OPTICAL CHARACTERISTICS OF SULPHUR-PASSIVATED n-GaAs (100) SURFACE

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A genuine GaAs surface is covered with a relatively thick layer (~10 nm) of native oxide pinning the surface Fermi level within the band gap of semiconductor. The method presented in this work is related to the sulphur passivation by treating n-GaAs(100) and (110) in sulphide solutions (e.g pure ammonium sulphide and sulphur monochloride) that combines both chemical electronic passivation by reducing the surface state density. The effects of passivation were put into evidence by Photoluminescence measurements where it was observed the variation of state density. The presence of sulphur dipoles at surface was presented in a diagram of Second Harmonic Generation analysis and the general aspect of sulphur compound was identified by SEM images. The presence of the covalent bond Ga-S and the variation of surface barrier as well as the effect of crystal orientation were put into evidence by micro-Raman Spectroscopy. At the surface of n-GaAs it is developed an adherent layer of sulphur compound as a resul of chemical interaction of sulphur ions with n-GaAs surface.

1. Introduction

The electronic quality of surfaces and semiconductor insulator interfaces at III-V compounds is very important for broader use of the materials in microelectronic and optoelectronic applications.

GaAs is one of the most promising semiconductor compounds material due to its characteristics as direct energy gap or high carrier mobility at room temperature, characteristis exploited for optoelectronic devices as LEDs and Laser Diodes or for high frequency devices as HEMT.

The expansion of the electronic industry requires constant improvement in the fabrication of III-V semiconductors in the form of high-quality atomically thin surface layers. Apart from growth kinetics , which are as yet poorly understood at the atomistic level, the surface passivation remains a key issue in heterostructures composed of III- V semiconductors as GaAs [1]. One way to successful surface passivation is the use of an atomically thin layer of pseudomorphic Si to terminate GaAs(100) surface bonds, followed by a partial nitridation of Si layer in order to form a high-quality interface Si_3N_4/Si [1]. Another passivation technique involves the epitaxial growth of a single-crystal Gd_2O_3 dielectric film on GaAs(100) with the advantage of existing low interfacial density of states with a electrical and thermodynamical stable insulating character [1].

A real GaAs surface is covered with a relatively thick layer (a few nanometers) of native oxide which is the origin of a high density of surface states $N_{SS} \sim 10^{12}$ cm^{-2} (under technological

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conditions) [2,3] pinning the surface Fermi level within the band gap of the semiconductor. This fact can lead to a disadvantage effect on operation of different semiconductor devices [2].

The aim of surface passivation is to reduce the surface state density, or preferably, to remove them from the band gap. The sulphur treatment of the GaAs surface in sulphide solutions results in the removal of the native oxide layer and the formation of As-S and Ga-S covalent bonds [4]. These processes are accompanied by a marked reduction of surface recombination velocity which is indicated by an enhancement of band edge photoluminescence yield of sulphur treated GaAs

As it was stated a special experimental interest is directed towards the effect of chemical treatments on semiconductor surface, which should lead to an electronic surface passivation with sufficient stability, which means non-reversible reduction in surface states and surface charge density as well as lowering of the band bending Φ_b [3]. In This perspective in he case of GaAs the chemical treatment by sulphur or selenium tend to minimize the values of N_{SS} and v_S (surface recombination velocity)~ 10^7 cms^{-1}. From a chemical point of view sulphur passivation involves a removal of native oxide layer and the formation of thin protective layer on n-GaAs in order to prevent its oxidation in atmosphere. From the electrical point of view the passivation is related as was stated before with the reduction of surface state density and as a consequence is the change of surface potential barrier on GaAs.

In this paper there are presented some optical characteristics of sulphur passivated n-GaAs(100) and n-GaAs (110) recorded by photoluminescence, second harmonic generation and Raman spectroscopy experiments , as well as SEM analysis.

2. Experimental techniques and sample preparations

The investigations were performed on n-GaAs (100) Te doped and n-GaAs (110) Te doped wafers with a carrier concentration n~10^{18} cm^{-3}. Prior to sulphur treatment the wafers were degreased in trichloroethylene (boiling for 2 minutes), rinsing in acetone and than chemical etched in HCl:H$_2$O (DIW) (1:1) for 100 seconds at room temperature. The n-GaAs wafers presented the aspect of an optical polished surface. The sulphide treatment was carried out in two different solutions namely: (a) pure ammonium sulphide (NH$_4$)$_2$S (50% H$_2$O) –as stated an aqueous solution and (b) solution of sulphur monochloride (S$_2$Cl$_2$) in carbon tetrachloride (CCl$_4$) (1:10). The few drops of sulphide solutions were added on n-GaAs (100) and n-GaAs (110) surfaces and afterwards the wafers chemical treatment was stabilized by drying at a spinner.

Regarding the photoluminescence (PL) experiments for GaAs the resulting PL signal is collected from the same sample surface upon which the exciting light was incident and is referred to as "front surface photoluminescence". The position of PL line closely follows the absorption edge as a function of temperature at least to 200 K indicating that the transition does not turn into free electron-free hole recombination at higher temperatures [5]. As expected the absorption cut off is much larger for n-type GaAs because the emission is very close to band edge. For thin deposited layers on GaAs the front-surface PL is the only method that can be used. For GaAs in the range 1,5 eV to 1.0 eV the S1 response photomultiplier is the best, because at the low signal level, the best signal-to-noise ratios are obtained by reducing the dark current of the photomultiplier to a minimum. In our experiment the PL spectra have been recorded using a lock-in technique with a standard luminescence set-up composed of two monochromators for excitation and emission, A Xe-150 W lamp as light source a photomultiplier (with long-tail infrared S1 cathode) as light detector. The recorded spectra were not corrected for the spectral sensitivity of the experimental set-up.

The Second Harmonic Generation (SHG) technique is used in basic research on the physical and chemical properties of surfaces and interfaces. The existence of a dipole layer at the interface (as liquid-air) responsible for the observed signal implies the surface sensitivity of this technique. Using the SHG technique as a surface-specific probe is based on the principle that SHG is electric-dipole forbidden in the bulk media with inversion symmetry (e.g. Si and Ge) but allowed at the surface where the inversion symmetry is broken. Since the SHG technique is an optical probe, it can have access to buried interfaces if the top medium is transparent to the

excitation laser light.. The significant advantages of the SHG probe include capabilities of non-contact, non-invasive and *in situ* sampling. The GaAs material from the symmetry point of view is not centro-symmetric and therefore the origin of any SHG signal is not known a priori [6]. The experimental set-up for SHG experiments is 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 azimuthal 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 as presented for GaAs(100) that illustrates the symmetry of the rotational SH anisotropy
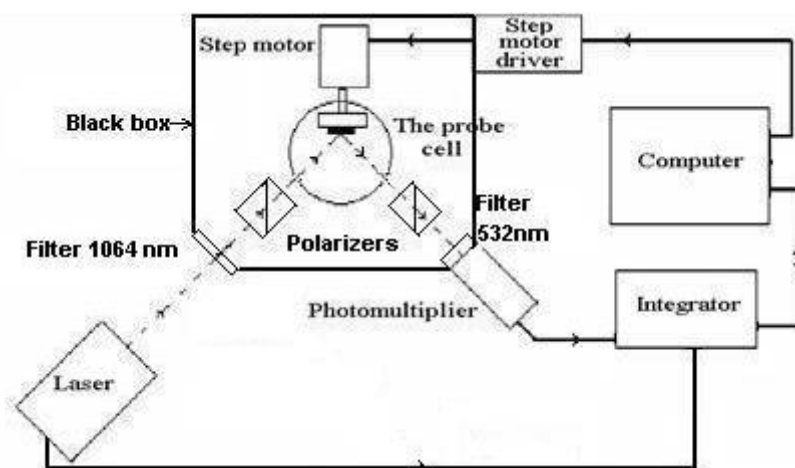

Fig.1 Experimental set-up for SHG measurement

The Scanning Electron Microscopy (SEM) analysis was performed using a HITACHI S 2 600 N type operating at 25 kV in vacuum.

Raman spectroscopy is a spectroscopic technique used to study vibrational, rotational and other low-frequencies in a system.The shift in energy gives information about the phonons modes in the system. Raman spectra can be collected as in the present case from a very small volume (< 1μm in diameter) and these spectra allow the identification of species present in that volume. Raman spectra on GaAs were performed in a backscattering geometry at room temperature and in air using a LabRAM HR 800 UV-VIS-NIR Horiba SCIENTIFIC. A micro-Raman set –up begins with a standard optical microscope, adds an excitation laser, a monochromator and a sensitive detector. In this perspective in our experiment the main characteristics are: an Ar laser (514.5 nm), power on surface sample : 2.5 mW, measurement range : (130-600) cm^{-1}, laser spot size: 1μm^2 objective x100, without attenuation filter, spectra rising parameters(exposure time: 2 sec, accumulation time: 5 sec, accumulation numbers: 5 cycles), resolution: 0.5 cm^{-1}, laser spot :1 μm^{-2}, lattice: 1 800 l/mm.

3. Results and discussion

3.1 Photoluminescence

The photoluminescence intensity of n-GaAs increases following the sulphide treatment is presented in Fig.2. The intensity varies and the position of the maximum for PL band indicates a radiative transition of the band-to-band type. The band-to-band transition is related to the variation of carriers number that recombine at GaAs/sulphide interface. As the intensity of the PL signal increases, it increases also the number of carriers that recombine due to the variation of the density of states at the interface GaAs/dielectric. The intensity of the signal depends on the electron number present on the quasi-Fermi level F_n and the number of holes on the quasi-Fermi level F_p. The generated electrons and holes established a equilibrium distribution within the band gap very quickly by phononic processes. Since the exciting light is absorbed in creating e-h pairs, the greatest excitation of the sample is near the surface and therefore the resulting carrier distribution is both inhomogeneous and non-equilibrium. In attempting to regain homogeneity and equilibrium the excess carriers will diffuse away from the surface that will be depleted by both radiative and non-radiative recombination processes. Most of the excitation of the crystal is thereby restricted to a region within a diffusion length (or absorption length) of the illuminated surface. Since the recombination radiation is subjected to self-absorption, it will not propagate far from this region.

For sulphur passivated samples the self-absorption in the diffusion length in GaAs is weaker as S passivated layer is thicker as can be seen from SEM analysis (Fig.3 a and b). It follows that the recombination radiation rather escapes through the nearly illuminated surface. In our case the highest increase of the PL intensity is observed on the sample passivated with S_2Cl_2 as can be observed in Fig.2. The PL analysis on S passivated samples is a bit hard to perform from the involved physical phenomena due to the main disadvantage of a PL technique namely the increased remoteness of the row data from the physical phenomena of principal interest.
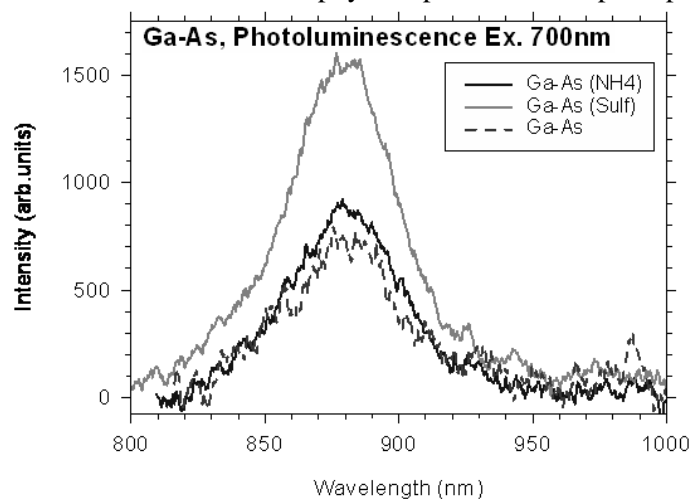

Fig. 2 Photoluminescence signal on n-GaAs(100) native and passivated with S_2Cl_2(Sulf) and $(NH_4)_2S(NH_4)$

3.2 Second Harmonic Generation

For the SHG measurement the existence of a dipole layer at the interface responsible for the observed signal implies the surface sensitivity of this technique.

SHG is related to a responsible technique for the surface sensitivity of non-linear optical properties of a material which does not have inversion symmetry. It is observed that the SHG signal is dependent on crystal orientation due to a bulk contribution. The separation of bulk and surface SH contributions is a problem of fundamental difficulty in the use of SHG as a strictly surface probe. However in most cases (e.g. GaAs(100)) the strict separation is not needed because SHG usually dominates over bulk SHG.

In our case was studied the SHG signal arisen from n-GaAs (100) covered with sulphide compound $(NH_4)_2S$ and S_2Cl_2 deposited in a thin layer. The native surface of GaAs is Ga-rich and

on the sulphur passivated surfaces there exists covalent bonds Ga-S and As-S (as presented in literature [2]) and confirmed by our experiments [7, 8]. On the GaAs(100) surface the nearest-neighbor distance is proportional to 5.653 Å [1]. In the case of sulphur passivation in the presence of covalent bonds to GaAs it would not make sense to talk about a surface reconstruction because the dangling bonds would not exist in the presence of sulphide film. At the interface, where these significantly different structures meet it might be a presence of an asymmetry of the bonding as observed in literature [1].

In Fig.4 is presented the SHG signal on n-GaAs (100), n-GaAs (100)NHS (passivated $(NH_4)_2S$) and n-GaAs (100) SCl (passivated S_2Cl_2) in a very thin layer. As can be observed the dominant contribution arises from the bulk material-the four lobes that maintains also on samples covered with a thin layer of sulphur compound-this is a volume dipole on GaAs. The surface contribution (sulphur dipoles) is observed as fluctuations of the basic structure of the signal. We assumed that at the surface is present an adsorption process especially for the sample covered with an adherent layer of S_2Cl_2 where the influence of the adsorbed dipoles is pointed.
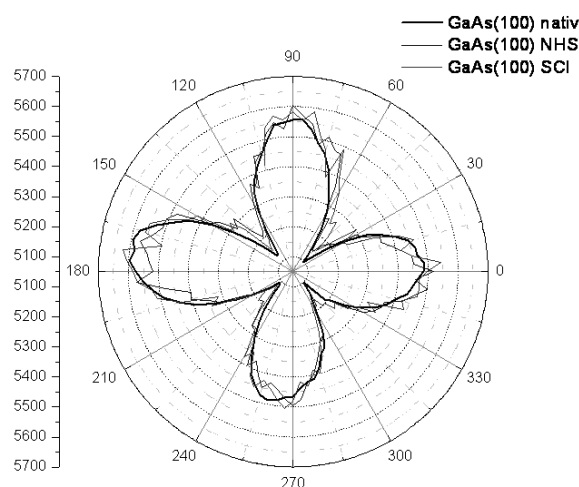

Fig.4 SHG signal on n-GaAs(100) native and passivated S_2Cl_2 (SCl) and $(NH_4)_2S$ (NHS)

3.3 Scanning Electron Microscopy

The SEM images provide the direct information regarding the morphology of the as-prepared samples and confirm the presence of a compound layer as the main result of passivation process. The SEM micrograph on sulphur treated n-GaAs (100) and n-GaAs(110) revealed a uniform deposition of Sulphur compounds (S_2Cl_2 and $(NH_4)_2S$) on different regions on the sample area of over 1 cm^2 as presented in Fig.3a and Fig.3b.
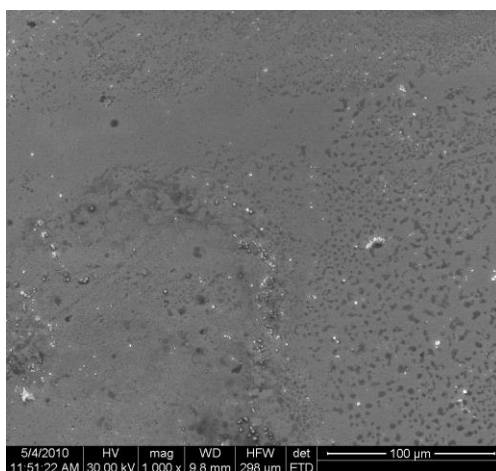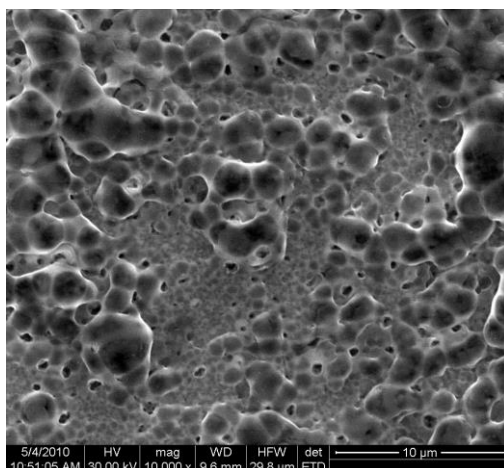

Fig.3a Sulphur passivated n-GaAs(100) in S_2Cl_2

Fig.3b- SEM image for (NH₄)₂S deposition on n-GaAs(100)

3.4 Raman Spectroscopy

For n-GaAs:Te (100) unpassivated sample there are present two main peaks as can be clearly seen in Fig.5a. The peak marked L^- (260 cm^{-1}) is caused by scattering from coupled phonon-plasmon modes in the bulk where the free carriers exist. The LO peak(290 cm^{-1}) stems from the surface depletion layer. The intensities of L^- and LO peaks for unpassivated GaAs are almost equal at this wavelength of excitation [2]. In the region of (500-550)cm^{-1} there is present a shoulder, a shift from the bulk probably as a result of crystal orientation on the (100)face. The sulphur treatment in different solutions results in a change of the balance between L^- and LO peaks which can be corroborated with the variation of the surface barrier [2]. The decrease of the surface barrier in n-GaAs means that the surface Fermi level shifts towards the conduction band of the semiconductor after sulphur passivation. For n-GaAs (100) passivated with S_2Cl_2 as can be seen in Fig.5a, the L^- and LO peaks are in the spectral range (250-300)cm^{-1} with the presence of the shoulder in the region (500-550)cm^{-1} and a peak at 220 cm^{-1}. The feature of Raman spectra namely the peak of 220 cm^{-1} is related to the presence of a thin GA-S rich layer on the surface as it was previous observed [2]. For n-GaAs(100) passivated with (NH₄)₂S as can be seen in Fig.5a the L^- and LO peaks are in the spectral range (250-300)cm^{-1}with the presence of a shoulder in the region (500-550)cm^{-1} and a small peak under 200 cm^{-1} that it is not assigned .

For n-GaAs:Te(110) unpassivated sample as can be seen in Fig.5b there is an intense L^- (260 cm^{-1}) peak and the absence of LO peak can be an effect of crystal orientation as long as Raman spectra is sensitive to the orientation. For n-GaAs (110) passivated (NH₄)₂S as can be seen in Fig.5b there is present an intense L^- much higher corroborated with the variation of surface barrier. For n-GaAs (110) passivated with S_2Cl_2 as can be seen in Fig.5b the Raman spectra have the main peaks: 150 cm^{-1} which is not assigned , 220cm^{-1} assigned to a Ga-S rich layer, 260 cm^{-1} L^- peak, and a shoulder at 470 cm^{-1} which was not assigned.

For TO mode at n-GaAs(110) samples there is no displacement for peak position, but the variation of integral intensity is modified as regarding the surface treatment. In Fig.5c is presented the variation of integral intensity on n-GaAs(110) and as can be observed for unpassivated sample the TO mode is more intense than for the sample passivated with S_2Cl_2 and the intensity rises for (NH₄)₂S passivation.
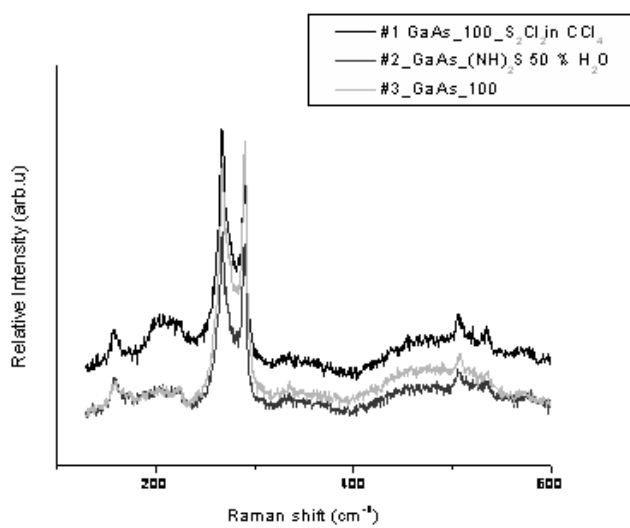
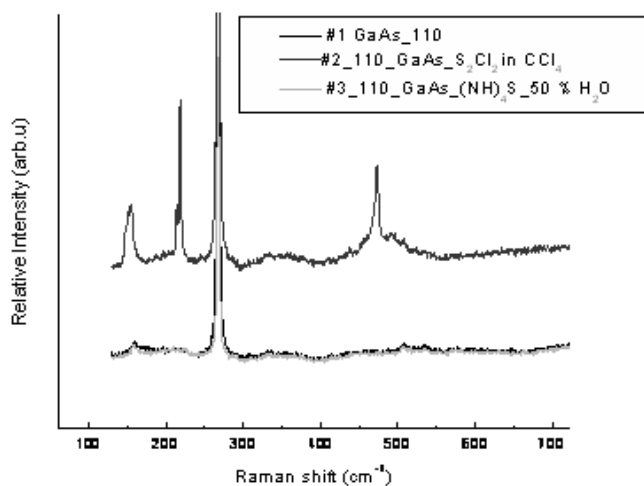*Fig.5a Raman spectra on n-GaAs(100)native(#3) and passivated S_2Cl_2(#1) and $(NH_4)_2S$(#2)*

Fig.5b Raman spectra on n-GaAs(110) native(#1) and passivated S_2Cl_2(#2) and
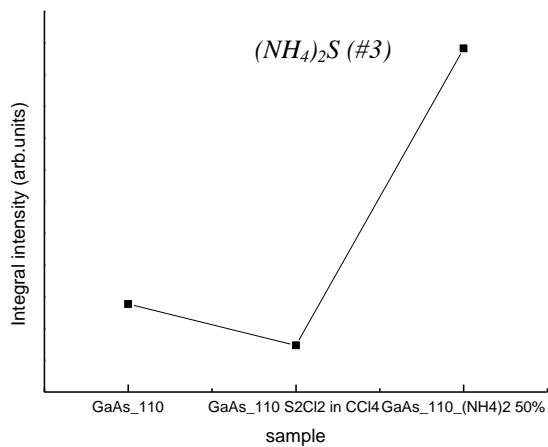

Fig.5c Integral intensity for Raman signal on n-GaAs(110) samples

4. Conclusions

It was shown by Photoluminescence experiment that the PL intensity of n-GaAs increases following the sulphide treatment. The intensity varies and the position of the maximum of PL band indicates a radiative transition of the band-to-band type. The variation of PL intensity is related with the variation of state density at the surface of n-GaAs (100), a result that is in accord with previous attempts in literature.

For the SHG measurement the existence of a dipole layer at the interface responsible for the observed signal implies the surface sensitivity of this technique. The SHG experiment on the surface of n-GaAs(100) put into evidence the presence of the surface contribution (sulphur dipoles) that is observed as fluctuations of the basic structure of the signal. We assumed that at the surface is present an adsorption process especially for the sample covered with an adherent layer of S_2Cl_2, where the influence of the adsorbed dipoles is pointed.

The aspect studies of sulphur passivated n-GaAs(100) and n-GaAs(110) observed by SEM images put into evidence the formation of a thin protective layer on semiconductor surface in order to prevent its oxidation in atmosphere.

It was shown by Raman spectroscopy that the treatment of n-GaAs(100) by sulphide compounds conduced to a in a change of the balance between L^- and LO peaks which can be corroborated with the variation of the surface barrier. For n-GaAs(110) was put into evidence the effect of crystal orientation together with the presence of new peaks in Raman spectra for the passivation with a solution of S_2Cl_2. The Raman spectroscopy reveal that a surface treatment in sulphide solutions results in an effective passivation of GaAs surface.

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