₅OH but an effective passivation process requires the second step - an encapsulation - to protect the surface for a long time.

ACKNOWLEDGMENTS

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