Cleaning of Si and GaAs Surface in the Atomic Hydrogen Flow Formed by the Source Based on Low-Pressure Arc Discharge

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Abstract – The experimental results on atomic hydrogen Si and GaAs surface treatment are presented. The atomic hydrogen surface cleaning from native oxide layer, carbon, and other contaminants results in atomically clean surface suitable for subsequent epitaxial regrowth and/or formation of micro- and nanoelectronics devices. Concentration values of impurities on Si and GaAs surface after treatment is leveled to their bulk concentration values being in the case of Si samples \(\cong 4 \times 10^{17} \text{ cm}^{-3}\). The controlled time-temperature treatment modes as well as the angle of atomic hydrogen flow incidence on the surface of samples allow manipulations with surface parameters, in particular, the surface roughness and obtained atomically glad surface. As a result of treatment, the surface roughness of Si and GaAs surface is decreased by \(\cong 2\) times and for Si samples it makes \(\cong 0.06\) nm.

1. Introduction

Rather fast demagnification of IC elements typical sizes and nanoelectronics development do stimulate elaboration of new technologies allowing formation of atomically clean and atomically smooth monocrystalline surface of semiconductor wafers presenting minimum introduced charges and defects. Treatment of semiconductor structures by kinetic-energy-enhanced neutral reactive particles beams is considered to be one of such perspective techniques [1], and surface cleaning of semiconductor materials by atomic hydrogen (AH) flow is today one of demanded methods of surface preparation [2, 3].

GaAs surface cleaning from native oxides by active hydrogen medium (high-frequency discharge hydrogen plasma) was first performed in [4], later [5] Si surface cleaning as well as surface cleaning of Al\(_x\)Ga\(_{1-x}\)As [6] with employing of hydrogen plasma were studied. Recently, in connection with development of technology of low-k dielectrics, the works on resist removal in plasma of hydrogen-containing gases (NH\(_3\), H\(_2\)/N\(_2\), and H\(_2\)/He) were carried out [7, 8]. The drawback of plasma treatment is energy charged particles action on semiconductive structure. It is possible to avoid that negative action of charged particles using flows of neutral reactive particles. Thus, for example, in the papers [9, 10] the possibility of GaAs cleaning by low-intensity flow of thermal hydrogen atoms was shown.

This paper reports on the results of surface cleaning of Si and GaAs wafers from native oxide, carbon and other contaminants by intensive kinetic-energy-enhanced hydrogen atoms flow formed by the source which has been developed by us for micro-and nanoelectronics tasks solution.

2. Experimental Techniques

The experiments on surface cleaning of semiconductor structures were carried out on the set-up described in [11]. The wide-aperture beam of kinetic-energy-enhanced hydrogen atoms was produced by the low-pressure arc discharge AH source [11]. Hydrogen with purity of 99.9999999% was used in experiments. The residual atmosphere pressure in the vacuum chamber exhausted by turbomolecular pump was \((60–4) \times 10^{-3}\) Pa at surface cleaning of GaAs samples and \((10–5) \times 10^{-2}\) Pa in the case of samples Si/SiGe/Si. IR heater heated the samples. The variable parameters during experiments were AH flow density \((5 \times 10^{14}–5 \times 10^{15} \text{ at.} \text{ cm}^{-2} \text{ s}^{-1})\), temperature of samples \((T = 18–650 \degree \text{C})\), and time of treatment by AH \((t = 0.3–40 \text{ min})\). Hydrogen pressure in the vacuum chamber during treatment was \(5 \times 10^{-3}–10^{-2}\) Pa. After cleaning was over, aiming at cleaned surface capsulation, the cleaned samples were deposited with Au thin film \((d = 0.05–0.1 \mu \text{m})\) using thermal deposition technique in situ. Not cleaned reference samples were capsulated with Au film too. Measurement of elements concentration distribution in samples depth was performed by time-of-flight secondary ion mass-spectroscopy (ToF SIMS) method. Atomic-forced microscope (AFM) measured surface roughness.

3. Basic Physics and Chemical Processes at Atomic Hydrogen Interaction with Semiconductor Surface

Removal of surface contaminants and subsequent etching of semiconductor material by AH flow occurs due to the mechanism of radical etching, and chemical reactions leading to GaAs surface cleaning may be written in the following form [12–14]:

\[
\text{H} + \text{GaAs} \rightarrow \text{GaAs} \rightarrow \text{H} + \text{GaAs} \rightarrow \text{GaAs} \rightarrow \text{H} + \text{GaAs} + \text{CH}_4.
\]
Modification of material properties

Ga₂O₃ + 4H⁺ → Ga₂O↑ + 2H₂O↑,
2Ga₂O₃ + 8H⁺ → 4GaOH↑ + 2H₂O↑,
As₂O₃ + 2H⁺ → As₂↑ + xH₂O↑.

As a result of reactions, on the surface of sample with native oxide-layer, first, oxides reduction occurs and volatile products form, namely, molecules of elements or their hydrides, as well as lower oxides appear. Further etching of GaAs sample occurs through formation of volatile hydrides of As and Ga. The volatile products of chemical reactions in the case of Si cleaning are water, and hydrides of Si and C. The experiments have shown that temperature dependencies of etching rates of oxides Ga, As, and Si are described by Arrhenius equation (Fig. 1). That speaks for the fact that at AH flow density of 5 ⋅ 10¹⁴–5 ⋅ 10¹⁵ at. cm⁻²s⁻¹ the etching rate is not limited by the flow density but is limited by the rate of one of the three processes: adsorption of reactive particles, chemical reaction occurred on the surface, or desorption of the products of reaction. The additional experiments made using simultaneous AH flow effect on the surface and continuous and/or pulsed UV irradiation (λ ≤ 200 nm) have revealed that at low cleaning temperatures of GaAs (T ≤ 100 °C) the rate of removal of GaAs oxides is probably limited by reaction products desorption rate [15].

On surface cleaning of semiconductor structures, simultaneously with the process of oxide etching by AH, the surface oxidation by active gas components presenting in the residual atmosphere of vacuum chamber and in hydrogen supplied into AH source does occur. The etching rate is determined by temperature of the sample, and oxidation rate depends on the partial pressure of oxygen-containing particles and sample's temperature increasing in the course of oxide film removal. Surface equilibrium concentration of oxygen established in the process of cleaning is determined by proportion between the rates of etching and oxidation. It is clear that it is impossible to realize such the experimental conditions with which oxidation rate would be equal to zero. Therefore, after cleaning, oxygen always is presented on the surface. From technological point of view, one may speak for maximal cleaning degree of the surface only in that case when surface oxygen concentration is equal to its concentration value in solid matter bulk.

4. Surface Cleaning of Semiconductor Materials by Atomic Hydrogen Flow

Surface cleaning of Si. In the experiments, the samples of Si/SiGe/Si, obtained by epitaxial growth of SiGe and Si layers on Si (100) substrate were used. The profiles of elementary distribution in depth of the initial sample of Au/Si/SiGe/Si, the surface of which before Au deposition was exposed to air, are presented in Fig. 2, a. At the boundary of Au/Si, oxygen and carbon are presented with relative concentration values exceeding their concentration in the bulk of Si about two orders of magnitude. That suggests existence of native oxide layer and surface carbonic contaminants. The sloping profile of carbon over the epitaxial layers of Si and SiGe is the evidence that carbon was introduced in these layers bulk during the process of epitaxial growth of SiGe and Si layers. Concentration values of Cl and F at the boundary exceeds their bulk concentration by 2.5–3 orders of magnitude being sharply decreased at deepening into the material (it is not shown in the figure).
The result of sample’s cleaning by AH at 580°C within 2 min is practically total oxygen removal from Si surface (Fig. 2, b). Its concentration at Au/Si boundary decreases up to $\leq 4 \times 10^{17}$ cm$^{-3}$ being comparable to oxygen concentration in Si bulk (Fig. 2, c). The analogous results were obtained for the cases of C, Cl, and F. It is the evidence that cleaning by AH leads to obtaining of atomically clean Si surface.

The dependencies of concentration of O, C, H, Cl, and F at Au/Si boundary versus temperature of treatment are presented in Fig. 3. Cleaning at temperature of 200°C results in decreasing of concentration values of O, C, Cl, and F by 1–2 orders of magnitude. With further increasing in treatment temperature, concentration values of these elements gradually decrease, and at temperature of 510–580°C verge towards their concentration values in Si bulk. Somewhat other behavior is observed for hydrogen. Treatment at 200 and 400 °C changes its concentration negligibly as compared to the initial sample. At $T = 510$ °C, concentration of H at Au/Si boundary sharply decreases being decreasing with temperature growth, hence even at $T = 580$ °C that H concentration steel exceeds the bulk one.

The analysis of hydrogen profiles distribution in depth of silicon has shown that excessive contains of H for the initial Si sample is being observed until 7–8 nm depth. Treatment at $T = 200$ °C and 400 °C results in hydrogen penetration in Si bulk in depth not less that 20 nm and 25 nm, respectively. At higher temperature values of treatment ($T = 510$ °C), the depth of hydrogen occurrence changes negligibly being leveled to 25 nm. As-cleaned at the mode $T = 580$ °C, $t = 2$ min, the depth of H penetration in Si only slightly exceeds H-profile width of the initial sample comprising 10 nm (Fig. 2).

Hydrogen penetration in Si (hydrogenation) may lead to passivation of dopants and change in electro-physical characteristics of the surface layer. The experiments carried out show that at the cleaning mode of $T = 580$ °C, $t = 2$ min penetration of H into Si is quite negligible, and probably it does not influence essentially on the electrophysical properties of the surface layer.

It has been established that the thickness of Si epitaxial layer is decreased with increase of treatment temperature by AH flow. In the case if after treatment at 200°C the Si-layer thickness corresponds to the initial thickness (20 nm), then after treatment at 400 and 510°C ($t = 10$ min) the thickness value decreases up to 17 nm, and after treatment at 580°C ($t = 2$ min) that one is 16.6 nm. The last fact does confirm that during treatment by AH flow the oxide is being removed, and it testifies that after oxide removal, etching of Si underlying layers is being realized. Etching rate of Si at 580°C is $\leq 0.03$ nm s$^{-1}$.

Surface cleaning of GaAs. Fig. 4, a shows profiles of elementary distribution in the initial $i$-GaAs sample the surface of which before Au film deposition was exposed to air. It is seen that at the boundary Au/GaAs there are impurities of oxygen, carbon and hydrogen, and oxygen is presented in chemically bound state as oxides of Ga and As. That testifies that there is the native oxide layer on GaAs surface, as well as carbon- and hydrogen containing contaminants.

The profiles of elementary distribution in the depth of $i$-GaAs sample, cleaned by AH flow ($T = 300$ °C, $t = 1$ min), the surface of which at once as-treated was deposited in situ with Au film, are shown in Fig. 4, b.
It is seen that oxygen contains at the boundary of Au/GaAs, which is probably in chemically bound state with Ga. That is evidenced by profiles forms coincidence for O and Ga+O. The small contain of Ga oxides at the boundary of Au/GaAs speaks for their incomplete removal at the given cleaning mode with temperature and treatment time. Concentration values of other impurities, including As+O, are leveled to their bulk concentrations being the evidence of their complete removal from GaAs surface at treatment by AH.

The profiles of elementary distribution in depth of the sample i-GaAs, cleaned by AH flow at \( T = 400 \, ^\circ C \) during 1 min are shown in Fig. 4, c. Concentration values of all contaminant elements at the boundary of Au/GaAs are leveled to their bulk ones being the evidence that the complete removal of native GaAs oxide layer was performed as well as surface carbon and hydrogen-containing contaminants was done as a result of treatment by AH flow, and atomically clean surface was formed. The cleaned surface and surface layer of GaAs have practically stochiometric composition that is testified by close by value relation between intensity of signal of As+Ga and As and similar profiles of those components in the case of as-treated initial sample.

Cleaning by AH flow did not lead to additional penetration of hydrogen in the surface layer of GaAs and, hence, the change in electrophysical properties of material could hardly occur.

5. Surface Roughness after Cleaning by AH Flow

At treatment of semiconductor materials by AH, not only removal of native oxide layer and surface contaminants but subsequent etching of the surface by atomic hydrogen occurs resulting in change of such important parameter as roughness.

\( \text{Si surface roughness.} \) Table 1 presents the values of surface roughness \( R_s \) of the initial sample \( p\)-Si (100) and \( n\)-samples treated by AH at various modes. The surface of the initial sample is characterized by roughness leveled to 0.128 nm at measurement area of \( 500 \times 500 \, \text{nm}^2 \).

Treatment by AH flow leads to roughness decrease from 0.128 nm to 0.055–0.068 nm (measurement area \( 500 \times 500 \, \text{nm}^2 \)). The minimal roughness value of \( R_s = 0.055 \, \text{nm} \) is characteristic of the sample treated at \( T = 300 \, ^\circ C \) during 2 min at the normal AH flow incidence on Si surface (\( \alpha = 90^\circ \)). The sample treated at analogous time-temperature mode but at sliding incidence of AH flow (\( \alpha = 30^\circ \)) gives slightly greater roughness (\( R_s = 0.064 \, \text{nm} \)). With the more greater roughness \( R_s = 0.068 \, \text{nm} \) is the sample treated at the room temperature (\( T = 22 \, ^\circ C, \, t = 2 \, \text{min}, \, \alpha = 30^\circ \)).

Increase in treatment duration of samples by AH up to 40 min (\( T = 300 \, ^\circ C, \, \alpha = 90^\circ \)) has shown an increase in roughness by 60% relatively to its initial value.

At increase in measurement area, the difference in surface roughness for the initial sample and the samples treated by AH is gradually decreases, and at scanning area of 12000×12000 nm\(^2\) becomes in practice not distinguishable. That speaks for the fact that total change in surface roughness is determined by modified shape of the objects that have small sizes, and it may be revealed on samples surface only at study of small areas. The listed below data do confirm that.

The two-dimension images of the initial Si sample surface as well as the samples treated by AH are shown in Figs. 5, 6. There are two types of irregularities on the surface of the initial sample (scanning area is 12000×12000 nm\(^2\)) observed. The first type irregularities are characteristic of a small difference in height and planar sizes leveled to 2000×2000 nm\(^2\). The second type of irregularities has the greater difference in height and planar sizes leveled to 20×20 nm\(^2\). Treatment by AH at the room temperature leads to the slight change in surface relief, nevertheless it shows a tendency to slight increase in height of irregularities of the first type and the more decrease in height of irregularities of the second type. Treatment at \( T = 300 \, ^\circ C \) and sliding incidence of AH flow has enhanced those tendencies. Much expressed the tendencies were revealed for the sample treated at \( T = 300 \, ^\circ C \) and normal AH flow incidence.

The surface images of samples obtained at area scanning of 500×500 nm\(^2\) testify that treatment by AH at the room temperature has really resulted in height decrease of second type irregularities. The surface becomes smoother, and the characteristic planar sizes of irregularities occur to be greater up to \( \approx 80 \times 80 \, \text{nm}^2 \) (Fig. 6). After treatment of the samples at 300 °C, the second type irregularities are not observed.

\( \text{GaAs surface roughness.} \) Fig. 7 presents two-dimensional surface images of the initial sample of GaAs with epitaxial layer of \( n\)-GaAs, as well as the surface images of the samples treated by AH flow at various modes. The surface roughness and irregularities data of such samples are shown in Table 2.

<table>
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<tr>
<th>Parameters</th>
<th>No. 1</th>
<th>No. 3</th>
<th>No. 4</th>
<th>No. 5</th>
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<tr>
<td>Roughness, nm; area: 500×500 nm(^2)</td>
<td>0.128</td>
<td>0.068</td>
<td>0.055</td>
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Fig. 5. Two-dimensional images of Si samples surface prior (No. 1) to and after AH treatment at $T = 22^\circ C$, $t = 2$ min, $\alpha = 30^\circ$ (No. 3); $T = 300^\circ C$, $t = 2$ min, $\alpha = 90^\circ$ (No. 4); $T = 300^\circ C$, $t = 2$ min, $\alpha = 30^\circ$ (No. 5); scanning area is 12000×12000 nm².

Fig. 6. Two-dimensional images of the Si samples surface prior (No. 1) to and after AH treatment at $T = 22^\circ C$, $t = 2$ min, $\alpha = 30^\circ$ (No. 3); $T = 300^\circ C$, $t = 2$ min, $\alpha = 90^\circ$ (No. 4); $T = 300^\circ C$, $t = 2$ min, $\alpha = 30^\circ$ (No. 5); scanning area is 500×500 nm².

Fig. 7. Two-dimensional images of the GaAs samples surface; scanning area 500×500 nm²; initial sample (No. F0); samples treated in AH at $T = 400^\circ C$, $t = 1$ min, $\alpha = 90^\circ$ (No. F1); $T = 400^\circ C$, $t = 5$ min, $\alpha = 90^\circ$ (No. F2); $T = 400^\circ C$, $t = 5$ min, $\alpha = 30^\circ$ (No. F4).
Table 2. Characteristics of surface irregularities and roughness of GaAs samples before and after treatment by AH; initial sample (No. F0); samples treated by AH at \( T = 400 \, ^\circ C, t = 1 \, \text{min}, \alpha = 90^\circ \) (No. F1); \( T = 400 \, ^\circ C, t = 5 \, \text{min}, \alpha = 90^\circ \) (No. F2); \( T = 400 \, ^\circ C, t = 1 \, \text{min}, \alpha = 30^\circ \) (No. F3); \( T = 400 \, ^\circ C, t = 5 \, \text{min}, \alpha = 30^\circ \) (No. F4); scanning area is 500×500 nm²

<table>
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<tr>
<th>Parameter</th>
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<th>No. F1</th>
<th>No. F2</th>
<th>No. F3</th>
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<td>Peak to peak, nm</td>
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<td>2.8</td>
<td>2.75</td>
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<td>Mean, nm</td>
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<td>1.97</td>
<td>1.56</td>
<td>1.37</td>
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<tr>
<td>Roughness, nm</td>
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<td>0.63</td>
<td>0.39</td>
<td>0.39</td>
<td>0.36</td>
</tr>
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</table>

At the normal AH flow incidence to surface, treatment of GaAs sample at 400 °C during 1 min does not essentially change the surface characteristics. An increase in treatment time up to 5 min results in the smoother surface obtained. Both the average value of surface irregularities from \( R_{\text{mean}} = 1.7 \) nm to 1.56 nm, and surface roughness from 0.65 nm to 0.39 nm are observed.

At sliding incidence of AH flow, the treatment by AH just during 1 min leads to decrease in average values of surface irregularities and roughness. Thus, \( R_{\text{mean}} \) decreases from 1.7 to 1.37 nm, and \( R_s \) does it from 0.65 to 0.38 nm. An increase in treatment time up to 5 min gives some more decrease in roughness value reaching 0.36 nm.

Thus, there are the treatment modes of Si and GaAs samples by AH flow with which smoothing etching of the surface of semiconductor materials is realized. The morphology and roughness of surface is being determined by treatment temperature and time, as well as by the angle of incidence of AH flow to sample’s surface. In the optimal modes of treatment it is possible to obtain atomically smooth surfaces of both Si and GaAs samples.

6. Conclusion

The performed experiments have shown that treatment of Si and GaAs semiconductor structures by intensive flow of kinetic-energy-enhanced hydrogen atoms allows obtain of atomically clean and atomically smooth surfaces of Si and GaAs with further use of them for epitaxial growth and formation micro- and nanoelectronics devices. The controlled time-temperature treatment modes as well as the angle of AH flow incidence on the surface of samples allow manipulations with surface parameters, and, in particular, the surface roughness.

Treatment by hydrogen atoms is characterized as high-controllable and precision process, and low-degree of introduced defects, rather well compatible with low-k dielectrics technology.

References