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Surface passivation and morphology of GaAs(100) treated in HCl-isopropanol solution

V.L. Alperovich, O.E. Tereshchenko^{*}, N.S. Rudaya, D.V. Sheglov, A.V. Latyshev, A.S. Terekhov

Institute of Semiconductor Physics, Novosibirsk State University, 630090 Novosibirsk, Russia

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Abstract

A promising chemical surface preparation technique, which consists in the treatment of GaAs(1 0 0) in HCl-isopropyl alcohol (HCl-iPA) solution under nitrogen atmosphere, is further developed. It was shown earlier [Tereshchenko et al., J. Vac. Sci. Technol. A 17 (1999) 2655] that HCl-iPA treatment and subsequent anneals in vacuum yielded atomically clean GaAs(1 0 0) surface with the whole range of surface reconstructions characteristic of this crystal face. In the present work the mechanisms of the passivation of GaAs(1 0 0) surfaces by arsenic overlayers as a result of HCl-iPA treatment are experimentally studied by X-ray photoelectron spectroscopy, low-energy electron diffraction and atomic force microscopy. The HCl-iPA treatment of clean As-stabilized GaAs(1 0 0) surfaces results in chemical passivation of the surface by submonolayer amount of excess arsenic. For the initially oxidized surfaces the treatment leads to the formation of 1-3 monolayers of amorphous arsenic on the surface, with the major part of the arsenic originating from the surface oxides dissolved in HCl-iPA. The HCl-iPA treatment preserves the atomic flatness of the GaAs(1 0 0) surface, keeping the mean roughness on a very low level of approximately ~0.1 nm.

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1. Introduction

Preparation of atomically flat surfaces is a necessary prerequisite for atomic-scale manipulations on semiconductor substrates. Only atomically flat surfaces yield opportunities for reproducible fabrication of nanoscale atomic structures due to self-assembling

fax: +7 3832 332771.

phenomena or by manipulations with single atoms using the atomic-probe techniques. Atomically flat surfaces should be also atomically clean because oxides and contaminations introduce atomic-scale roughness. Atomically flat and clean surfaces are also needed for many applications in micro- and optoelectronics.

Along with the preparation of atomically flat surfaces, an important problem is the preservation of these surfaces from contamination, corrosion and oxidation in air. To solve this problem, various kinds

^{*}Corresponding author. Tel.: +7 3832 343508;

E-mail address: teresh@thermo.isp.nsc.ru (O.E. Tereshchenko).

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of chemical passivation of surfaces by protecting overlayers are used in semiconductor science and technology. The general requirements to a passivation layer are the following: (i) the layer should be easily removed by thermal desorption at relatively low temperatures, well below the threshold of surface decomposition; and (ii) the formation and removal of the passivation layer are not accompanied by surface corrosion and introduction of defects. Various passivation techniques were developed for III-V semiconductor surfaces. These include passivation by sulfur-contained overlayers [1,2], special oxidation used in the production of "epiready" substrates [3], and in situ deposition of arsenic cap layers after molecular beam epitaxy (MBE) growth [4]. The latter proved to be a very effective passivation technique for GaAs(100). Thermal desorption of the As cap layer in vacuum at progressively increasing temperatures yielded atomically clean and structurally ordered surface with various atomic reconstructions [4]. However, for many applications it is necessary to obtain clean and well-ordered GaAs surfaces by chemical procedures.

Promising chemical procedures based on the surface treatment of GaAs in aqueous or alcohol solutions of HCl were proposed previously [5-11]. It was shown that HCl removed native oxides and formed thin, of about 1-3 monolayers (ML), elemental arsenic As⁰ overlayers on the surface. The evidences of GaAs surface chemical passivation by the As⁰ overlayers are as follows. First, carbon contaminations are easily removed from the HCl-treated surfaces by annealing in vacuum at relatively low temperatures of about 400 °C. On the contrary, on the oxidized GaAs surfaces the carbon contaminations are often converted into the surface carbides which cannot be removed by annealing at temperatures below the surface decomposition threshold $T \approx 600 \,^{\circ}\text{C}$ [12]. Second, if hydrocarbon contaminants were adsorbed on the clean GaAs(100) surface, they could be removed only by annealing at substantially higher temperatures (exceeding 500 °C) as compared to the contaminants which were adsorbed on the protective As⁰ layer formed by HCl treatment. Third, the elemental As⁰ overlayer prevents the surface from oxidation in air for at least a few minutes needed to load the chemically treated sample into UHV chamber. Satisfactory results were obtained by loading HCl-treated GaAs samples via air within ~ 5 min, although more stable and reproducible method consists in the sample treatment under inert atmosphere and transfer into UHV without exposure to air [7,11]. It was shown earlier in Ref. [7] that sample treatment in HCl-isopropanol solution under nitrogen atmosphere and subsequent annealing in UHV yielded atomically clean and well-ordered GaAs(1 0 0) surface with the whole set of reconstructions characteristic of this crystal face. The structural quality of the GaAs(1 0 0) surface prepared by the HCl-iPA treatment [7,13] was comparable with the quality of the MBE-grown As⁰-decapped GaAs(1 0 0) surface [4].

Despite a well-proved practical efficiency of the HCl-iPA treatment for preparation of the GaAs(100) surface, a number of essential problems are still not resolved. Firstly, the mechanism of the As⁰ layer formation remains unclear. Secondly, from the data obtained on HCl-iPA-treated surface [7,13,14] it is difficult to evaluate the morphology of the surface. Indeed, conventional low-energy electron diffraction (LEED) pictures can be observed even on relatively rough and disordered surfaces containing multi-level steps and islands, with only small part of the overall area having long-range order. To evaluate the surface morphology, either more elaborate spot profile analysis of LEED patterns (SPA-LEED technique) [15], or scanning probe techniques like atomic force microscopy should be used. Scanning tunneling microscopy (STM) images presented in Ref. [13] yield local picture of the atomic structure and do not allow to evaluate the smoothness of the surface on a larger scale.

The available data on the smoothness of HCl-treated surfaces are contradictory and related only to the aqueous solutions. In Ref. [6] atomically flat surfaces of n-GaAs(1 0 0) with height fluctuations of ± 1 ML over the area of $1 \times 1 \mu m^2$ were obtained by treatment in concentrated HCl and subsequent rinsing in deionized water. On the other hand, in Ref. [16] the treatment of p-GaAs in HCl under zero or anodic potentials led to the formation of large truncated pyramids. Later it was shown that the smoothness of GaAs(1 0 0) surfaces depended on the concentration of HCl in aqueous solution and on the time of treatment [6,17]. The morphology of the GaAs surface treated in alcohol solutions of HCl was not studied so far. The purpose of the present paper is to study the mechanism of the formation of arsenic passivation layers and the influence of the HCl-iPA treatment on the surface morphology.

2. Experimental

The experiments were performed on GaAs epitaxial layers in order to avoid possible influence of structural defects, which are present near the surfaces of commercial substrates prepared by mechanical and chemo-mechanical polishing. We used GaAs layers grown by liquid-phase epitaxy (LPE) on conventional GaAs(1 0 0) substrates and on patterned GaAs(1 0 0) substrates [18] with square-shaped mesa areas of various sizes ranged from 0.2 to 2 mm². The thicknesses and doping levels of the layers were $d = 4-6 \ \mu m$ and $p = (1-10) \times 10^{17} \ cm^{-3}$, respectively.

The preparation of the HCl-iPA solution consisted in the isopiestic saturation of the iPA by HCl vapor, which was performed as follows. A glass with 100 ml of high-purity doubly distilled iPA was put in a 3-1 desiccator filled with 300 ml of high-purity concentrated 37% hydrochloric acid. To determine the time dependence of HCl concentration $C_{\rm HCl}$ in the solution, 1-ml probes of HCl-iPA were taken from the glass. The concentration $C_{\rm HCl}$ was calculated from the acidity of the probes diluted in H_2O in the proportion of 1:40. The accuracy of these measurements was about $\pm 5\%$ and was verified by the method of titration. The measured time dependence of C_{HCl} is shown in Fig. 1 by closed circles. It is seen that at $t \le 50$ h the concentration increased linearly up to $C_{\rm HCl} \sim 10\%$ and saturated at $C_{\text{HCl}} \approx 20\%$ for t > 100 h. Except for special experiments with diluted HCl-iPA solutions (see below), the saturated 20% solution was used for the GaAs treatment. As compared to the direct dilution of hydrochloric acid in iPA, the isopiestic method minimizes the amount of water and contaminations in the resulting HCl-iPA solution.

In principle, the reaction of alcohol chlorination may occur in the HCl-iPA solution, producing isopropyl chloride and water [19]:

$$C_3H_7-OH + HCl \rightarrow C_3H_7-Cl + H_2O \tag{1}$$

Reaction (1) would diminish the concentration of chlorine Cl⁻, which is the active component of the HCl-iPA solution. In the available literature we found

Fig. 1. The time dependence of HCl concentration C_{HCl} in HCliPA solution measured during the process of saturation of iPA by HCl vapor (filled circles). Stability of C_{HCl} is shown by open circles. The solid and dashed lines are drawn to guide the eye.

no data on the rate and equilibrium constants of the reaction (1). In order to check a possible adverse effect of the reaction (1) on the stability of the HCl-iPA solution, at t = 100 h a 30-ml probe of the solution was put in a separate tightly closed glass. The time dependence $C_{\text{HCl}}(t)$ measured in this probe is shown in Fig. 1 by open circles. It is seen that within experimental error the concentration was constant up to $t \sim 500$ h. Moreover, the HCl concentration remained the same after $\sim 10^4$ h (not shown in Fig. 1). Thus, at room temperature the HCl-iPA is quite stable and may be used for a period of about 1 year.

The treatment of GaAs(1 0 0) was performed in a glove-box with dry nitrogen atmosphere. The sample was dipped into the HCl-iPA solution, then rinsed in clean iPA and dried by nitrogen flow. Other details of the HCl-iPA treatment are given in Refs. [7–9]. The morphology of the as-grown and HCl-iPA-treated surfaces was studied at ambient conditions by atomic force microscopy (AFM), using the scanning probe microscope Solver P-47H (NT-MDT).

For studying the composition and atomic structure of the surface, the HCl-iPA-treated samples were transferred into the UHV spectrometer ADES-500 in a hermetic transfer vessel, under nitrogen atmosphere, without air contact. The anneals were performed in the analytical chamber with the base pressure of 4×10^{-11} mbar. The pressure did not exceed 10^{-10} mbar during measurements and 5×10^{-10} mbar during annealing. The sample temperature during annealing was measured by means of the specular back side reflectance spectroscopy [7].



All measurements were done after cooling the sample down to room temperature. The surface reconstructions were studied by LEED. The composition of the surface was determined by X-ray photoelectron spectroscopy (XPS). The Al K α (1486.6 eV) and Zr M ζ (151.4 eV) lines were used for XPS measurements. Surface roughness may distort the results of the XPS measurements, and therefore special attention was paid to the morphology of the films. Fig. 2 shows a typical AFM image of an epitaxial film grown by liquid-phase epitaxy on a conventional substrate. It is



Fig. 2. A typical AFM image (in 3D mode) of an epitaxial GaAs(1 0 0) film grown by liquid-phase epitaxy (a); a cross-section profile of the film relief measured along the *x*-axis at $y = 3 \mu m$, which contains two step bunches (b); a fragment of the cross-section profile (b) within the flat area between the step bunches (c). Note different *x* and *zy* scales in (b, c).

seen that the surface contains atomically flat areas, several microns in width, separated by steps bunches of 10 nm height. Well-resolved monatomic steps, 0.28 nm in height, are seen within the flat areas. As the most part of the surface is atomically flat, these films can be considered as suitable for XPS experiments.

3. Results and discussion

3.1. Mechanism of As⁰ layer formation

It was shown in Ref. [7] that the HCl-iPA treatment of the oxidized GaAs(100) surface led to enrichment of the surface by several monolayers of elemental arsenic As^0 . The As^0 enrichment of the GaAs(100) surface was deduced from XPS experiments with an Al anode, by decomposition of the As 2p photoemission line. Here the presence of the As⁰ overlayer is confirmed by the evolution of Ga 3d and As 3d photoemission lines measured with a Zr anode (photon energy of 151.4 eV) at various angles of photoemission θ . The kinetic energies of emitted electrons $E \sim 110-130 \text{ eV}$ correspond to the photoelectron escape depth of approximately $\lambda \approx 0.6$ nm, which provides high surface sensitivity of the method. Photoemission spectra shown in Fig. 3 were measured on $GaAs(1 \ 0 \ 0)$ etched in $H_2SO_4:H_2O_2:H_2O = 20:1:1$ for 1 min at 40 °C and then treated in 20% solution of HCl-iPA for 3 min at 18 °C. It is seen that with increasing θ the Ga 3d line decreased more rapidly than the As 3d line. At $\theta = 75^{\circ}$ the line Ga 3d



Fig. 3. XPS spectra measured at various emission angles θ on the GaAs(1 0 0) surface treated in the HCl-iPA solution.



Fig. 4. Angular dependencies of the Ga 3d/As 3d intensity ratio measured on the HCl-iPA-treated GaAs(1 0 0) surface (filled circles), and on the clean surface with As-rich $(2 \times 4)/c(2 \times 8)$ reconstruction obtained by annealing at 450 °C (filled triangles). The solid line shows the angular dependence calculated by the formula (2) (see text). The dashed line is drawn to guide the eye.

practically vanished, while the line As 3d remained relatively intensive. The observed increase of As 3d/ Ga 3d intensity ratio with increasing angle proves that there is a uniform arsenic layer covering the surface [20]. In addition, the As 3d line shifted to higher binding energies by ~ 0.4 eV. This shift is due to a relative increase of the elemental arsenic As⁰ component, which is chemically shifted with respect to the bulk arsenic component.

In Fig. 4 the angular dependence of the Ga 3d/As 3d intensity ratio $K(\theta)$ measured at the HCl-iPA-treated surface is shown by filled circles. It is seen that the ratio decreased from 0.36 to 0.08 with increasing the emission angle from $\theta = 0^{\circ}$ (corresponding to normal emission) to 75°. The angular dependence $K_0(\theta)$ measured on the GaAs(1 0 0) surface with As-stabilized $(2 \times 4)/c(2 \times 8)$ reconstruction, which is denoted by filled triangles, was much weaker than that obtained on the HCl-iPA-treated surface, as expected. The solid line in Fig. 4 shows the dependence $K(\theta)$ calculated in the model of a uniform As⁰ layer on a GaAs substrate according to the following formula [20]:

$$K(\theta) = \frac{K_0(\theta)}{1 + r[\exp(d/\lambda\cos\theta) - 1]}$$
(2)

where r = 2.08 is the ratio of the volume arsenic concentration in the amorphous As⁰ layer to the arsenic concentration in the GaAs crystal. The thickness of the amorphous arsenic layer *d* was used as a fitting parameter and was found to be equal to $d = 0.33 \pm 0.03$ nm, which is equivalent to ≈ 2.5 ML. A good agreement between the calculated curve and experimental angular dependence confirms the existence of a uniform As overlayer on the HCl-iPAtreated GaAs surface.

It was shown in Ref. [6] that properties of the GaAs surface treated in aqueous HCl solutions critically depended on the HCl concentration. To check concentration dependence of the properties of the GaAs surface treated in HCl-iPA solutions, we performed chemical treatment in the solutions with various $C_{\rm HCl}$. In Fig. 5 the As 2p/Ga 2p photoemission intensity ratio, which characterizes the amount of elemental As⁰ on the surface, is shown for the $GaAs(1 \ 0 \ 0)$ surfaces treated for 3 min in HCl-iPA solutions with C_{HCl} equal to 20, 7, and 2.5%. After the measurements of As 2p/ Ga 2p ratio on the treated surface, each sample was thermally cleaned for 10 min at 450 °C to obtain Asstabilized surface with the $(2 \times 4)/c(2 \times 8)$ reconstruction. The ratio measured on the $(2 \times 4)/$ $c(2 \times 8)$ surfaces is also shown in Fig. 5. As expected, the measured values for the $(2 \times 4)/c(2 \times 8)$ surfaces coincide within experimental error for all three samples. On the other hand, it is seen from Fig. 5 that the As 2p/Ga 2p ratio measured on the chemically treated surfaces decreases substantially with the decrease of $C_{\rm HCl}$. The observed decrease of the ratio corresponds



Fig. 5. Photoemission lines As 2p/Ga 2p intensity ratio measured on the GaAs(1 0 0) surface after the treatment in HCl-iPA solutions with various concentrations of HCl (filled symbols) and subsequent annealing in vacuum at 450 °C, which yielded the As-stabilized $(2 \times 4)/c(2 \times 8)$ reconstruction (open symbols).

to the reduction of the amount of passivating elemental As⁰ on the surface. We also observed some deterioration of the LEED images (dimming of the diffraction spots and increase of the diffuse background) and about $\sim 30\%$ increase of carbon contaminations on the surfaces treated in diluted HCl-iPA solutions. These effects are explained by worse passivation properties of thin As⁰ layers obtained in diluted solutions. The same is true for aqueous HCl solutions: for small C_{HCI} , corresponding to acidities pH > 3, the elemental As^0 is soluble [21], and this may be the reason for the increased roughness of GaAs(100) surfaces obtained in diluted aqueous HCl solutions [6]. All further experiments were done using HCl-iPA solutions with the highest available concentration $C_{\rm HCl} \approx 20\%$.

The results presented in this paper along with the direct observation of chemically shifted components of photoemission lines [14] prove the fact of accumulation of amorphous arsenic on the GaAs surface under the HCl-iPA treatment. However, the mechanism of this accumulation remains unclear. Presumably, the interaction of HCl-iPA with the GaAs surface is as follows. On the first stage gallium and arsenic oxides are dissolved. We proved experimentally that at room temperature it took less than 10 s to remove the oxides. On the second stage an arsenic overlayer is formed on the GaAs surface due to the following reaction [22]:

 $GaAs + 3H^+ + 4Cl^- \rightarrow GaCl_4^- + As^0 + \frac{3}{2}H_2 \uparrow (3)$

In course of the reaction (3), chlorine attacks gallium, forms soluble gallium chlorides, which are dissolved in the solution, while elemental As⁰ accumulates on the surface [7]. It is possible that monolayer or even submonolayer amount of excess As⁰ blocks the access of chlorine to underlying gallium atoms. Thus, the surface is passivated, and the reaction (3) is stopped. However, the experimental observation of As⁰ layers with thicknesses exceeding 1 ML allows one to suggest that after the formation of the first monolayer, further accumulation of As⁰ takes place due to GaAs dissolution according to the reaction (3). If this is the case, the reaction (3) is presumably limited by diffusion of reagents and reaction products through the layer of amorphous arsenic. Due to exponential decrease of the diffusion transfer with the increase of the layer thickness, a logarithmic increase of the thickness d(t) is expected. Also, for this mechanism the accumulation of As^0 should be facilitated by the increase of the temperature of HCl-iPA solution. Thus, in order to test this mechanism of As^0 accumulation, the kinetics of the As^0 layer thickness d(t) should be studied at various temperatures of the solution. One more possible source of As^0 accumulated on the surface under the HCl-iPA treatment is the arsenic which is present in the surface oxide layer and on the oxide–GaAs interface [23]. Some portion of this arsenic may be left on the surface after the dissolution of the oxides on the first stage of HCl-iPA treatment.

To clarify which of the two proposed mechanisms of As⁰ accumulation is valid, we performed HCl-iPA treatment of oxide-free, atomically clean GaAs(100) surfaces with a well-defined composition and structure. To this end, an as-grown surface with native oxide was stripped of oxides in HCl-iPA, then the sample was loaded in the UHV setup and thermally cleaned at T = 450 °C. In this way the atomically clean As-stabilized surface with the $(2 \times 4)/c(2 \times 8)$ reconstruction was obtained. After that the sample was unloaded under nitrogen atmosphere to the nitrogenfilled glove-box, treated in HCl-iPA again, and then reloaded back to the UHV chamber. The determination of the surface composition using surface-sensitive photoemission lines (As 2p, Ga 2p for the Al anode and As 3d, Ga 3d for the Zr anode) was performed by XPS on each stage. The ratio As 3d/Ga 3d measured in this experiment is shown in Fig. 6. It is seen that the As 3d/Ga 3d ratio is substantially larger after the HCl-iPA treatment of as-grown oxidized surface than after the treatment of the clean surface (the triangle and square, respectively). Therefore, a substantial portion of As⁰, which accumulates on the initially oxidized surface under the HCl-iPA treatment, originates from the surface oxide.

In order to exclude the contribution of As⁰ originating from surface oxides, in further studying of the As⁰ layer formation, oxide-free atomically clean GaAs(1 0 0) surfaces with the $(2 \times 4)/c(2 \times 8)$ reconstruction were treated in HCl-iPA solution. The As 3d/ Ga 3d ratio measured on GaAs(1 0 0) surfaces treated at various temperatures of the HCl-iPA solution $(T = 0, 18 \text{ and } 45 \,^{\circ}\text{C})$ and for treatment durations from 10 s through 30 min are shown in Fig. 7(a) by filled symbols. For comparison, open symbols show



Fig. 6. As 3d/Ga 3d intensity ratio after the HCl-iPA treatment of an initially oxidized GaAs(1 0 0) surface (filled triangle), after annealing at 450 °C (filled circle), and after the second HCl-iPA treatment of the obtained As-stabilized $(2 \times 4)/c(2 \times 8)$ reconstruction without exposure to air (filled square).

the values of As 3d/Ga 3d ratio measured in corresponding experiments on the clean $(2 \times 4)/c(2 \times 8)$ surfaces. The scattering of the open data points around the mean value (denoted by the dashed line) characterizes the error in determination of the As 3d/Ga 3d ratio. It is seen that at T = 0 and 18 °C the As 3d/Ga 3d ratio did not appreciably change with treatment duration and corresponded to submonolayer effective As⁰ coverages $d \sim 0.3-0.5$ ML. Substantial increase of the As 3d/Ga 3d ratio with increasing treatment duration t was observed only at higher temperature $T = 45 \,^{\circ}\text{C}$ of the HCl-iPA solution. For $T = 45 \,^{\circ}\text{C}$ and t = 30 min the effective thickness of As⁰ layer increased up to $d = 1.2 \pm 0.2$ ML. In this experiment a substantial deterioration of the LEED picture of the $(2 \times 4)/c(2 \times 8)$ reconstruction took place. In Fig. 7(b) this deterioration is seen as an increase of the ratio of the diffuse background to diffraction spot intensity by a factor of 2. The increase of the amount of As⁰ and of the diffuse background at T = 45 °C can be presumably assigned to temperature activation of the reaction (3) and, consequently, to the beginning of the surface corrosion. It should be noted that at low temperature $(T = 0 \,^{\circ}\text{C})$ the increase of the diffuse background also took place, although without substantial accumulation of As⁰.

Thus, at room and lower temperatures the HCl-iPA treatment of clean oxide-free GaAs(100) surfaces leads to the formation of submonolayer arsenic coverages. A monolayer arsenic coverage is formed under



Fig. 7. (a) As 3d/Ga 3d intensity ratio vs. time of treatment at various temperatures *T* of the HCl-iPA solution (filled circles: T = 0 °C; filled squares: T = 18 °C; filled triangles: T = 45 °C). The open symbols correspond to the As 3d/Ga 3d ratio measured at the annealed As-stabilized $(2 \times 4)/c(2 \times 8)$ surfaces in the respective experiments (see text). (b) The ratio of the diffuse background to the diffraction spot intensity in the LEED images of the GaAs(1 0 0)– $(2 \times 4)/c(2 \times 8)$ surface vs. treatment time and temperature of the HCl-iPA solution. The symbol notations are the same as in (a).

the treatment at T = 45 °C. For the range of treatment conditions used in this work the rate of GaAs diffusion-limited dissolution is negligible and the accumulation of As⁰ over one monolayer does not take place. One can conclude, firstly, that a relatively small enrichment of the $(2 \times 4)/c(2 \times 8)$ surface by about 0.3–0.5 ML of excess arsenic effectively blocks the access of chlorine to the underlying Ga atoms and thus passivates the GaAs surface from further dissolution. Secondly, the amorphous arsenic in the passivation layers, which are formed by HCl-iPA treatment of oxidized GaAs surfaces, originates mainly from the surface oxides.

3.2. Structure and morphology

The angular dependence of photoemission spectra shown in Fig. 4 allows us to suppose that HCl-iPA treatment of the oxidized GaAs(1 0 0) surface leads to the formation of a uniform As⁰ passivation layer and preserves the atomic flatness of the surface. LEED and AFM data presented in this section yield direct proofs of this supposition. LEED image of the HCl-iPAtreated surface is shown in Fig. 8(a). On this surface the (1×1) structure is observed at electron energies $E \ge 130$ eV, while at $E \sim 40-60$ eV no diffraction spots are seen on the diffuse background. Annealing in vacuum at 250 °C removed most part of the As⁰ layer, so that the (1×1) diffraction pattern was observed at low energy E = 42 eV (see Fig. 8(b)). After annealing at T = 450 °C (Fig. 8(c)) the diffraction pattern corresponding to the As-stabilized $(2 \times 4)/c(2 \times 8)$ reconstruction is clearly seen in the LEED image. Annealing at higher temperatures transformed the As-stabilized to Ga-stabilized surface via a set of intermediate reconstructions [7]. The Ga-stabilized $(4 \times 2)/c(8 \times 2)$ reconstruction obtained after annealing at T = 550 °C is shown in Fig. 8(d).



Fig. 8. LEED images of the GaAs(1 0 0) surface with (1 × 1) structure observed after the HCl-iPA treatment at electron energy E = 130 eV(a); (1 × 1) structure after annealing at T = 250 °C, E = 42 eV (b); $(2 \times 4)/c(2 \times 8)$ reconstruction after annealing at T = 450 °C, E = 45 eV(c); $(4 \times 2)/c(8 \times 2)$ reconstruction after annealing at T = 550 °C, E = 46 eV (d).



Fig. 9. Typical AFM images of the as-grown epilayer surface (left column (a, b)) and the same surface treated in HCl-iPA for 3 min at room temperature (right column (d, e)). The top (a, d) and middle (b, e) panels show the large-scale and small-scale images, respectively. The bottom panel (c, f) shows the *z*-*x* cross-section profiles measured along the directions denoted by dashed lines in the middle panels (b, e).

The influence of the HCl-iPA treatment on the morphology of the $GaAs(1 \ 0 \ 0)$ surface was studied by the atomic force microscopy. The AFM images of the epitaxial films grown by LPE on conventional

GaAs(100) substrates (see Fig. 2) show that the surfaces of these films contain atomically flat regions of several micron size. However, the irregularities of the surface relief, which are mainly due to the

presence of step bunches and also a small number of other defects like pits and pyramids, hinder studying the influence of the HCl-iPA treatment on the atomically flat regions. To overcome this difficulty, we used epitaxial films grown on the patterned substrates with square-shaped mesa areas. In agreement with the results presented in Ref. [18], on these mesa areas the dislocation-controlled facet growth yielded extremely flat surfaces of the epitaxial films, without step bunches or other macroscopic defects. A $12 \times 14 \ \mu m^2$ AFM image of such surface is shown in Fig. 9(a). In the central part of the image one can see a spiral monatomic step, d = 0.28 nm in height, originating from a dislocation which has the Burgers vector component perpendicular to the surface. The width of terraces between the monatomic steps is about 2 µm. The spiral step configurations were the only macroscopic morphological features on these atomically flat surfaces.

Fig. 9(b) and (c) shows an enlarged AFM image of a $400 \text{ nm} \times 400 \text{ nm}$ fragment of the as-grown facet surface and the z-x cross-section profile of the film relief along the x-axis measured at y = 140 nm, respectively. Monatomic height anisotropic islands with sizes of about 20-50 nm are seen in Fig. 9(b) and (c). The islands are elongated in the $[-1\ 1\ 0]$ direction presumably due to the anisotropy of the adatom diffusion coefficients and incorporation probabilities on the growing surface. Similar anisotropy of the island shapes was observed earlier on the MBE-grown films [24,25]. Mean roughness ρ of the surface determined on $300 \times 300 \text{ nm}^2$ is equal to $\rho = 0.12 \text{ nm}$. The oxide thickness measured by XPS on as-grown LPE films after several days in air was approximately equal to 0.5 nm.

The right column of Fig. 9 is related to the HCl-iPAtreated surface. The AFM image of a $3 \times 3 \mu m^2$ part of the surface measured within 1 h after HCl-iPA treatment is shown in Fig. 9(d). It shows that the treatment preserves the character of the film relief with wide terraces and monolayer height islands. However, on the enlarged images more subtle distinctions between the as-grown and HCl-iPA-treated surfaces can be seen. Fig. 9(e) shows a 400 nm × 400 nm fragment of the AFM image measured after HCl-iPA treatment on the same mesa area as the image shown in Fig. 9(b). Although after the treatment the mean roughness remained practically the same, $\rho = 0.11$ nm, the relief seems more amorphous, with smeared edges of islands. These distinctions are due to the formation of an amorphous layer of elemental arsenic on the surface. Interestingly, the atomic flatness of the HCl-iPA-treated surface remained intact for rather long period of about 2 years. One can conclude that HCl-iPA treatment of the atomically flat GaAs(1 0 0) surfaces does not lead to their corrosion during the treatment and passivates the surfaces against subsequent corrosion in air.

4. Conclusions

Composition, morphology and structure of the GaAs(100) surface treated in the solutions of HCl in isopropyl alcohol are studied by XPS, LEED and AFM. The HCl-iPA treatment of the clean As-stabilized GaAs(1 0 0)–(2 × 4)/c(2 × 8) surface results in chemical passivation of the surface by submonolayer of excess arsenic. This arsenic blocks the access of chlorine to underlying gallium atoms and, thus, stops the reaction which leads to further accumulation of arsenic by GaAs dissolution. The treatment of the oxidized GaAs surfaces leads to the formation of 1-3 monolayers of amorphous arsenic on the surface, with the major part of the arsenic originating from the surface oxide. AFM measurements performed before and after treatment on atomically flat epitaxial films grown on special patterned substrates prove that HCliPA treatment preserves the atomic-scale smoothness of the GaAs(100) surface.

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