Study of thiols deposition on GaAs

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A genuine GaAs surface is covered with a relatively thick layer (~nm) of native oxide pinning the Surface Fermi level within the band gap of semiconductor. The method presented in this work is related to sulfur passivation by treating n-GaAs in different solutions of alkane thiols. At the surface of GaAs it is developed an adherent layer of sulfur compound as a result of chemical interaction of sulfur ions with GaAs(100) face, that are putted in evidence by scanning electron microscopy (SEM) images and second harmonic generation (SHG) analysis. Using X-ray photoelectron spectroscopy (XPS) is presented a detailed analysis of XPS data at the surface of thiols on GaAs together with the presence of the covalent bond As-S. The electric characteristics of the AuGeNi/Thiol/GaAs structure are presented in I (V) curves recorded in the region of small currents.

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1. Introduction

GaAs is the most promising III-V semiconductor compounds due to its electronic properties as direct energy band gap and the high mobility at room temperature of its charge carriers.

The technological importance is related to its applications in optoelectronics as laser diodes, light emitting diodes or solar cells of high concentration factor. The native oxides of GaAs have a complicated chemistry where both As_2O_3 and Ga_2O_3 compounds will form when a clean GaAs surface is exposed to oxygen and light [1]. The formation of Ga_2O_3 is thermodynamically favored, leaving bare arsenic atoms embedded within the oxide near the oxide/GaAs interface. The As_2O_3 is also mobile at grain boundaries, resulting in a no uniform oxide in which an As_2O_3-rich layer is found near the oxide/air interface. It is worth to mention that both Ga_2O_3 and As_2O_3 are somewhat soluble in water, and their solubilities are dependent on pH. In addition, the high density of surface/interface states that exists between the native oxide and GaAs caused either stoichiometric deficits or structural defects, and this is a major inconvenience for device performances [2].

The real GaAs surface covered with native oxide (~few nm) is the origin of a high density of surface states pinning the surface Fermi level within the band gap of semiconductor, affecting the operation of different semiconductor devices where the elemental As is believed to be responsible for the surface state density) [3].The complicated chemistry of the GaAs native oxides has prevented the development of a simple and robust passivation scheme for this surface.

Sulfur and other chalcogenides have been explored as electrical passivating agents for GaAs, that started with the work of Sandroff et all in 1987 [4], by treating the GaAs surface with $Na_2S•9H_2O$, a treatment that improve the electrical characteristics of GaAs. Following the discovery of GaAs passivation with inorganic sulfides, several groups have demonstrated passivation of III-V semiconductors with thiol-type self-assembled monolayers (SAMs) [5-9]. The surface –active sites with respect to surface-S bond formation were Lewis acidic in nature, consistent with As-S and Ga-S bond formation putted in evidence by XPS measurements. From the study of surface morphology of GaAs passivated with alkanethiol SAMs, Allara and co-workers [7, 8] have shown that the SAM structure is similar to that for alkane thiols on Au surfaces and that the SAMs can be used as resists and as insulating spacer in Schottky barrier devices.

In this paper we examine the formation of SAMs from alkane thiols namely dodecanethiol (DDT) and octadecanethiol (ODT) on n-GaAs (100) and p-GaAs (100). There are presented morphological aspects, a XPS-analysis for Ga-S and As-S bond formation, SHG studies together with electrical characteristics measured in normal laboratory conditions.

2. Experimental

The experiments were performed on n-GaAs (100) and p-GaAs (100). Prior to sulfur treatment the wafers were washed in water and then degreased in trichloroethylene (boiling for 1 minute) and rising in acetone at room temperature. The samples were chemical etched in $HCl:H_2O$ (DIW) (1:1) for t=30 sec. at room temperature, followed by rising in DIW at room temperature. The GaAs wafers maintained the initial aspect of the optical polished front surface. The sulfide treatment was carried out in two different solutions: (a)-1-dodecanethiol 98% catalog Alfa Aesar Johnson Matthey Company (DDT)-CH_3-$(CH_2)_{11}$-SH and (b) –solution of octadecanethiol (ODT) - CH_3-$(CH_2)_{17}$-SH in ethylic alcohol concentration: 0.5443×10^{-5}M. The few drops of sulfide solutions were added on GaAs surface and afterwards the wafers were dried in air flux at room temperature (aprox. 24-25^{0}C) for 2 or more days. In the

case of n-GaAs, for the electric measurements, on the back side of wafers is deposited a metallic contact of AuGeNi.

The SEM images for morphological aspects of thiols deposition on GaAs were recorded on a Zeiss EVO 50 XVP system.

The signal of Second Harmonic Generation analysis was performed in the experimental set-up presented in Fig. 1. The SHG investigations were performed by using the fundamental of a Q-switched YAG:Nd laser (1064 nm at 20 Hz, with 16 nsec. pulse length and 25 mJ in a spot size of 0.2 cm^2). As can be observed in Fig. 1 in the experimental set-up there exists a black-box where there are placed the sample and the photomultiplier. At the entrance in the black-box is placed an interferential filter for laser radiation at 1064 nm. A polarized prism is placed after filter and it selected only the p-polarized wave before it reached the sample and the analyzer prism is placed between the sample and photomultiplier and let it pass only the radiation p-polarized after reflection on sample. A step-by-step motor rotates the sample around an axis perpendicular on its surface plane. In this way is recorded an anisotropy of the amplitude of second harmonic as a function of azimuthally angle. The incidence angle of fundamental radiation on the sample is usually 45^0. The optical filter that allows the pass of the radiation at 532 nm is fixed before the entrance window of photomultiplier, in order to block the penetration of radiation of fundamental wavelength. The signal at the photomultiplier is integrated on 30 laser pulses. The computer acquires the signal from integrator and from command unit of step-by-step motor. By measuring the rotational anisotropy of second harmonic signal is obtained a complete description of the shape and amplitude for the variation of nonlinear susceptibility of the surface. The SHG signal generated at single crystalline n-GaAs during a complete rotation around their normal axis in a p-in/p-out configuration closely reflects the surface symmetry.

The XPS recorded spectra were obtained using SPECS XPS spectrometer based on Phoibos analyzer with monochromatic X-rays emitted by an anti-cathode of Al (1486.7 eV). The hemispherical analyzer was operated in the constant energy mode with pass energy of 5 eV giving an energy resolution of 0.4 eV, which was established as FWHM (full width half maximum) of the Ag 3d5/2 peak. The analysis chamber was maintained in ultra high vacuum conditions (~10^{-9} torr). As a standard practice in some XPS studies, the C (1s) line (285 eV) corresponding to the C-C line bond had been used as reference Binding Energy (BE) [10]. The recorded XPS spectra were processed using Spectral Data Processor v 2.3 (SDP) software. In its structure SDP soft uses the deconvolution of a XPS line as a specific ratio between Lorentzian and Gaussian shape and these characteristics ensures a good fit of experimental data.

The analysis of electrical behavior included the recorded of current that passed through the structure AuGeNi/thiol(DDT &ODT)/n-GaAs at an applied voltage. The registration was done on the instrument Keithley Electrometer/ high resistance meter 6517 A.

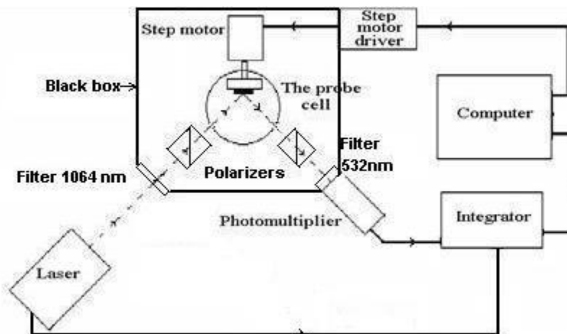

Fig. 1. Experimental set-up for SHG measurement.

3. Results and discussion

The samples of n-GaAs (100) and p-GaAs (100) exposed to thiols (ODT) deposition have been examined by SEM facilities as can be observed in Fig. 2(a & b).

As can be observed a composed layer with a good uniformity is present on n-GaAs (100) passivated with ODT, is worth to mention that are also present foreign fragments that had have the source from the air flow drying (for the image with the index 20μm). The adherence on n-GaAs (100) is good and we remarked as regards the samples with thiols on p-GaAs (100) a static charge during the measurement doubled with a less adherence on the substrate as can be observed on Fig. 2 (b).

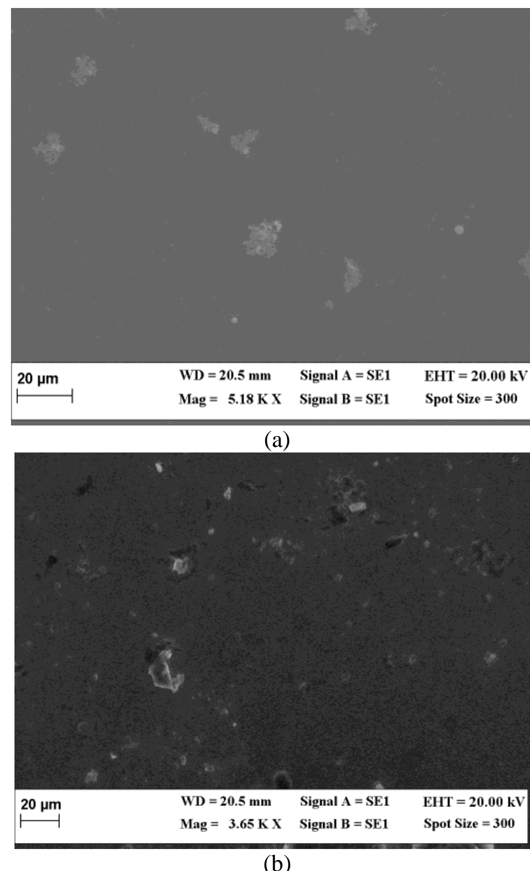

Fig. 2. SEM image n-GaAs(100) passivated ODT (a) and p-GaAs(100) passivated ODT (b).

The analysis of SHG signals on n-GaAs(100) passivated ODT and p-GaAs(100) samples passivated ODT put into evidence the typical structure of four lobes that is characteristic to the face GaAs(100) together with amplitude variations of SHG signal at the passivated surface as can be seen in Fig. 3 (a and b). The measurements have been made in the configuration polarized p-wave at the entrance (p-in) and s-out at the exit. (Fig. 3 a).

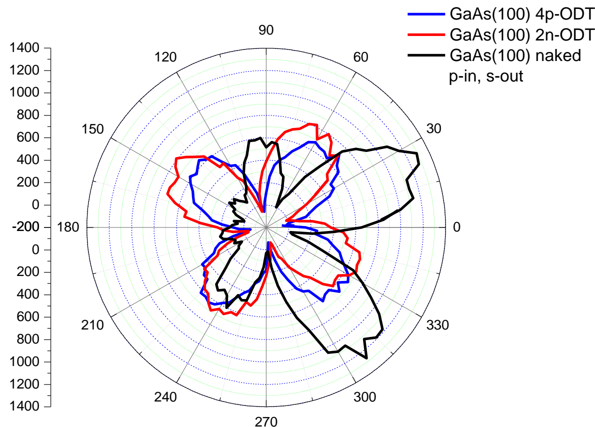

Fig. 3 (a)- The SHG signal on GaAs(100) samples passivated ODT in configuration p-in/s-out.

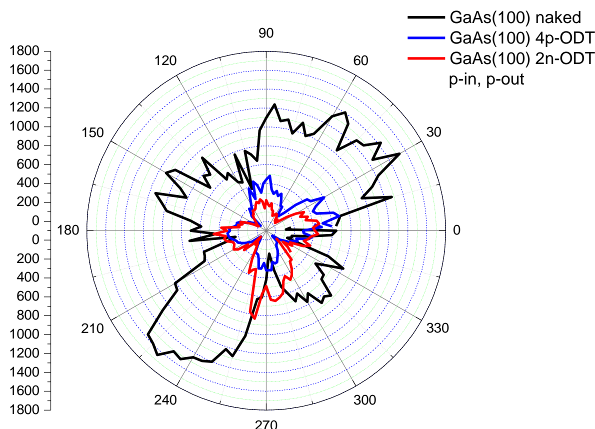

Fig. 3. (b) - The SHG signal on GaAs (100) samples passivated ODT in configuration p-in/p-out.

In Fig. 3 (b) there are presented the SHG data in the configuration of polarized wave p-in/p-out. As a general remark we can say that the dominant contribution is related to the bulk material on GaAs (100) face and this is a volume dipole with 4 lobes. The surface contribution due to the thiols passivation (sulfur dipoles) is observed as fluctuations of the basic signal. It can be assumed that at the surface is present an adsorption process, on the samples covered with an adherent compound as a result of passivation with ODT.

The analysis of X-ray Photoelectron Spectroscopy (XPS) shows that the exposure of GaAs surfaces to the organic compounds from this system enrich the semiconductor surface in thiols but this exposure did not remove the excess of elemental As and do not form a compound As_2S_3 as a protective layer to GaAs. This result implies that the complete removing of As^0 or the formation of monolayer of As_2S_3 it is not a condition *sine qua non* in order to induce a decreasing of recombination rate at the etching surfaces of GaAs [11].

The systems of self-assembled mono-layers (SAM) have been studied with interest ant the application of the system thiol/Au at electrodes and modified sensors [12, 13, 14] is of considerable interest as an example of SAM systems related directly to a semiconductor. From this point of view the present study is related to a new class of self-organized mono-layers derived from SAM-s of alkanethiol deposited directly on GaAs surface [15]. The viability of sulfur chemistry on GaAs (S/GaAs) that allows the existence of self-assembling is presented in literature [15] as well as in our laboratory experience which indicated that at room temperature there exists coverage with inorganic sulfides [16]. In the case of ODT the literature [15] indicates that the mono-layer consists in chains of alkali conformational ordered, stabile and with a high organization related directly to the GaAs surface. The chemical processing in the preparation of GaAs surface conduced to o surface covered with As [17]. The SAMs obtained at room temperature has an incomplete aspect (as observed in SEM images) and are disordered. The technological solution can be a thermal treatment at 100^0C [15] that would conduce to a good quality for mono-layers.

In order to investigate the composition for the GaAs samples treated with thiols at their surfaces it was done a XPS analysis, on n and p-GaAs (100). We present in Fig.4 the XPS spectrum for As 3d on n-GaAs (100) treated with DDT.

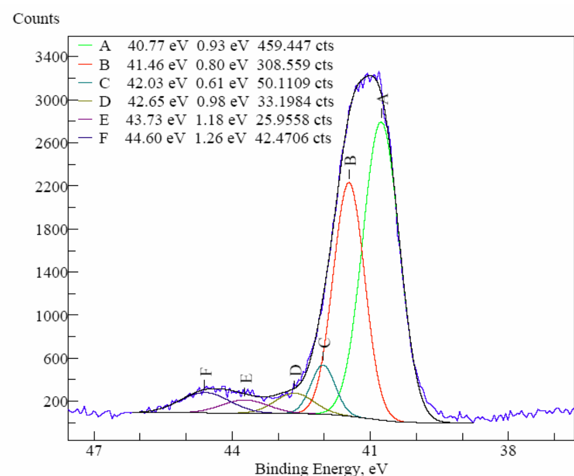

Fig. 4. XPS signal for As 3d on n-GaAs treated with DDT.

The As 3d line is composed of two peaks 3d5/2 and 3d 3/2 positioned at approximately 0,7 eV one to the other and with a surface ratio of 3/2. For noisy and small peaks the two lines can not be seen, so the deconvolution was

done using one larger peak. The A and B peaks represents the doublet for As in GaAs compound, the C and D peaks represents the doublet for elemental As and E peak is related to the bond As-S and F peak represents the oxidized As : As_2O_3. In Fig. 5 we present the signal for Ga 3d.

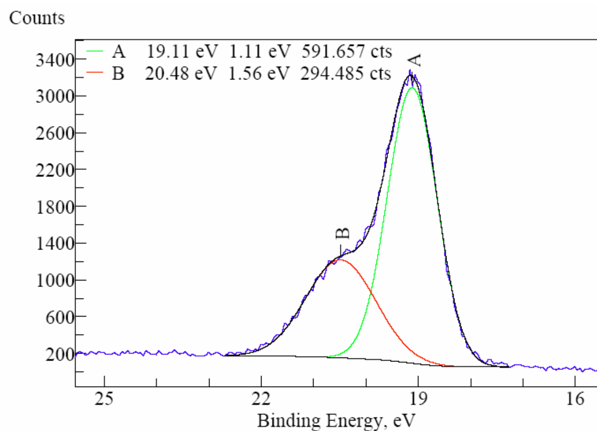

Fig. 5. XPS signal for Ga 3d on n-GaAs treated with DDT.

In this spectrum the A peak represents Ga in GaAs and B peak represent Ga oxide. For the sample of n-GaAs (100) treated with ODT is presented in Fig. 6 the As signal.

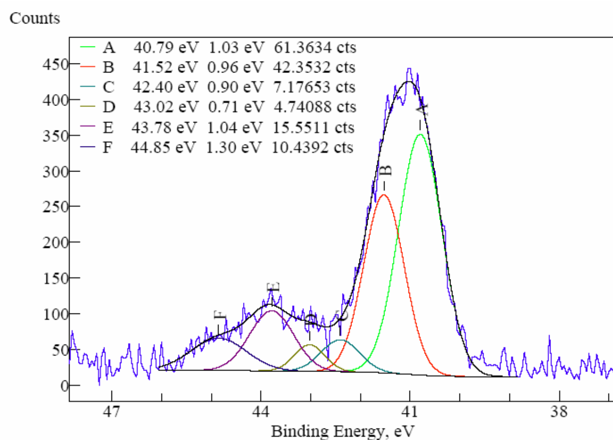

Fig. 6. XPS signal for As 3d on n-GaAs treated with ODT.

In XPS spectrum, The A and B peaks are related to As in GaAs, C and D peaks are related to elemental As, and the bond As-S presented in E peak it is much stronger than in the case of DDT on GaAs; the F peak is related to As_2O_3. In Fig. 7 we present the XPS spectrum for Ga 3d on n-GaAs (100) treated with ODT.

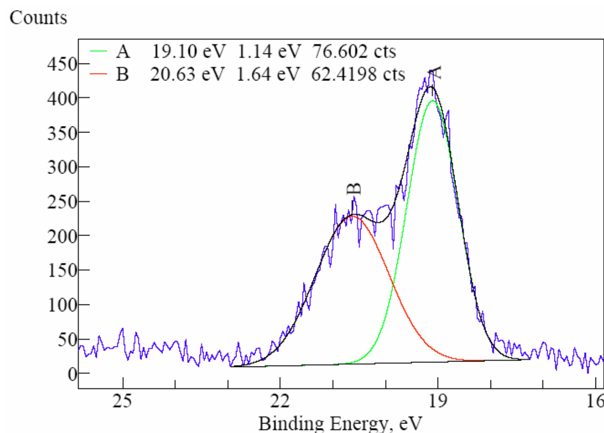

Fig. 7. XPS signal for Ga 3d on n-GaAs treated with ODT.

In this spectrum, the A peak is related to Ga in GaAs and B peak is related to Ga oxide. As a general remark as in the case of GaAs treated with DDT there are not observed the Ga-S bonds in XPS spectrum.

In Fig. 8 is presented XPS signal together with the deconvolutions with SDP program for the As 3d in the case of p-GaAs (100) treated with DDT. The peaks A and B represents the doublet of As in GaAs, The C and D peaks represents the doublet of elemental As, the E peak is related to As-S bond and F peak represents As oxide and is more extended.

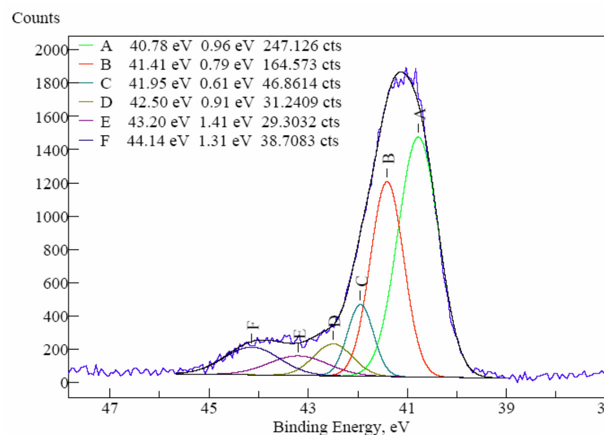

Fig. 8. XPS signal for As 3d on p-GaAs treated with DDT.

In Fig. 9 we present the XPS signal for Ga 3d on a p-GaAs sample treated with DDT.

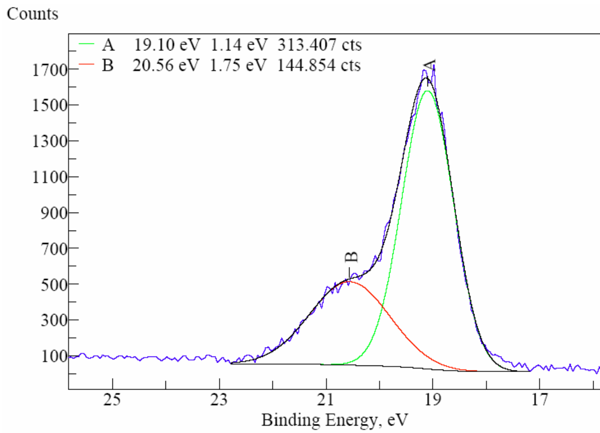

Fig. 9. XPS signal for Ga 3d on p-GaAs treated with DDT.

The A peak represents Ga in GaAs; the B peak is related to Ga oxide and is a large peak. In Fig. 10 present the XPS signal and the respective deconvolution for As 3d on p-GaAs (100) treated with ODT. The assignment of the peaks is the same as in precedent cases, where E peak stands for the As-S bond.

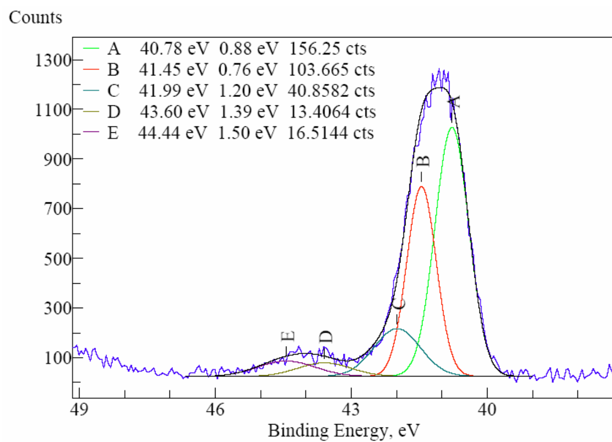

Fig. 10. XPS signal for As 3d on p-GaAs treated with ODT.

In Fig. 11 we present the Ga 3d signal on p-GaAs (100) sample treated with ODT.

The A peak is related to Ga in GaAs and B peak is related to Ga oxide. The results from As 3d and Ga 3d on n-GaAs and p-GaAs treated with DDT and ODT are sustained by similar results of XPS signals of As 2p and Ga 2p. From the signal arisen from S 2p we came to the conclusion that there are no Oxygen bonds , and the Binding Energy situated in that range can be assigned to an As bond or to thiol. It can be observed in the literature [15] that the width of intrinsic line for S 2p (165 eV) is superimposed on Ga 3s peak (160 eV), which is an impediment in a detailed interpretation for the interface bond. The thiols passivation of GaAs surfaces is active in the reduction in the recombination velocity at GaAs surface.

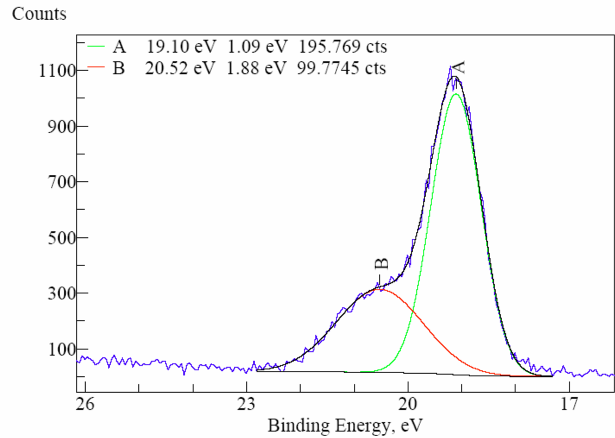

Fig. 11. XPS signal for Ga 3d on p-GaAs treated with ODT.

The analysis of electric behavior was performed on different samples in the system AuGeNi/Thiol (DDT&ODT)/n-GaAs. In Fig. 12 (a, b, c) we present the I-V characteristics.

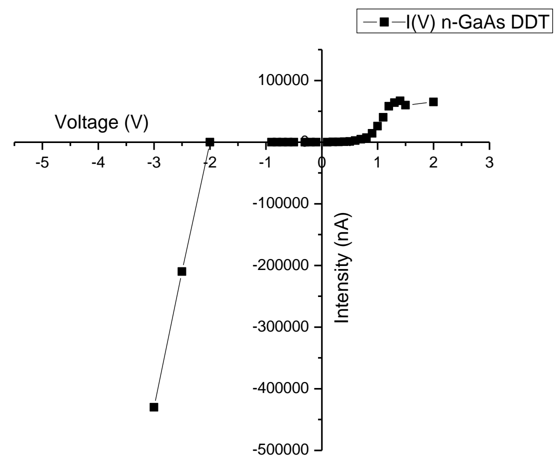

Fig. 12. (a) - I-V characteristic on n-GaAs (100) treated with DDT.

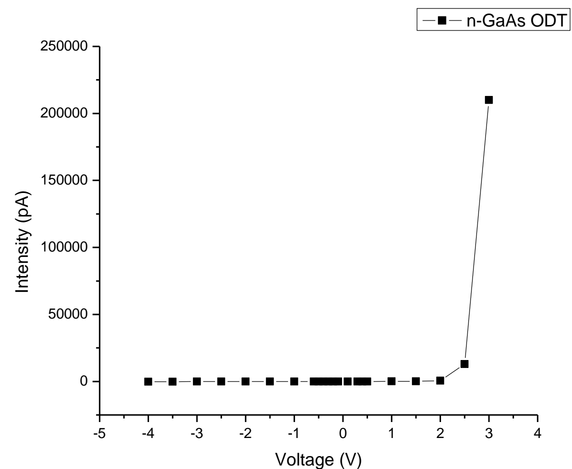

Fig. 12 (b)- I-V characteristic on n-GaAs (100) treated with ODT.

The general characteristics for I(V) curves is the presence of small currents (nA) for n-GaAs samples treated with DDT and the presence of extremely small currents(pA) for n-GaAs treated with ODT, and the conclusion is that the thiols passivated at the surface GaAs. It is interesting to underline the general feature of a diode-especially on n-GaAs treated with ODT but with breakdown regions (especially for n-GaAs treated with DDT), a feature that can be related with the non-uniformity of deposited thiol as it was observed in SEM images. The analysis of these samples in the region of small currents indicates strong instabilities probably due to the contact during the measurement. As can be observed in Fig.12(c), in the region of negative voltages the behavior is almost linear for the case of n-GaAs treated with ODT.

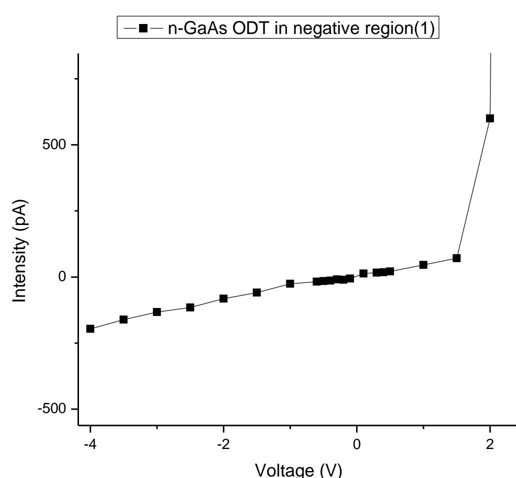

Fig. 12(c) I-V characteristics in negative voltage region on n-GaAs treated with ODT.

Regarding the electric behavior our general remark concerning the thiols passivation is that the passivation with ODT (in alcohol solution used in the laboratory) is more effective than the passivation with DDT (in standard concentration from the firm in catalog).

4. Conclusions

The passivation study with sulfur organic compounds of aliphatic types as dodecanethiol (DDT) and octadecanethiol (ODT) put into evidence the presence of a thin protective layer on the surface of n-GaAs (100) and p-GaAs (100). There are presented detailed analysis of SEM, SHG and XPS on the protective sulfur compound layer. At the surface of GaAs treated with DDT and ODT the analysis highlights the presence of chemical bond As-S which is the result of the passivation of GaAs surface. The electrical analysis of I (V) characteristics indicates the presence of small currents of 10^{-9}A order in the case of DDT/n-GaAs and of 10^{-12} order in the case of ODT/n-GaAs. The n-GaAs samples passivated with ODT had a slight rectifier character.

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