



Analysis of mechanism of carbon removal from GaAs(1 0 0) surface by atomic hydrogen

P. Tomkiewicz^{a,*}, A. Winkler^b, M. Krzywiecki^a, Th. Chasse^c, J. Szuber^a

^a Department of Electron Technology, Silesian University of Technology, 44-100 Gliwice, Poland

^b Institute of Solid State Physics, Graz University of Technology, A-8010 Graz, Austria

^c Institute of Physical and Theoretical Chemistry, University Tübingen, 72076 Tübingen, Germany

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ABSTRACT

Etching of carbon contaminations from the GaAs(1 0 0) surface by irradiating with atomic hydrogen, which is one of the key reactions to promote high-quality thin films growth by molecular beam epitaxy (MBE), has been investigated by mass spectrometry (MS), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). It is shown that during the cleaning process at room temperature a total reduction of the Auger carbon signal, accompanied by desorption of methane as major reaction product, can be observed. The reaction pathways as well as the processes responsible for the observed carbon removal are discussed in detail to give a support for etching and growth quality enhancement not only in thin films epitaxy but in all atomic hydrogen promoted gas-phase III–V semiconductor processes.

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1. Introduction

It is known that carbon is strongly bonded to the III–V surfaces and for this reason the carbon contamination is very hard to remove [1–5]. Unfortunately, these carbon impurities, commonly found on the III–V surfaces, adversely affect the growth and quality of MBE layers [3–5] resulting in surface morphology deterioration even for buffer layers with thickness of up to 100 nm [2,3]. Thus, removing of carbon contaminations is strongly desired, since it is suggested that the presence of carbon at the growth interface is a major origin of carrier depletion [4].

Recently, the behavior of hydrogen atoms, frequently called hydrogen radicals, at semiconductor surfaces has attracted the attention of scientists as an important subject in gas-phase semiconductor processes [6–10]. Among different approaches, many papers have also addressed specifically the utilization of

atomic hydrogen for the low-temperature cleaning of semiconductor surfaces [8–14].

In spite of significant progress in smooth and high-quality surface production [15–19], very little is currently understood at the atomic level concerning the chemical processes responsible for the contaminations removal. For example, some authors have demonstrated that it is possible to remove carbon from the surface by room temperature atomic hydrogen irradiation [2,8,20] whilst others [4,9,12,13] claimed that it is impossible.

With respect to the abundance of inconsistent experimental data, we revisit the role of atomic hydrogen irradiation in carbon film removal from the GaAs(1 0 0) surface, not only of its importance for epitaxial growth by molecular beam epitaxy (MBE) of high-quality thin films, but also for academic reasons.

The objectives of these studies are to reveal the etching process during atomic hydrogen irradiation of the GaAs(1 0 0) surface, and to provide a basic theoretical interpretation for the differences in the degree of etching between different carbon contaminations. Thus, in this paper we focus our attention on the first interaction stage of the atomic hydrogen interaction with the native

* Corresponding author. Tel.: +48 32 237 10 09; fax: +48 32 237 20 57.

E-mail address: ptomkiewicz@polsl.pl (P. Tomkiewicz).

GaAs(100) surface [14] by applying mass spectrometry (MS), Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). Using this set of surface analysis methods, it was possible for the first time to show directly that one of the major reaction products is methane. Moreover, our AES carbon signals and XPS signals allow us to distinguish between different carbon species which is the key issue in the understanding of the processes involved during carbon film removal. Our results support the etching and growth quality enhancement, not only in thin film epitaxy but in all atomic hydrogen promoted gas-phase III–V semiconductor processes.

2. Experimental

In the experiments two types of (100) oriented n-type GaAs wafers were used, one real obtained by standard cut and one epi-ready delivered by AXT [21]. After the standard degreasing in acetone, methanol and rinsing in deionized water, one of the real type samples, which will hereafter be called R1, and one of the epi-ready type samples, which will hereafter be called EPI, were transferred into the ultra high-vacuum system (UHV), operating at the base pressure of 10^{-8} Pa, without any other treatments.

Both samples were then subjected to a subsequent short-time atomic hydrogen etch steps. Typically, these steps have carried out under low-hydrogen feeding pressure of 5×10^{-6} Pa for about 100–500 s. It is noteworthy that during the cleaning cycles the temperature of the samples has never been found to increase more than 10 K above the room temperature (298 K), as measured by a thermocouple. After each cleaning cycle as well as during the treatments the surface chemistry as well as the reaction products have been controlled by AES and MS, respectively. The Auger dN/dE spectra were taken by a cylindrical mirror analyzer (CMA) equipped with a coaxial electron gun operating at 2000 eV. The mass spectra were recorded by a quadrupole type mass spectrometer (QMS) placed at 10 cm away from the sample.

As an atomic hydrogen doser a cracking source similar to that developed in [22] has been used. The atomic hydrogen doser was kept about 3 cm away from the sample. In such a construction, for low-feeding pressure maintaining during the experiments, the cracking efficiency was almost unity [23]. With respect to the fact that the absolute exposure of atomic hydrogen has not been calibrated, the total background pressure of hydrogen multiplied by the treatment time is used as the relative measure for atomic hydrogen exposure (given in Langmuirs, L).

In the second part of the experiment, the atomic hydrogen doser was shifted toward the sample by 2 cm while the QMS spectrometer was placed 2 cm from the sample. In that part of experiment, real samples, which will hereafter be called R2, R3 and R4, have been introduced into the UHV system, but contrary to the previous samples without any prior treatment. At this time, the temperature of the sample has been found to increase up to 50 °C depending on the treatment time as a result of sample illumination by the hot tungsten capillary operating at 2100 K.

The difference in surface chemical composition of both sample types, EPI and R1, has been examined by XPS in a separate multi-chamber UHV system, operating at a base pressure of 10^{-8} Pa. The XPS spectra were taken at normal emission using a monochromatic Al $K\alpha$ source with energy of 1486.6 eV and a SPECS PHOIBOS 100 hemispherical analyzer (pass energy of 10 eV). The XPS C 1s peaks were then analyzed by curve fitting with a product of Gaussian and Lorentzian lines using a minimum number of peaks to obtain an acceptable fit to the experimental data. The whole fitting procedure was strict so that stringent conditions were imposed on the fitted components as described in detail in [24]. Namely, (i) the mixing ratios of the components were fixed, (ii) the FWHMs of

the main carbon components, i.e. C–C, were fixed, (iii) the oxide components were allowed to vary in a narrow margin of FWHMs, to take into account a possible mixture of different oxidation states. Finally, for both samples, (iv) the chemical core level shifts were kept constant and (v) the FWHMs of the components originating from the same species were fixed. Then the intensities were determined as the integrated peak areas assuming Shirley's background.

3. Results and discussion

In the top of Fig. 1, variations of the Auger carbon peak at 273 eV kinetic energy versus increasing atomic hydrogen exposure are presented for all of investigated samples. From these results it is clear that independent of the samples used, degreased or non-degreased, real or epi-ready, an increasing atomic hydrogen dose results in a very fast reduction of the carbon signal. Indeed, in the case of R1, R3 and EPI samples an exponential-like decrease in intensity is observed, while in the case of the R2 and R4 sample a slightly weaker, almost linear decrease is observed. A carbon free EPI sample is obtained after 150 L of H-exposure, while in the case of the real samples, R1, R2, R3 and R4, higher exposures of 200, 600, 600 and above 800 L, were needed, respectively.

These differences are mainly a result of the contamination level of the as-introduced samples before the atomic hydrogen treatments. As expected, since the EPI-ready term has been originally coined for samples with a special surface preparation procedure [21], the EPI sample shows the lowest content of carbon impurities. Accordingly, it is not surprising that from the degreased R1 sample the carbon can be removed faster than in the case of the non-degreased R2, R3, and R4 samples. Thus, our results reveal that there exists the possibility to remove carbon contaminations from differently pretreated GaAs surfaces even at room temperature, in contradiction to some other reports [4,9,12,13].

It seems that the reported discrepancies are the result of the additional “unknown” peak at 252 eV, which appears to grow after

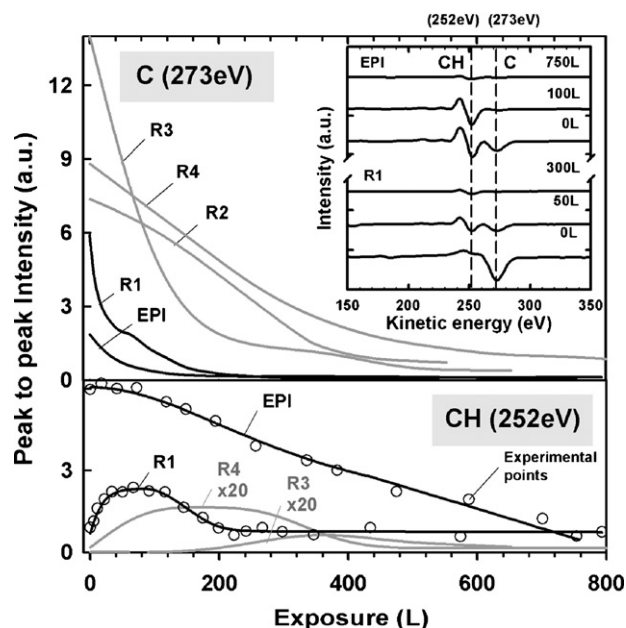


Fig. 1. Variations of the Auger carbon peak-to-peak intensity at 273 eV of kinetic energy denoted by C (upper panel) and at 252 eV denoted by CH (lower panel) vs. atomic hydrogen exposure for all samples (the same sensitive factor was used for both peaks [25]). In the inset the corresponding Auger spectra for the selected set of atomic hydrogen exposures for the EPI and R1 sample are summarized.

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