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Comparative study of the GaAs(1 0 0) surface cleaned by atomic hydrogen

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Abstract

In attempt to correlate electronic properties and chemical composition of atomic hydrogen cleaned GaAs(1 0 0) surface, high-resolution photoemission yield spectroscopy (PYS) combined with Auger electron spectroscopy (AES) and mass spectrometry has been used. Our room temperature investigation clearly shows that the variations of surface composition and the electronic properties of a space charge layer as a function of atomic hydrogen dose display three successive interaction stages. There exists a contamination etching stage which is observed up to around 250 L of atomic hydrogen dose followed by a transition stage and a degradation stage which is observed beyond 700 L of exposure. In the first stage, a linear shift in the surface Fermi level is observed towards the conduction band by 0.14 eV, in agreement to the observed restoration of the surface stoichiometry and contamination removal. The next stage is characterized by a drop in ionization energy and work function, which quantitatively agrees with the observed Ga-enrichment as well as the tail of the electronic states attributed to the breaking As-dimers. As a result of the strong hydrogenation, the interface Fermi level $E_F - E_v$ has been pinned at the value of 0.75 eV what corresponds to the degradation stage of the GaAs(1 0 0) surface that exhibits metallic density of states associated with Ga_{As} antisites defects. The results are discussed quantitatively in terms of the surface molecule approach and compared to those obtained by other groups.

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1. Introduction

The preparation of clean and atomically flat polar GaAs(1 0 0) surfaces is a critical step in the epitaxial growth by molecular beam epitaxy (MBE) of high-quality thin films [1–3]. Many ex situ and in situ cleaning procedures have been explored, including chemical etching, thermal desorption and ion bombardment [4,5].

Among them, the most often used thermal desorption has been typically employed in molecular beam epitaxy to remove the native oxides prior the epitaxial growth [6–12]. In this process the GaAs(1 0 0) oxides are removed by direct heating of the substrate to the temperature in the range of 600 °C. This is a result of the layered structure [13–15] of the native oxides which come off in two steps: at first the outer arsenic oxides evaporate at around 400 °C, since they are more volatile than the inner gallium oxides, which then come off over a narrow temperature interval, typically above 580 °C [9–11].

As has been shown by different studies [7–12], the thermal desorption of the native oxides in the case of a GaAs(1 0 0) surface produces an atomically rough and pity surface. This has been attributed to a spatially inhomogeneous bulk reaction between the GaAs surface and the arsenic oxides:

$$2GaAs + As_2O_3 \rightarrow 4As + Ga_2O_3, \quad (1)$$

as well as to the temperature activated Ga oxides decomposition in which the bulk GaAs from the substrate is consumed in the following process:

$$Ga_2O_3 + 4GaAs\,(bulk) \rightarrow 3Ga_2O + 2As_2\,(As_4). \quad (2)$$

Apart from this, a high overpressure of the group V species is also required, not only for buffer growth, but also during the oxides removal stage of the process to prevent excessive

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desorption of the group V element from the surface and irreversible surface damage.

On the other hand, an alternative method for oxides removing, which can lead to a smooth GaAs surface has been proposed [16–22]. By annealing under a flux of atomic hydrogen, surface oxides, carbons and other contaminants can be effectively removed by chemical reactions with atomic hydrogen and subsequent desorption of the reaction products.

In this manner, the atomic hydrogen cleaning is usually carried out at moderately elevated temperatures, typically from 300 °C to 400 °C [17–22]. Under such conditions, the removal of As oxides and Ga_2O oxide may be completed thermally without further presence of atomic hydrogen [6–8]. Thus the aim of the cleaning procedure is to reduce Ga_2O_3 oxide, which naturally occurs at the interface, into Ga_2O suboxide as shown by Yamada et al. [18,19]. Moreover, the problem of the observed instability of the native oxides in this temperature range can be significantly reduced by introducing two hydrogenation steps as shown by Petit and Houzay [20,21]. The first one reduces the outer As oxides at room temperature in order to prevent the formation of Ga oxides from reaction (1) and finally, Ga oxides are etched separately during the second step at 300 °C.

The main advantage of this technique is that the annealing temperatures required are lower than those needed for the standard oxides desorption [6–8] without the presence of atomic hydrogen, and thus the problem of group V desorption and surface roughening can be reduced as shown by excessive LEED and STM studies [23–26,3].

Most of the presented studies deal with the goal to obtain clean and smooth GaAs(1 0 0) surfaces for the growth of high-quality thin epitaxial layers, while not much work is presented in the context of the electronic properties of GaAs surfaces upon atomic hydrogen exposure, especially at room temperature. Moreover, in these studies of the electronic properties of the GaAs(1 0 0) surface cleaned by atomic hydrogen mainly classical XPS and UPS photoemission techniques have been applied [20,21]. 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 special emphasis on the electronic band gap states and Fermi level position are in demand [27].

Furthermore, the problem of atomic hydrogen diffusion into the GaAs bulk is also often neglected, despite the fact that the H atoms can well diffuse into the bulk at temperatures below 200 °C [28–30]. Due to the inadvertent formation of dopant–hydrogen complexes, which neutralize the dopant atoms, as well as to the observed passivation and/or compensation of deep or shallow level impurities or defects, the presence of hydrogen in the subsurface region is sometimes problematic in controlling the critical electronic properties of semiconductor devices [28–30].

Thus, a better understanding of the mechanism of atomic hydrogen cleaning of GaAs(1 0 0) surfaces, especially at room temperature, as well as a comprehensive model which can relate electronic properties and chemical processes is a challenging issue in the technology of modern devices [16–30].

In this work, we aim at gaining a better understanding of the processes involved during atomic hydrogen interaction with real GaAs(1 0 0) surfaces at room temperature by use of photoemission yield spectroscopy (PYS) developed by Sebenne and co-workers [31], Auger electron spectroscopy (AES) and mass spectrometry (MS). By applying such a unique composition of examination techniques, which allows determination, among others, of precise values of the ionization energy and work function, the three interaction stage processes are displayed against the atomic hydrogen exposure. In terms of the presented room temperature investigations, the roles of different mechanisms which are responsible for the observed surface electronic and chemical variations are carefully discussed and compared to literature data [16–22]. Finally, in attempt to correlate the chemical composition and electronic properties of the space charge layer, a quantitative correlation with others by use of a surface molecule approach is introduced.

2. Experimental

Two types of (1 0 0) oriented n-type Te doped GaAs wafers with a carrier concentration of the same level of 10^{17} cm^{-3} were used. After the standard degreasing in acetone, methanol and rinsing in deionized water, both types of samples (real obtained by standard cut and epi-ready delivered by AXT) were transferred into the ultra high vacuum system (UHV) without any other treatments (the epi-ready sample differs from the real one by controlled oxidation in well defined condition [32]).

In the first part of the experiments, the atomic hydrogen cleaning, as well as the PYS experiments were performed using an atomic hydrogen cracking cell similar to that developed by Sugaya and Kawabe [17]. In this approach, the molecular hydrogen is thermally dissociated on the resistively heated coiled tungsten filament placed at normal angle to the sample at a distance of 5 cm. The filament temperature was estimated, based on the thermal change of the filament resistance, to about 2100 K. In this temperature range, the cracking efficiency of molecular hydrogen is confirmed to be below 10%, as presented by others [17,33] for a constant pressure maintained at 2×10^{-4} Pa during sample exposures.

These results were then verified in an additional separate UHV apparatus operating at the same base pressure of 10^{-7} Pa. In this part of AES and MS experiments, a cracking source similar to that developed by Bischler and Bertel [34] has been used. In this case the atomic hydrogen is generated by passing molecular hydrogen through a tungsten capillary operating at 2100 K, as measured by a pyrometer. The atomic hydrogen doser was kept about 3 cm away from the sample at 50° to the surface normal. In this temperature range, for low feeding pressure maintained at 5×10^{-6} Pa during the experiments, the cracking efficiency was almost unity as estimated from the analysis performed by Winkler and co-workers [35].

The absolute exposure of atomic hydrogen was not been calibrated. Instead, the total background exposure of hydrogen (given in Langmuirs denoted by L) multiplying by the cracking efficiency is used as the relative measure for atomic hydrogen dosage in both experiments.