

High resolution photoemission yield study of the GaAs(100) surface cleaned by atomic hydrogen

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High-resolution photoemission yield spectroscopy (PYS) has been used to study the electronic properties of space charge layer of the real GaAs(100) surface cleaned by atomic hydrogen. The ionization energy, work function and interface Fermi level position were determined as a function of hydrogen dose. Moreover, the evolution of effective density of filled electronic states localized in the band gap and in the upper part of the valence band was observed. Our experiments showed that for the hydrogen dose up to 10^4 L H₂ the contamination etching stage occurs for which the interface Fermi level position $E_F - E_v$ reaches a value of 1.06 eV. For the higher hydrogen dose at the level 10^5 L H₂ the interface Fermi level position $E_F - E_v$ reaches a value of 0.75 eV which corresponds to the degradation of GaAs(100) surface that becomes covered by metallic Ga.

Keywords: GaAs, atomic hydrogen cleaning, photoemission yield spectroscopy (PYS), surface states, interface Fermi level pinning, work function, ionization energy.

1. Introduction

In high technology of III-V semiconductor devices, particularly made using the MBE technology, the well ordered and contamination free polar GaAs(100) surface is of great importance [1, 2]. However, the real GaAs surface has been found to be very reactive with gaseous atmosphere resulting in immediate growth of 2–3 nm of native oxide layer [3, 4]. It predominantly consists of Ga₂O₃ with inclusions of As₂O₃ at the top-most layer and a free-As monolayer beneath the oxide layer [5].

Up to now, various surface treatments, including the most popular – ion bombardment and annealing as well as thermal or plasma assisted etching, have been extensively studied [6, 7]. However, all of these procedures use the elevated temperature which causes that GaAs clean surface exhibits an evident nonstoichiometry combined with surface reconstruction, therefore drastically influencing its electronic interface properties [1, 6, 7].

During the last few years other methods have been explored for cleaning the real GaAs surface without the above mentioned limitations.

One of the most promising methods seems to be removing the native oxide on the GaAs surface by atomic hydrogen cleaning. It has been found that atomic hydrogen can efficiently reduce both carbon contaminations, giving good-quality III-V surfaces for epitaxial growth [8, 9] and native oxides which are known to be responsible for the high density of surface midgap states [10]. However, it is also well documented that H atoms can also etch bulk components inducing damage of III-V surfaces [10] and remove the excess of free bulk arsenic from the interface which is known to be one of the species present within the native oxide responsible for pinning of the surface Fermi level [8, 9].

In spite of considerable efforts undertaken to study the mechanism of atomic hydrogen cleaning of GaAs surface, a comprehensive model which can relate electronic and chemical processes and explain the mechanism of modification of the surface electronic structure is still lacking.

Up to now, in the study of the surface chemistry and electronic properties of GaAs(100) surface cleaned by atomic hydrogen mainly classical photoemission techniques like XPS and UPS have been applied [8, 9]. Because of their evident limitations (resolution of energy analyzer, weak procedure of spectra deconvolution *etc.*), other techniques which allow the determination of the electronic properties of the space charge layer with the special emphasis on electronic band gap states and Fermi level position are in demand [11].

In this article, the electronic properties of the space charge layer for the *n*-GaAs(100) surface after atomic hydrogen treatment are investigated in detail, using photoemission yield spectroscopy (PYS) developed by the group of Sebenne [12]. It consists in measuring the total number of photoemitted electrons per incident photon at a given light energy E (usually up to 6.2 eV). Because of a large dynamic range (up to eight orders of magnitude) and very high energy resolution (up to the level of kT), it allows the determination, among others, of the values of work function ϕ and ionization energy Φ of the semiconductor surface [12]. Moreover, with debatable but usual assumption that the transition matrix elements and escape depth remain constant in a usually small photon energy range (about 3 eV), the derivative of the photoemission yield with respect to the photon energy $dY(E)/dE$ is proportional to the effective density of the filled electronic states $N(E)$ localized in the band gap below the Fermi level E_F and in the upper part of the valence band (within the escape depth of photoelectrons).

2. Experimental

The (100) oriented *n*-type Te doped GaAs samples with the carrier concentration at the level of 10^{17} cm^{-3} were used as the samples. After the standard degreasing in acetone, methanol and rinsing in deionized water, the samples were transferred to the ultra high vacuum (UHV) system without any other treatments.

The atomic hydrogen cleaning, as well as PYS experiments have been performed using a self-constructed UHV multiple-technique electron spectrometer with the base pressure of 10^{-7} Pa. In order to clean the GaAs(100) surface by atomic hydrogen, the UHV chamber was additionally equipped with an atomic hydrogen cracking cell similar to that developed by SUGAYA and KAWABE [13]. Thus, molecular hydrogen of the 99.99 purity, from a glass flask was introduced to the system through a leak valve at the constant pressure maintained at 2×10^{-4} Pa and different time of exposure. Molecular hydrogen was thermally dissociated on the resistive heated tungsten capillary placed at normal angle to the sample at a distance of 5 cm. The filament temperature was estimated basing on thermal change in filament resistance as about 2100 K. In this temperature range, the efficiency of molecular hydrogen dissociation was confirmed to be below 10%, as presented by the others [13, 14].

The photoemission yield spectra $Y(E)$ were recorded after each cleaning procedure at room temperature. The $Y(E)$ spectra were taken at 1 nm intervals up to 200 nm (6.2 eV) and recorded by self-constructed digital counting electronics for subsequent analysis.

Details of the home-built atomic hydrogen cracking cell and PYS apparatus can be found elsewhere [15].

3. Results and discussion

Figure 1 shows a set of the effective densities of filled states $N(E)$ spectra calculated as the first derivative of measured photoemission yield spectra with respect to photon energy as a function of hydrogen dose in L (1 langmuir = 10^{-6} torr \times s).

The $N(E)$ spectra consist of the effective density of both filled electronic states localized in the band gap and in the upper part of the valence band [16].

In order to separate valence band contribution, the high energy tail of the $N(E)$ spectra was fitted by the theoretical power law: $N(E) \sim B(h\nu - \Phi)^\alpha$, proposed by KANE [17], where Φ denotes the ionization energy. In turn, the work function ϕ , which gives the position of the Fermi level E_F with respect to the vacuum level can be obtained by fitting the low-energy tail of $N(E)$ spectra either with the Fermi distribution function or the tail corresponding to the photon energy at the threshold [12]. Thus, the accuracy of determination has been estimated to be 0.05 eV, since the density of states at the photon energy threshold is not very high [11].

Figure 2 shows the variation of ionization energy Φ , work function ϕ and surface Fermi level $E_F - E_v$ as a function of hydrogen exposure (dose).

For the starting of the real GaAs(100) surface covered by natural oxide, the respective values of ionization energy Φ were equal to 5.42 ± 0.05 eV, the work function ϕ was equal to 4.54 ± 0.05 eV, and finally the surface Fermi level position $E_F - E_v$ was equal to 0.88 ± 0.05 eV, which was in good agreement with the recently published data [11].

With the increasing hydrogen dose up to 10^3 L, the work function ϕ and ionization energy Φ decrease to the values of 5.28 and 4.22 eV, respectively. A similar variation

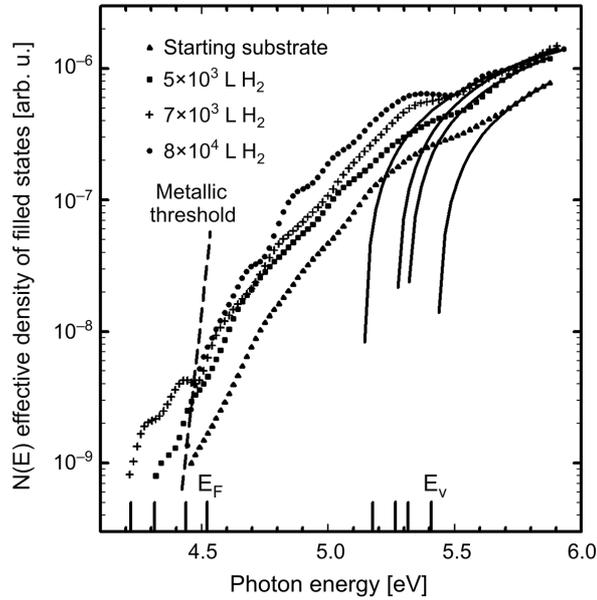


Fig. 1. Semilogarithmic plot of the effective density of the filled surface states $N(E)$ vs. the photon energy for a selected set of GaAs(100) surface with different hydrogen exposures. The solid lines are the known contribution of the GaAs valence band to the $N(E)$ spectra. The dashed line corresponds to kT slope at 25°C, which fits the 8×10^5 L spectrum at a low photon energy threshold.

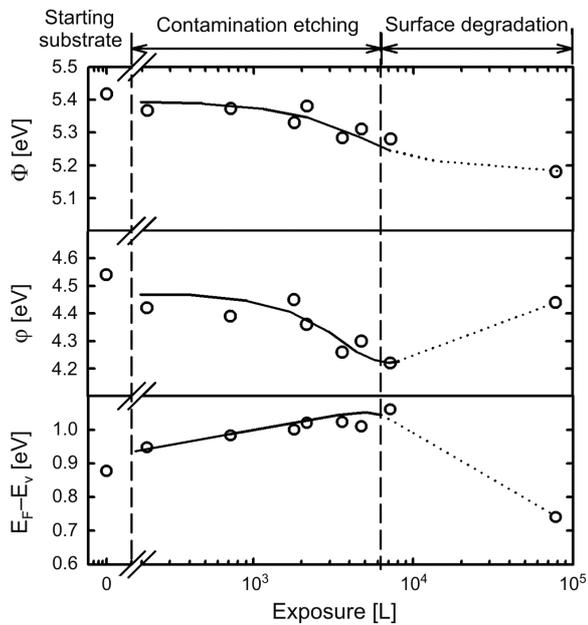
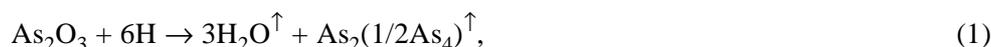


Fig. 2. Variation of ionization energy Φ , work function ϕ and surface Fermi level $E_F - E_v$ as a function of hydrogen exposure in L (1 langmuir = 10^{-6} torr \times s).

of the values of ionization energy and work function after the atomic hydrogen exposure indicates that there are no significant changes in the band bending eV_s [18, 19].

It is the proof of existence of positive charge on the outside adatom and an increased negative, electron charge forming the covalent bonds between adatom and surface atoms. It can be attributed to the Ga adatoms as the products of the following reactions [20, 21]:



This approach is in good agreement with the information presented by PETIT and HOUZAY [8, 9] who found that during atomic hydrogen cleaning of GaAs(100) surface, the ionization energy remains constant at 5.5 eV and is reduced to 5.1–5.2 eV when the surface is degraded. They proposed that the reduction of ionization energy is due to metallic Ga on the surface and constant during the cleaning thanks to a rapid loss of As form deoxidized areas.

From the additional analysis of $N(E)$ spectra shown in Fig. 2, one can conclude that the shape of occupied surface states in the gap remains constant up to the hydrogen exposure of 7×10^3 L. Above this value, the new tail of occupied surface states is observed, which shifts the interface Fermi level by 0.18 eV towards the conduction band to its extreme. One can refer these states to the breaking of As dimmers, since they do not contribute at lower and higher hydrogen doses. Moreover, it is well correlated with subsequent and small decrease in ionization energy up to 5.18 eV for 10^6 L of hydrogen exposure. It is probably the result of removing of arsenic atoms from deoxidized areas, since their electronegativity is higher than for the GaAs.

As a result of further increase in hydrogen dose up to of 8×10^5 L, the Ga enrichment is observed on the GaAs(100) surface and the new electronic states close to the Fermi level at 0.75 eV are also perceived. This low energy tail of occupied states exhibits metallic character, the since several last points of the energy distribution can be well fitted by a straight line having a slope equal to kT at 25°C. A similar behavior was observed by the group of Sebenne [12, 16, 22] and interpreted as the result of metal atoms deposition on clean semiconductor surfaces. The same effect was observed by Spicer *et al.* [23], who found that the Ga deposition leads to pinning of the interface Fermi level at the position equal to 0.75 eV, almost the same as in our paper. This level of states has been attributed by Spicer *et al.* [23] to the Ga_{As} antisite defects. It is in good correlation with our explanation of taking into account the existence of Ga_{As} antisite defects at the Ga-rich surface.

From the results presented in Figs. 1 and 2, it is clear that the atomic hydrogen interaction with the real GaAs(100) surface can be divided into two successive stages. The first interaction stage, which can be referred to as the contamination etching stage

of GaAs(100) surface, is observed until about 10^4 L of hydrogen dose, and the degradation stage which leads to the Ga-rich surface.

4. Conclusions

In this article, the electronic properties of space charge layer for the *n*-GaAs(100) surface after atomic hydrogen treatment with different exposure times are investigated. Our PYS experiments showed that:

- after hydrogen exposure to 10^4 L the surface Fermi level is depinned by 0.18 eV;
- the effect of depinning of the surface Fermi level is correlated with removing of native oxides as well as breaking As-dimmers;
- at higher hydrogen exposures the surface electronic properties drastically changed, resulting in pinning of the surface Fermi level at the semiconductor midgap, 0.75 eV, which corresponds to the effect of Ga enrichment of the cleaned surface.

In attempt to correlate both electronic properties and chemical composition of the atomic hydrogen treated GaAs(100) surface, further works are needed. These include a study of the temperature-dependent behavior of the intensity of the bulk components as a function of hydrogen dose, which are in progress in our laboratory.

Acknowledgements – The authors wish to thank Dr. L. Grządziel and S. Arabasz for their consistent support and motivation. The work was carried out within the CESIS CoE (Project VPRUE: G6MA-CT-2002-04042) and NANOMET CoE (Project MSI: 135/E-367/CD/DFS-51/2004).

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*Received June 6, 2005
in revised form September 7, 2005*