

## ON THE PASSIVATION OF GaAs SURFACE BY SULFIDE COMPOUNDS

R.V.GHITA\*, C.C.NEGRILA, C.COTIRLAN, C.LOGOFATU

*National Institute of Materials Physics, P.O.Box MG 7, Magurele, Bucharest, Romania,*

A genuine GaAs surface is covered with a layer (~few nm) of native oxide pinning the surface Fermi level within the band gap of semiconductor. In this work is presented a study of GaAs surface passivation by sulfur compounds inorganic and organic (alkane thiols), a method that combines both chemical and electronic passivation. 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 surface, a compound putted into evidence by scanning electron microscopy (SEM) images, photoluminescence analysis, second harmonic generation (SHG) measurement and Raman spectroscopy. Using X-ray photoelectron spectroscopy (XPS) it is putted into evidence the presence of covalent bonds Ga-S and As-S as a result of chemical interaction with sulf ions. Electrical characteristic of AuGeNi/thiol/GaAs structure is presented in I (V) recorded in the region of small currents.

(Received July 2, 2013; Accepted September 31, 2013)

*Keywords:* Sulfur passivation, GaAs, SEM, XPS, Photoluminescence, SHG, Micro-Raman Spectroscopy, Electrical measurements

### 1. Introduction

The electronic quality of surfaces and semiconductor/insulator interfaces in III-V semiconductor compounds is very important for a broader use of these materials in microelectronic and optoelectronic applications. GaAs is one of the most promising semiconductor compounds due to its characteristics as direct energy gap and high carrier mobility at room temperature which are exploited in optoelectronic devices (LEDs and Laser Diodes) or in high frequency devices as HEMT. The development of electronic industry requires constant improvement in fabrication of III-V devices a quality related to the present status of thin surface layers. The device surface needs to be passivated in order to reduce electronically active surface states that cause noise [1, 2]. The deficiencies in the surface properties of GaAs have stimulated many attempts to passivate the surface, reduce the surface state density and unpin the surface Fermi level. It is worth to mention that the poor quality of native oxide on GaAs has made the surface passivation challenging and necessitated the use of deposited insulators. The native oxides of GaAs have a complicated chemistry where both  $\text{As}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3$  compounds will form when a clean GaAs surface is exposed to oxygen and light, and these oxides presents water solubility with a pH dependency [3]. The formation of  $\text{Ga}_2\text{O}_3$  is thermodynamically favored, leaving bare arsenic atoms embedded within the oxide near the oxide/ GaAs interface. The  $\text{As}_2\text{O}_3$  is also mobile at grain boundaries, resulting in a non uniform oxide in which an  $\text{As}_2\text{O}_3$ -rich layer is found near the oxide /air interface. 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, affected as is stated the operation of GaAs semiconductor devices. It is believed that the presence of elemental As is responsible for stoichiometric deficits that affects the device performances as being responsible for a high surface state density ( $N_{ss} \sim 10^{12} \text{ cm}^{-2}$  in technological conditions) [4].

---

\*Corresponding author: ghitar@infim.ro

Sulfur and other chalcogenides have been explored as electrical passivating agents for GaAs, a research that started with the work of Sandroff et al in 1987 [5], by treating GaAs surface with  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ , a treatment that improve the electrical characteristics of GaAs. The superior effects of sulfur passivation were demonstrated by a significant enhancement of the photoluminescence (PL) intensity of the treated GaAs surface. As a general remark from the literature [6], the simple sulfur treatment by dipping the GaAs in  $(\text{NH}_4)_2\text{S}_x$  or  $\text{Na}_2\text{S}$  aqueous solutions can provide good electronic passivation, but the chemical passivation is rather poor due to the sulfur compound instability. The ordinary sulfur treatment results in a layer of sulfur atoms bonded to GaAs surface, which can be easily replaced by oxygen after a long time of exposure to air especially illumination [7]. In order to solve the problem of longevity and durability a possible solution is to use the sulfur passivation in oxygen-free solution of  $\text{S}_2\text{Cl}_2 + \text{CCl}_4$ , which is effective for removing the native oxides of GaAs and forming Ga-S bonds [7]. The positive result of sulfur passivation was observed in GaAs surface stability [8, 9] and reduce surface state density and surface recombination velocity ( $v_s \sim 10^7 \text{ cm s}^{-1}$ ), with the consequence of the modification of surface barrier potential on GaAs ( $V_B$  genuine: 0.78 eV) [10] The surface chemistry after sulfide treatment includes the identification of sulfur bonds to GaAs and the efficient remove of native oxide by various pre-treatment methods as presented in literature [11]. 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) [12-16]. The surface active sited with respect to surface-S bond formation were Lewis acidic in their nature consistent with As-S and Ga-S bond formation putted into evidence by XPS measurements. From the study of surface morphology of GaAs passivated with alkane thiol SAMs, Allara and co-workers [14, 15] have shown that the SAM structure is similar to that for alkane thiols on Au surfaces.

In this paper we present a review of the main properties starting with the formation of Ga-S and As-S bonds on GaAs surfaces as identified by SEM, EDS and XPS measurements. Representative optical properties of inorganic sulfur passivated n-GaAs (100) and n-GaAs (110) are related to photoluminescence measurement, second-harmonic generation (SHG) and Raman studies at passivated surface. The formation of Sims from alkanet thrills namely dodecanethiol (DDT) and octadecanethiol (ODT) on n-GaAs and p-GaAs (100) are studied by XPS analysis as regards the formation of Ga-S and As-S bonds, together with electrical characteristics in I-V measurement.

## 2. Experimental

The experiments were performed on n-GaAs (100), n-GaAs (110) Te doped ( $n \sim 10^{18} \text{ cm}^{-3}$ ) and p-GaAs (100) Si doped. 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<sub>2</sub>O (DIW) (1:1) for  $t=30$  sec. at room temperature, and after this procedure the wafers maintained the initial aspect of the optical polished front surface. The sulfide treatment were performed in (a): pure ammonium sulfide  $(\text{NH}_4)_2\text{S}$  (50% H<sub>2</sub>O); (b): sulfur monochloride ( $\text{S}_2\text{Cl}_2$ ) in carbon tetrachloride ( $\text{CCl}_4$ ) (1:10); (c) dodecanethiol 98% catalog Alfa Aesar Johnson Matthey Company (DDT)- $\text{CH}_3-(\text{CH}_2)_{11}-\text{SH}$  and (d): solution of octadecanethiol (ODT)- $\text{CH}_3-(\text{CH}_2)_{17}-\text{SH}$  in ethylic alcohol of concentration  $0.5443 \times 10^{-5}$  M. The few drops of inorganic sulfide solutions were added on n-GaAs surface and afterwards the wafer treatment was stabilized by drying at a spinner. For the sulfur treatment with organic compounds few drops were added on n-GaAs and p-GaAs surface and afterwards the wafers were dried in air flux at room temperature (aprox. 24-25°C) for 2 or more days. For the electrical measurements, in the case of n-GaAs it was deposited the AuGeNi ohmic contact on the back side of wafer.

The SEM images recorded for the morphological aspect of sulfur compound deposition it was used a HITACHI S2 600 N type, operating at 25 kV in vacuum and equipped with an energy dispersive X-ray attachment (EDAX/2001) device.

The XPS spectra were obtained using a SPECS XPS spectrometer based on Phoibos analyzer 150 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 a pass energy of 5 eV giving an energy resolution of 0.4 eV, which was established as FWHH of the Ag 3d 5/2 peak;

analysis chamber is maintained at high vacuum conditions ( $\sim 10^{-9}$  torr). As a standard practice in XPS studies, the C (1s) line (285 eV) corresponding to the C-C line bond has been used as reference Binding energy (BE). The recorded XPS spectra were processed using Spectral Data Processor v 2.3 (SDP) software that in its structure 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.

In photoluminescence experiment, the PL spectra were recorded using a lock-in technique with a standard luminescence set-up composed of two monochromators (excitation and emission), a Xe-150 W lamp as light source a photomultiplier with S1 response as analyzer. The recorded spectra were not corrected for spectral sensitivity of experimental set-up. The PL signal on GaAs was collected from the same sample surface upon the exciting light was incident and is referred to as “front surface photoluminescence.”

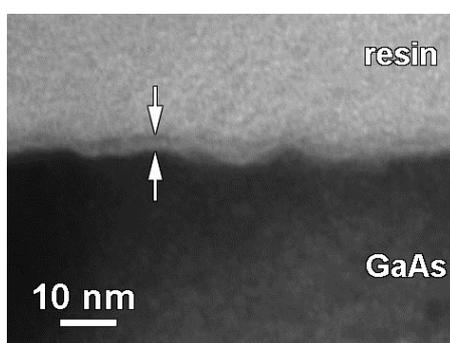
The second harmonic generation (SHG) investigations were performed by using the fundamental of a Q-switched Nd: YAG laser. The experimental set-up includes a black-box where the sample and the photomultipliers (PM) are placed. A polarized prism is placed after the filter and only the p-polarized wave is selected before it reached the sample, the analyzer prism is placed between sample and PM and allows the passing of the p-polarized radiation after reflection on sample. A step-by-step motor rotates the sample around an axis perpendicular to its surface plane, and 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 is usually  $45^{\circ}$ . The optical filter that allows the passing of 532 nm radiation is fixed before the entrance window of PM and the signal of PM is integrated on 30 laser pulses. A computer system acquires the signal from the integrator and from the command unit of the motor. By measuring the rotational anisotropy of the SHG signal, is obtained a complete description of nonlinear susceptibility variation at the surface.

Raman spectra on GaAs were performed in a backscattering geometry at room temperature in air, using a LabRAM HR 800 UV-VIS-NIR Horiba SCIENTIFIC system. The work parameters in our experiment were as follows: an  $\text{Ar}^+$  laser (514.5 nm), power on surface sample: 2.5 mW, measurement range ( $130\text{-}600$ )  $\text{cm}^{-1}$ , laser spot size:  $1\ \mu\text{m}^2$ , objective x100, without attenuation filter, spectra rising parameters (exposure time: 2 sec, accumulation time: 5 sec, accumulation numbers: 5 cycles), resolution:  $0.5\ \text{cm}^{-1}$ , grating: 1800 l/mm.

Analysis of electrical behavior included the recorded of the current that passed through the structure AuGeNi/thiol/n-GaAs at an applied voltage. The recorded signal implies the use of the instrument Keithley Electrometer/ high resistance meter 6 517 A.

### 3. Results and discussion

As it was stated the real surface of GaAs is covered by a layer of compound oxides as can be observed in Fig.1 in TEM image.



*Fig.1 Cross-section TEM image of the GaAs surface at higher magnification showing the presence of an amorphous layer (indicated by vertical arrows)*

The characteristics of native oxides are presented in Fig.2 as XPS recorded spectra of As 3d and Ga 3d lines on GaAs surface. The result of deconvolution by SDP software is as follows: **(a)** for As 3d : 1-BE 40.79 eV(As in GaAs); 2-BE 41.55 eV (As in GaAs); 3-BE 42.19 eV( As-Ga-O); 4- BE 44.12 eV ( $\text{As}_2\text{O}_3$ ), 5- BE 45.07 eV ( $\text{As}_2\text{O}_5$ ) and **(b)** for Ga 3d: 1- BE 19.32 eV (Ga in GaAs); 2-BE 20.13 eV(As-Ga-O), 3-BE 20.81 eV ( $\text{Ga}_2\text{O}_3$ )

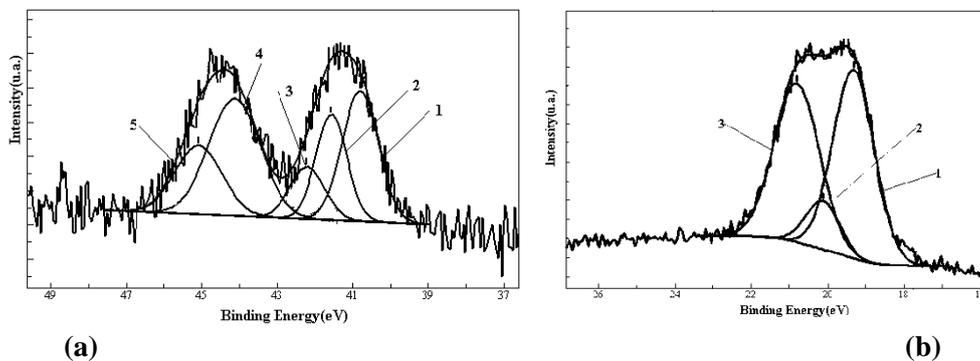


Fig.2 XPS spectra for (a)-As 3d ( $\text{TOA}=30^\circ$ ); (b)-Ga 3d ( $\text{TOA}=30^\circ$ ).

The SEM images provide the direct information regarding the morphology of as prepared samples and confirm the presence of a compound layer as the main result of passivation process. In Fig.3 (a) is presented the micrograph of  $(\text{NH}_4)_2\text{S}$  deposited on n-GaAs (100) and as can be observed the deposition looks like a cluster of sulfur compound. In Fig. 3(b) is presented the micrograph of p-GaAs (100) passivated ODT and as can be observed the sulfur compound is more uniform.

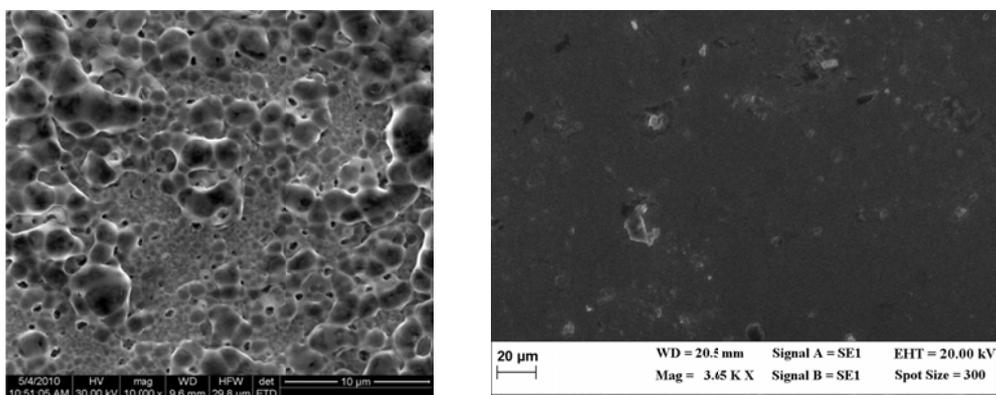


Fig.3 (a)-SEM image of n-GaAs (100) passivated  $(\text{NH}_4)_2\text{S}$  (b) - SEM image of p-GaAs (100) passivated ODT.

The EDS spectrum presented in Fig.4 shows well defined lines of Ga, As, S and O (O signal arises from the aqueous solution of  $(\text{NH}_4)_2\text{S}$ ) and the presence of S line is a consequence of the bond of sulfur ions to GaAs surface. The result of sulfur treatment is a passivated surface that can be used further in technological process.

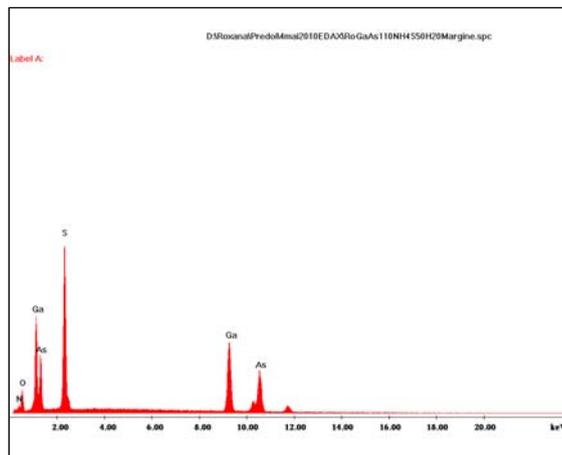


Fig.4 EDS spectrum of  $(\text{NH}_4)_2\text{S}$  deposited on *n*-GaAs (100)

The XPS spectra for *n*-GaAs (100) and *n*-GaAs (110) passivated with  $\text{S}_2\text{Cl}_2$  put into evidence for Ga 2p and As 2p signals the line corresponding to Ga-S and As-S covalent bonds as can be observed in the deconvolution from Fig.5 (a and b). The line identification is as follows: for Ga 2p the B-line corresponds to Ga-S and for As 2p the BE-1323.76 eV (As in GaAs), BE-1325.68 eV (As-S), BE-1327.14 eV (As in  $\text{As}_2\text{O}_3$ ), BE-1329.22 eV (As in  $\text{As}_2\text{O}_5$ ).

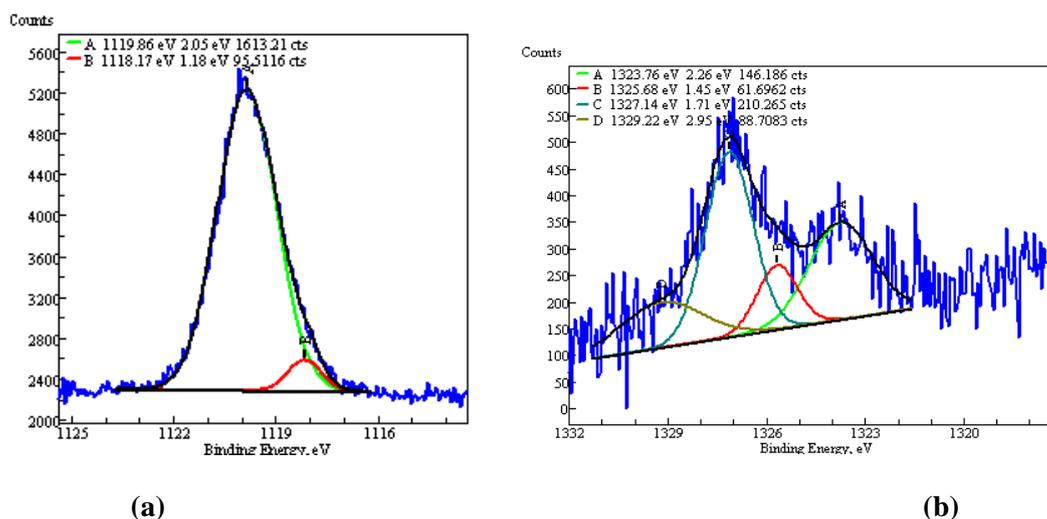


Fig.5 (a) - XPS spectrum of Ga 2p on  $\text{S}_2\text{Cl}_2$  passivated surface of *n*-GaAs (100); (b)-XPS spectrum of As 2p on  $\text{S}_2\text{Cl}_2$  passivated surface of GaAs (110)

The XPS spectra related to the compositional analysis for GaAs surface treated with thiols put into evidence both for *n*-GaAs (100) and *p*-GaAs (100) treated with DDT and ODT the presence of As in GaAs, elemental As, As in oxide and the presence of As-S bond. The XPS analysis involved the signal arisen from As 3d and Ga 3d and it is worth to mention that the Ga-S bond was not put into evidence in both cases of DDT and ODT surface treatment. In Fig.6 we present the XPS spectra for As 3d on *p*-GaAs(100) treated with ODT and As 3d spectra on *n*-GaAs(100) treated with ODT, the line corresponding to As-S bond is marked E (BE-43.20 eV)

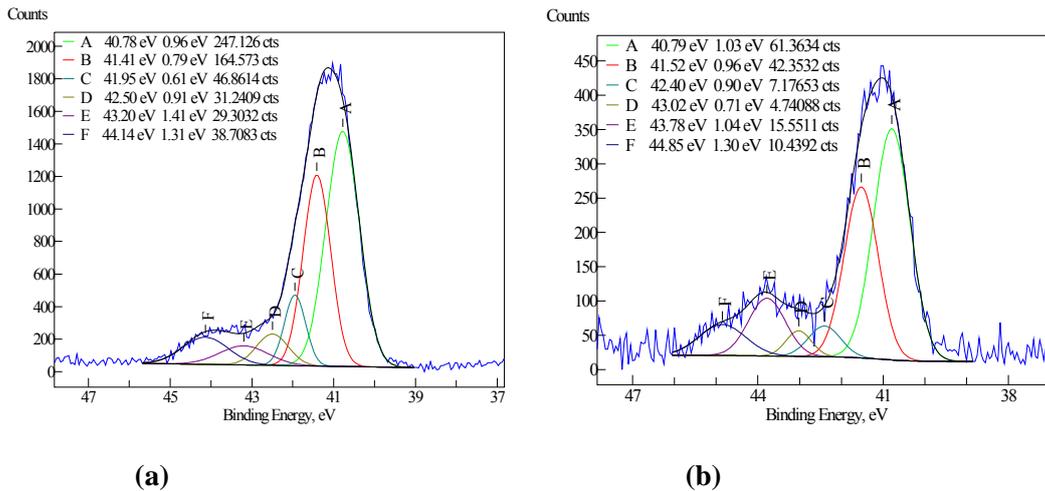


Fig.6 XPS spectra for As 3d on (a) p-GaAs treated ODT and (b) n-GaAs treated ODT

Some remarks regarding the XPS data are related to the fact that sulfur signal can not be easily identified in a XPS measurement. From the signal arisen from S 2p we conclude that there are no oxygen bonds and the BE situated in that range is assigned to an As bond or to thiol. The width 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 photoluminescence intensity of n-GaAs (100) is raising when follows the sulfur treatment of the two inorganic compounds:  $(\text{NH}_4)_2\text{S}$  and  $\text{S}_2\text{Cl}_2$ . The intensity varies and the peak position for PL band indicates a radiative transition band-to-band. This transition is related to the variation of carrier's number that recombines at the interface GaAs/sulfidic compound. The PL signal raises as a consequence of the growth for carrier number that recombine due to the variation of state density at the interface GaAs/dielectric. In Fig.7 we present the recorded PL spectra on n-GaAs (100) surface.

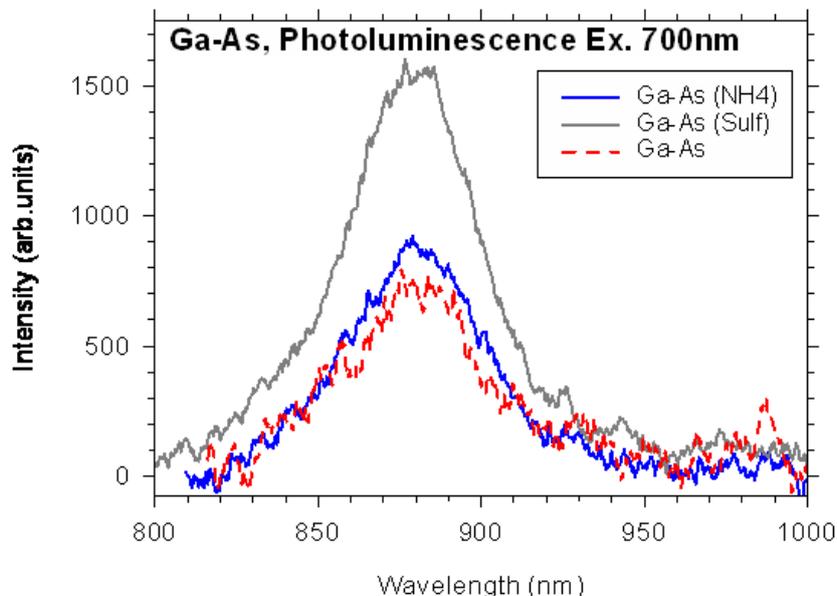


Fig.7 PL spectra at n-GaAs (100) surface treated with inorganic sulfide compounds

In the case of passivation with sulfide compounds it does exist the tendency to minimize the state density at the surface  $N_{ss}$  and the recombination velocity at the surface  $v_s$ . Since the exciting light is absorbed to create electron-hole pairs, the intense excitation for the sample is near the surface and as a consequence the carriers distribution is non-homogeneous and far from

equilibrium. For the excess carriers in their act to gain homogeneity and equilibrium they will diffuse far from the surface and the surface suffers a depletion by recombination processes both radiative and non-radiative. IN this condition the most part of the crystal is restricted to a region in the limit of diffusion length (or absorption length) for illuminated surface. As can be observed the highest intensity of PL signal was observed on n-GaAs (100) passivated in S<sub>2</sub>Cl<sub>2</sub> solution, and as regards a detailed analysis, the PL signal is difficult to interpret due to the involved physical phenomena.

Having large second-order susceptibilities that potentially offer high conversion efficiency of the nonlinear optical devices such as frequency doublers and parametric oscillators, GaAs is one of the most frequently studied materials for generating second-harmonic of laser light [17, 18]. SHG technique is used for studying the physical and chemical properties of surfaces and interfaces and as an optical method can have access to buried interfaces if the top medium has transparency. Besides the bulk electric dipole contribution allowed in the noncentrosymmetric materials, there are additional optical second-harmonic contributions coming from both the structural discontinuity of the surface, along with the physical/chemical changes in the interfacial region. For GaAs as a non centro-symmetric material the origin of any SHG signal is not recognized *a priori*. Because they are very sensitive to the surface symmetry, SHG measurements in the p-in/p-out polarization combination can detect surface-localized resonance and surface reconstruction phenomena. The SHG signal from single crystal GaAs during a complete rotation around the normal axis in p-in/p-out configuration reflects the surface symmetry.

In Fig.8 we present the SHG signal on n-GaAs (100) native and with inorganic sulfide passivation, in a polar diagram in p-in/p-out configuration where the orientation with respect to crystal axes is arbitrary.

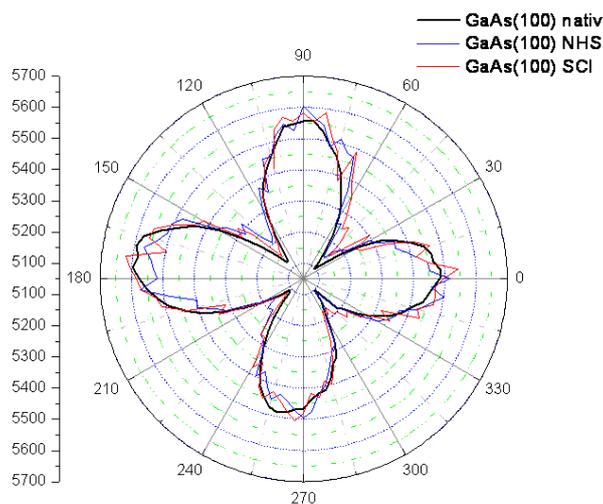


Fig.8 SHG signal on n-GaAs (100) treated in inorganic sulfides in polar diagram

On passivated surfaces with sulfide compounds there are covalent bonds Ga-S and As-S and as a consequence are the absence of “dangling bonds “in sulfide film. In the case of GaAs (100) the dominant contribution raises from the bulk (the four lobes are maintained on the native and covered sample-this is a bulk dipole on GaAs). The surface contribution (sulf dipoles) on n-GaAs (100) passivated with inorganic compounds is observed as fluctuations of the basic signal. From the observed rotational dependence where the intensity of SHG signal has the dependency  $I \sim |A+B \sin(2\phi)|^2$  where : A-isotropic surface contribution, B-bulk dipole and (small) surface anisotropic terms,  $\phi$ -rotation angle it results  $I \sim 0$  at  $0^\circ, 90^\circ, 180^\circ, 270^\circ$ . Any contribution of SHG signal in this area is related to the bulk isotropic surface contribution. These studies in the perspective of sulfide passivated GaAs are among the first experimental data reported in literature beside Yamada [19]. We assume that at the surface are present adsorption phenomena especially in the case of S<sub>2</sub>Cl<sub>2</sub> dipoles besides chemical reaction.

General information regards micro-Raman spectroscopy analysis involved this technique used in the study of vibration, rotational frequencies and other low frequencies in the analyzed system. In Raman scattering of monochromatic light the laser interacts with phonons or excitons from the system and it results a shift of laser photon energy up or down and this energy shift brings information regarding the phonon modes in the system. In Fig.9 we present the Raman spectra on n-GaAs (100) where the peak identification is in the view of Bessolov study [4].

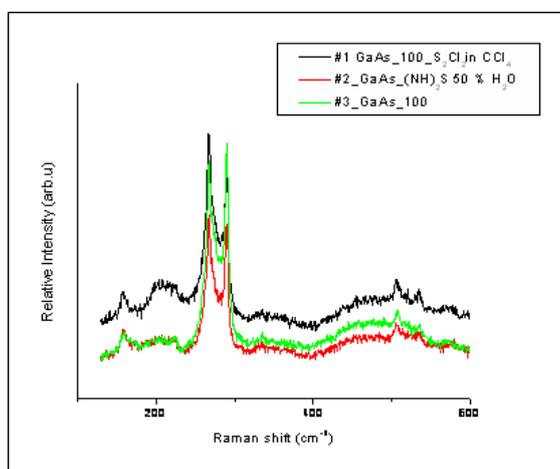


Fig.9 Raman spectra on n-GaAs (100) native and with inorganic sulfide passivation

The peak marked  $L^-$  ( $268.6 \text{ cm}^{-1}$ ) is caused by scattering from coupled phonon-plasmon modes in the bulk where the free carriers do exist. The LO peak ( $291.3 \text{ cm}^{-1}$ ) stems for optical longitudinal phonons from the depletion layer present at the surface. The sulf treatment in different sulfide solutions conducted to a modification of the balance between  $L^-$  and LO that can be assigned with the variation of surface barrier. The GaAs(100) passivated with  $\text{S}_2\text{Cl}_2$  has a peak in the range  $220 \text{ cm}^{-1}$  related with the presence of a thin layer of Ga-S at surface. All the analyzed samples have a shoulder in  $500 \text{ cm}^{-1}$  range that comes from substrate. In GaAs the surface depletion layer is of  $33.6 \text{ nm}$  and the barrier height for sulfide treatment  $V_s$  at GaAs passivation is  $\sim 0.3 \text{ eV}$  [4]. As can be observed the sulfide treatment decreased the surface barrier on GaAs from  $0.78 \text{ eV}$  [10] to  $\sim 0.3 \text{ eV}$  and this decrease are related to the fact that the surface Fermi level on n-GaAs shifts towards the conduction band of the semiconductor.

The electrical measurements as  $I(V)$  characteristics put into evidence the presence of small currents as can be observed in Fig.10. The presence of small currents (nA) for n-GaAs treated with DDT and extremely small (pA) for n-GaAs treated with ODT conducted to the conclusion that thiols passivated the GaAs surface. The analysis of samples in small currents region indicated strong instabilities as a result of imperfect ohmic contacts. The passivation with ODT is more efficient than the DDT passivation and has a well defined rectifier character.

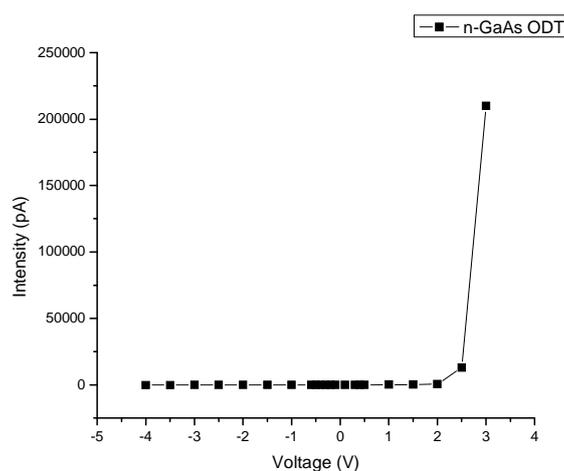


Fig.10 I-V characteristic on n-GaAs(100) treated with ODT

#### 4. Conclusions

Composition analysis at the surface regarding the aspect and the physical nature of the protective layer was explored on n and p-GaAs wafers passivated with inorganic ( $(\text{NH}_4)_2\text{S}$  (50%  $\text{H}_2\text{O}$ ),  $\text{S}_2\text{Cl}_2$  in  $\text{CCl}_4$ ) and organic (DDT, ODT) sulfide compounds. The thin protective layer developed on GaAs surface was exposed to different analysis techniques as; SEM, EDS, XPS, PL, SHG, Micro-Raman spectroscopy, I-V characteristics.

The measurements put into evidence the appearance of covalent bonds Ga-S and As-S where the chemical passivation prevents semiconductor surface oxidation (PL studies indicate variation of surface state density, Raman analysis indicates the presence of Ga-S bond, and in SHG measurement the sulf dipoles are observed as fluctuations of the basic signal.).

The XPS study indicates a technique devoted to a surface analysis composition showing that the birth of chemical bonds Ga-S and As-S is independent of crystal orientation.

The electrical I (V) characteristics indicates the presence of small currents and for n-GaAs passivated ODT has a slight rectifier feature.

Our experiments confirm the information in literature dedicated to the chemical passivation with sulfide compounds of GaAs wafer with the main application in technological process related to device fabrication.

#### References

- [1] M. Richardson, contract FA95500510397 Femtosecond laser passivation GaAs detector material- Final Report
- [2] Gottscho, Patent 5179029, Hydrogen plasma passivation of gallium arsenide (1993).
- [3] T.Hou, C.M.Greenlief, S.W.Keller, L.Nelen, J.K.Kauffman, Chem.Mater, **9**, 3181 (1997).
- [4] V.N.Bessolov, M.V.Lebedev, D.R.Zahn, J.Appl.Phys. **82**, 2640 (1997).
- [5] C.J.Sandroff, R.N.Nottenberg, J.C. Bishoff, R.Bhat, Appl.Phys.Lett, **51**,33 (1987).
- [6] B.A.Cowans, Z.Dardas, W.N.Delgass, M.S.Carpenter, M.R.Melloch, Appl.Phys. Lett, **54**, 365 (1989).
- [7] Xun Wang, Xiao-yuan Hou, Zhe-shen Li, Xi-ying Chen, Surface and Interface Analysis, **24**,564 (1996).
- [8] J.L.Lee, D.Kim, S.J.Maeng, H.H.Park, J.Y.Kang, Y.L. Lee, J.Appl.Phys. **73**, 3539 (1993).
- [9] Z.L.Yuan, X.M.Ding, H.T.Hu, Z.S.Li, J.S.Yang, X.Y.Miao, X.Y.Chen, X.A.Cao, X.Y.Hou, E.D.Lu, S.H.Xu, Y.Y.Zhang, Appl.Phys.Lett, **71**, 3081 (1997).
- [10] G.P.Schwartz and G.J.Gualtieri, J.Electrochem.Soc. **133**, 1266 (1986).
- [11] S.Arabasz, E.Bergignat, H.Hollinger, J.Szuber, Vacuum, **80**, 888 (2006).
- [12] S.R.lunt, G.N.Ryba, P.G.Santangelo, N.S.Lewis, J.Appl.Phys. **70**, 7449 (1991).

- [13] Y.Gu, Z.Lin, R.A.Butera, V.S.Smentkowski, D.H.Waldeck, *Langmuir*, **11**,1849 (1995).
- [14] O.S.Nakagawa, S.Ashok, C.W.Sheen, J.Martensson, D.L.Allara, *Jpn. J.Appl.Phys, Part I*, **30**, 3759 (1991).
- [15] R.C.Tiberio, H.G.Craighead, M.Lercel, T.Lau, C.W.Sheen, D.L.Allara, *Appl.Phys.Lett* **62**, 476 (1993).
- [16] M.J.Lercel, G.F.Redinbo, H.G.Craighead, C.W.Sheen, D.L.Allara, *Appl.Phys.Lett* **65**, 974 (1994).
- [17] V.Lazarescu, R.Scurtu, M.F.Lazarescu, E.Santos, H.Jones, W.Schmickler, *Electrochimica Acta*, **50**, 4830 (2005).
- [18] V.Lazarescu, R.Scurtu, M.F.Lazarescu, A.M.Toader, E.Volanschi, E.Santos, H.Jones, G.Gotz P.Bauerle, *Langmuir*, DOI 10.1021/la900043k (2009).
- [19] C.Yamada, T.Kimura, *Phys. Rev.Lett*, **70**, 2344 (1993).