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XPS study of chemically sulphur-passivated n-GaAs

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A genuine GaAs surface was 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 the sulphur passivation by treating n-GaAs in sulphide solutions (e.g. pure ammonium sulphide and sulphur monochloride) that combines both chemical and electronic passivation by reducing the surface state density. The presence of the covalent bonds As-S and Ga-S was putted into evidence by XPS analysis. It is presented the independence of XPS measurements on n-GaAs substrate orientation for (100) and (110) planes. At the surface of n-GaAs it is developed an adherent layer of sulphur compound as a result of chemical interaction of sulphur ions with n-GaAs surface.

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1. Introduction

GaAs is the most promising III-V semiconductor compounds due to the 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 are soluble in water and thus they are very easy to lose. 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 the device performances [1].

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) [2].

The sulphur passivation technique by treating GaAs surface with Na_2S•9 H_2O was developed for the first time by Sandroff et all in 1987 [3]. The superior effects of sulphur passivation were demonstrated by a significant enhancement of the photoluminescence (PL) intensity of the treated GaAs surface. As a general remarks from the literature [4], the simple sulphur treatment by dipping the GaAs wafer in $(NH_4)_2S_x$ or Na_2S•9 H_2O aqueous solutions can provide good electronic passivation, but the chemical passivation is rather poor due to its instability. In this view the present work is dedicated to the study of chemical effect of passivation on n-GaAs (100) and n-GaAs (110). The ordinary sulphur treatment results in a layer of sulphur atoms bonded to GaAs surface, which can be easily replaced by oxygen after a long time of exposure to air especially under illumination [5]. The treatment in a saturated ammonium polysulphide $(NH_4)_2S_x$ solution has been shown to improve the GaAs surface stability [6, 7] and reduce surface state density and surface recombination [3]. In order to solve the problem of longevity and durability another way is to use for sulphur passivation an oxygen-free solution of S_2Cl_2+ CCl_4, which is effective for removing the native oxide of GaAs and forming Ga-S bonds [5]. The surface chemistry after sulphide treatment varies in literature both quantitatively and qualitatively as it includes the identification of sulphur bonds to GaAs, the efficient remove of native oxide by various pre-treatment methods and different identification techniques [8].

For understanding the passivation mechanism of chemical sulphur passivation on n-GaAs (100) and n-GaAs (110) we mainly used the XPS technique in order to study the chemical composition of the passivated layer and the bonding states of Ga and As atoms, in the neighbourhood of the passivated film/ substrate interface.

In this paper we present the partial results of a XPS study on sulphur passivated surface of n-GaAs in $(NH_4)_2S_2$ (50 % H_2O) and S_2Cl_2 in CCl_4 (1:10) solutions, with a general remark that the sulphur signal cannot be easily identified in XPS measurements.

In our work the existence of sulphur and the bonding states are related to signals of As 2p, Ga 2p and As 3d and Ga 3d peaks used in order to investigate the surface chemistry in the limit of 0.8 nm (as stated in literature [9] for the information that is surface sensitive.

2. Experimental

The experiments were performed on n-GaAs, Te doped (n~ 10^{18} cm^{-3}) wafers with different orientations, that mean n-GaAs (100) and n-GaAs (110). Prior to sulphur treatment the wafers were washed in water and then degreased in trichloroethylene (boiling for 2 minutes) and rising in acetone at room temperature. The samples were chemical etched in HCl:H_2O (DIW) (1:1) for 100 seconds at room temperature. The n-GaAs wafers maintained the initial aspect of the optical polished front surface. The sulphide treatment was carried out in two different solutions respectively: (a) pure ammonium sulphide $(NH_4)_2$ S_2 (50% H_2O) –as stated an aqueous solution and (b) solution of sulphur monochloride in carbon tetrachloride S_2Cl_2:CCl_4 (1:10). The few drops of sulphide solutions were added on n-GaAs surface and afterwards the wafer treatment was stabilized by drying at a spinner.

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 a pass energy of 10 eV giving an energy resolution of 1.18 eV, which was established as FWHM (full width half maximum) of the Au 4 f 7 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 were 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.

3. Results and discussion

Sulphur signal can not be easily identified in a XPS measurement. For the n-GaAs (100) sample treated with S_2Cl_2 the major peaks in XPS are Ga and As together with C line, which is mainly originated from the chemical adsorbed carbon dioxide. The existence of sulphur and surface bonding states is derived from the line shapes of Ga $2p_{3/2}$ as can be observed on the XPS signal on S_2Cl_2 passivated surface on n-GaAs (100) in Fig. 1. The binding energy (BE) of 1118.17 eV is related to elemental Ga in GaAs and the BE of 1120 eV is related to Ga-S bond as presented in literature [5]. The signal of As 2p arises from elemental As in GaAs at BE: 1323.9 eV and As probably in oxide due to the presence of O on semiconductor surface in the form As_2O_3 at BE: 1327.5 eV. The chemical bond with S can not be put into evidence due to the overlap of the more intense signals above. The electron escape depth of Ga 2p and as 2p electrons are around ~0.8 nm [9], so the information obtained is surface sensitive. The As 3d signal arises from elemental As in n-GaAs (100) treated with S_2Cl_2.

Regarding the passivation of n-GaAs (100) with $(NH_4)_2$ S_2 (50% H_2O) the XPS signal of As 2p was not clearly put into evidence and that for As 3d signal, the BE; 40.96 eV and 41.68 eV are related to atoms As in GaAs. As presented in Fig. 2 concerning to the peaks C (BE: 43.82 eV) and D (BE: 44.77 eV) the signal arises from As in the oxide As_2O_3 due to the conditions of passivation in an aqueous solution that favorized the oxygen bond. The analysis of As-S component on ammonium sulphide passivated surface of n-GaAs (100) is hidden due to the small intensity of S-line and due to the overlap with elemental As in GaAs [8]. As regards the Ga signal, it was put into evidence the 3 d line at a BE: 19.24 eV related to elemental Ga in GaAs and the peak at BE; 20.35 eV can be related to Ga-S bond as a chemical shift of 0.7 eV is presented in literature [8]. As an experimental observation the decomposition of the Ga 3d line on the surface it might be corrected with the signal of a predominant gallium oxide component (Ga_2O_3) that exists at a chemical shift of 1.4 eV due to the presence of water in ammonium sulphide [8].

The main characteristics of XPS spectra on sulphur compounds on n-GaAs (110) are the same as for n-GaAs (100)

The As 2p signal on S_2Cl_2 as deposited on n-GaAs represents in the best way the surface because the emitted photoelectrons have low kinetic energy and the escape depth is 6-7 Å; that is why the XPS spectra have a surface information.

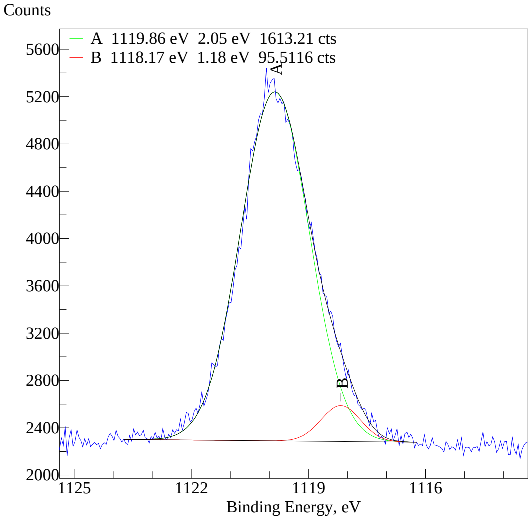

Fig. 1. XPS spectrum of Ga 2p on S_2Cl_2 passivated surface of GaAs (100).

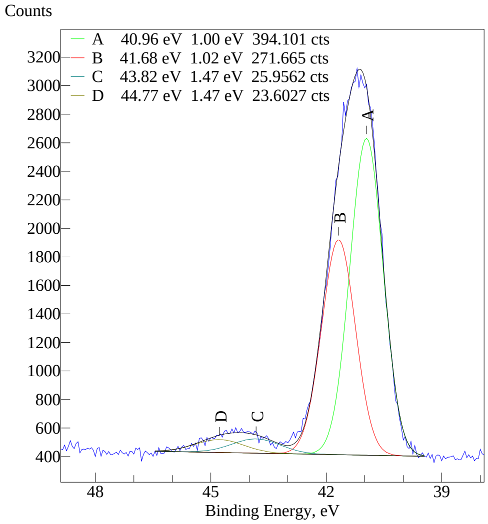

Fig. 2. XPS spectrum of As 3d on $(NH_4)_2S_2$ passivated surface of GaAs (100).

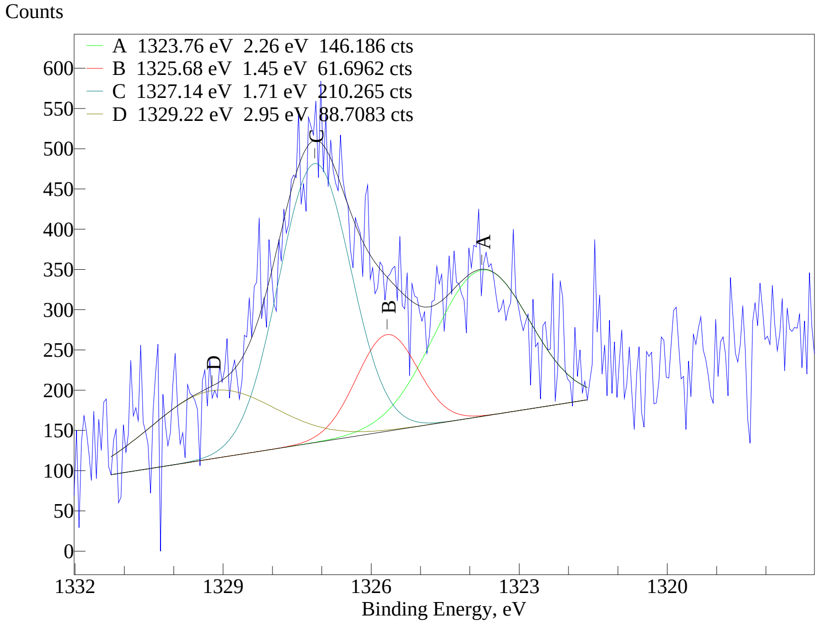

Fig. 3. XPS spectrum of As 2p on S_2Cl_2 passivated surface of GaAs (110).

As presented in Fig. 3 the As 2p signal is composed of four main peaks; A (BE: 1323.76 eV) related to As bond in GaAs, B (BE: 1325.68 eV) related to As – S bond, C (BE: 1327.14 eV) related to As_2O_3 presence and D (BE: 1329.22 eV) related to As_2O_5. The As 3d signal has an escape depth for photoelectrons of (25-30) Å and this means that the composition information is related to an inner volume from GaAs. The Ga 2p signal on n-GaAs (110) do not put into evidence the Ga-S bond, and also the Ga 3d signal is related to two peaks: A (BE: 19.35 eV) related to Ga in GaAs that hide the signal that can arise from Ga-S bond, and B (BE:20.79 eV) is related to gallium oxide (Ga_2O_3).

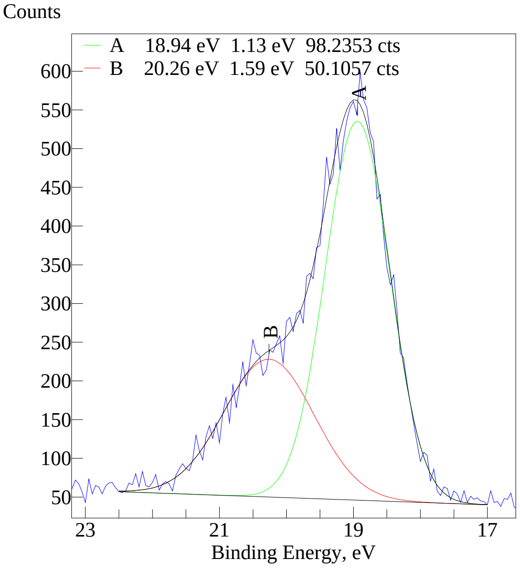

Fig. 4. XPS spectrum of Ga 3d on $(NH_4)_2S_2$ passivated surface of GaAs (110).

For the XPS signals on ammonium sulphide $(NH_4)_2S_2$ (50% H_2O) on n-GaAs (110) the experimental information regarding the sulphur signal do not put into evidence the As-S or Ga-S bonds. The sulphur layer in the limit of 10 Å escape depth it was not put into evidence in As 2p and Ga 2p spectrum. As for As 3d and Ga 3d signals, the BE: 40.95 are related to As in GaAs and BE: 18.94 for Ga in GaAs as presented in Fig. 4. In these deconvolutions the second peak (BE: 44.22 eV) and (BE: 20.26 eV) are related to As and Ga oxides.

4. Conclusions

The XPS study of sulphur passivated samples of n-GaAs (100) and n-GaAs (110) reveals the possibility for a compositional analysis of GaAs surface. The results regarding the chemical bonds As-S and Ga-S are independent of the wafer orientation for (100) and (110) planes. The effort for putting into evidence these covalent sulphur bonds depends on the sulphide treated solution. (the results are more evident for sulphur monochloride in carbon tetrachloride). Our work confirms the XPS results from literature on n-GaAs and can be applied in GaAs device technology.

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