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Nanometer Scale Modifications of Si/Sio_2 and Si/Sio_2/ Polymer Surfaces by Scanning Tunneling Microscope

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The article presents the results of STM investigations of the Si-SiO_2 and Si-SiO_2-polymer systems in air. Depending on the scanning parameters, such as the voltage applied and tunneling current, a modification of the Si-SiO_2 surface was observed during these experiments. The possibility of the reversible modification was demonstrated. A thin polymer film was used to exclude the adsorption–desorption and electrochemical processes on the Si surface. The modification of the Si-SiO_2-polymer surface was observed at the scanning parameters similar to those for the modification of the Si-SiO_2 system. The electronic mechanism of the surface modification based on the tunneling of a charge through the oxide layer and its influence on the STM tunneling current is discussed.

Keywords: charge transfer; polymer; scanning tunneling microscopy; Si-SiO_2 interfaces

1. INTRODUCTION

The Si-SiO_2 interfaces possess unique electronic properties. The peculiarities of the charge accumulation and transfer near this boundary underlie the operation of a wide range of semiconductor devices.

Native oxide on the Si surface makes it difficult to measure and maintain the tunneling current. So the STM investigations of such a surface require the application of various methods for etching and passivation of the silicon surface. The possibility of the STM study of the Si-SiO_2 interface properties was established late on.

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The results of some works showed a possibility for the silicon surface to be modified during the STM study in air [1–4]. The explanation of this fact was in the oxidation process on the Si-surface near the place of a flowing current. However, the analysis of the papers shows that the oxidation model cannot explain many of the surface modification phenomena.

2. EXPERIMENTAL

The work was carried out on a scanning multimicroscope SMM- 2000T (ZAO KPD, Moscow, Zelenograd) which is intended for the realization of researches in air with the resolution by coordinate along the surface up to 0.3 nm and along the z-axis perpendicular to the surface up to 0.1 nm. The range of changes of the tunnel current I is from 0.01 up to 160 nA, and the range for the voltage U on the probe–sample interval is from 0 up to ± 10 V. The probe was prepared by the oblique cutting of a copper wire.

The polished plates of the p-type Si with the (111) orientation were used in experiments. The Si surface, which was polished during the manufacturing process, was subjected to no additional treatment. There was a native oxide layer by a thickness of about several nanometers on the surface of silicon in this case. The thickness of the oxide film estimated by the ellipsometry method was less than 2 nm. Such oxide film thickness allows one to perform the measurements in the constant tunneling current mode. The current flowing through the system can be represented as a superposition of a few components: the current of direct tunneling, Fowler-Nordheim tunneling, and the surface current. Changes in the scanning parameters emphasize certain current components, which influences the image. Similar results were obtained earlier in [5].

3. RESULTS AND DISCUSSIONS

3.1. Si/SiO_2 Surface Modification

Figure 1 presents the typical STM image of the silicon surface in air.

Figure 2 presents the image of the Si surface with 5 separate modified areas under a positive voltage on the sample. The sequence reception of modified areas was carried out in the following order: a small site of the surface (the mode of modification) was scanned at first, then at first scanning of a site with greater size which includes the modified site was made (the mode of visualization). It was established that a stable picture can be obtained with certain scanning parameters:

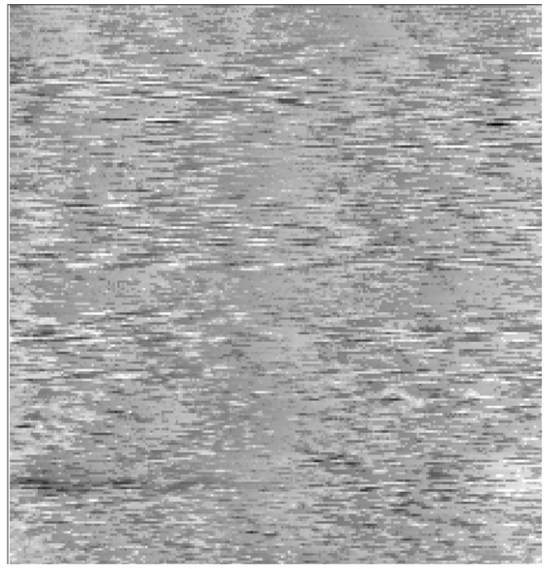

FIGURE 1 Typical image of the initial (unmodified) surface of silicon with the native SiO_2 layer.

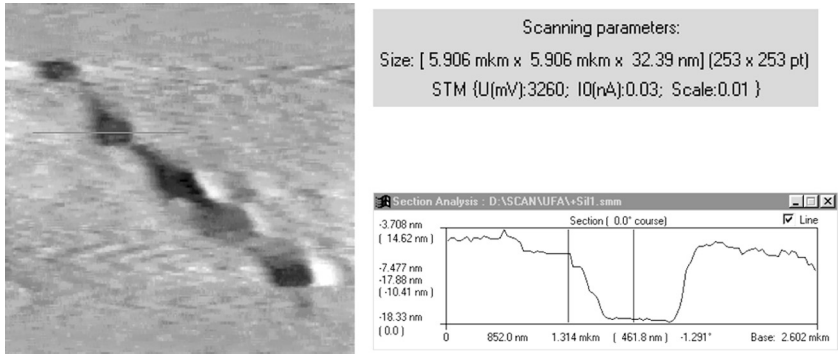

FIGURE 2 Image of a modified area of the silicon surface under the positive voltage (morphology and profile). The modification voltage: $U_{mod} = 3.7–5.3$ V, the visualization voltage: $U_{vis} = 3.26$ V. The size of modified areas – 0.5×0.5 μm, depth – 6–15 nm.

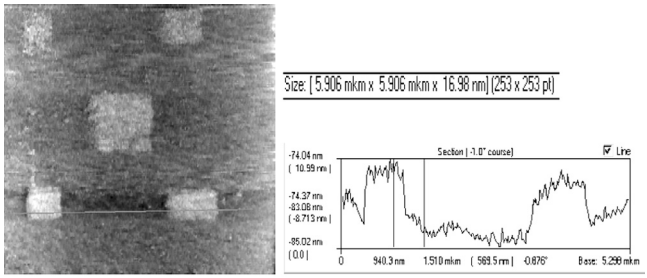

FIGURE 3 Image of a modified area of the silicon surface under the negative voltage (morphology and profile). The modification in the left top corner at $U_{\text{mod}} = -4.4\,\text{V}$, each subsequent modification was carried out with increase of the voltage by 0.4 V, the greatest modification voltage $U_{\text{mod}} = -6\,\text{V}$ in the left bottom corner of a snapshot. The visualization voltage: $U_{\text{vis}} = -4\,\text{V}$.

$3\,\text{V} < U_{\text{vis}} < 6\,\text{V}$, where U_{vis} is the bias voltage applied to the sample during the normal STM imaging; $10\,\text{pA} < I < 100\,\text{pA}$, where I is the tunneling current. The surface relief modification takes place if the modification voltage $U_{\text{mod}} > U_{\text{vis}} + 0.4\,\text{V}$.

If the same procedure is carried out with the reverse polarity (minus on the sample), the modified area is displayed as a protrusion. Figure 3 presents the image of the Si surface with 5 separate modified areas under a negative voltage on the sample. These areas were modified one after another with increase in the impressed voltage.

We note that the scanning parameters were almost the same in the measurements under different voltage polarities. However, the essential distinction was in the character of the modification obtained. Modified areas obtained under the negative polarity look like structured protrusions, i.e. they are composed of smaller elements (Fig. 2, profile). Those obtained under the positive polarity look like cavities, and no structure is observed (Fig. 3, profile).

3.2. Si-SiO_2-Polymer System: Surface Modification

As usual, the Si surface modification obtained during STM-measurements is explained by the irreversible oxidation [1–4,6,7]. The layer of adsorbate molecules is considered to assist with the oxidation. However, different functions are attributed to this layer in different papers. Thus, the role of this layer in the formation of structures on the surface of the Si-SiO_2 system is not clear. In this work, a thin polymer film was used to exclude the adsorption–desorption processes on the Si surface. It was shown earlier that the

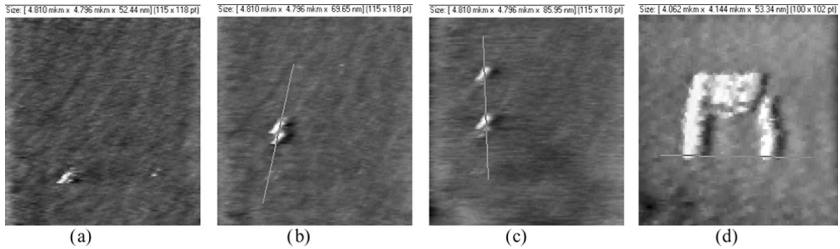

FIGURE 4 (a–d) Sequential modification of areas of the polymer surface on silicon. The modification voltage: $U_{mod} = -4.5\,V$, the visualization voltage: $U_{vis} = -3.4\,V$. The size of modified areas–$0.5 \times 0.5\,\mu m$, depth–30–50 nm.

poly (heteroarylene)s film up to 100 nm thick deposited onto a conductive surface can be investigated by the STM-method [8]. It is well known that the processes on the metal-polymer interface affect significantly the electronic properties of thin polymer films, particularly due to influencing the characteristics of the potential barrier on the interface. This makes it possible to use such films like unique charge sensors [9,10]. The polymer film was obtained from a solution in cyclohexanone by the centrifugation on a silicon surface. The thickness of the polymer films used in experiments varied in the range of 40–60 nm.

In Figure 4, the STM-image of consistently modified sites of a polymer surface on silicon is presented at a negative polarity on the sample. The modification was performed according to a way described above. At a change of the polarity (plus on the sample), the modified sites, as well as in the case where no polymeric film was drawn, are reproduced as cavities in Figure 5.

To interpret the data, this system was assimilated to the metal-insulator-oxide-semiconductor structure (STM probe-adsorbate

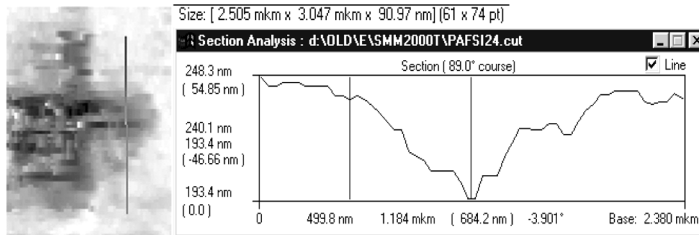

FIGURE 5 Image of a modified area of the polymer surface on silicon. The modification voltage: $U_{mod} = 4.5\,V$, the visualization voltage: $U_{vis} = 3.4\,V$.

layer-SiO_2-Si). The same structures were used as elements of the non-volatile memory, the operation principle of which is based on the capture of an injected charge in the insulator layer [11]. The charge captured in the insulator (adsorbate) layer can sufficiently affect the tunneling parameters, which is reflected on the STM image.

When the negative voltage is applied to the *p*-type semiconductor substrate, the concentration of minority carriers increases near the surface (the mode of depletion). At the greater enclosed voltage, the concentration of minority carriers can exceed the concentration of majority carriers (the mode of inversion) (Fig. 6a). At high voltages, the charge carriers tunnel through the oxide layer following the Fowler-Nordheim law. This occurs when the voltage applied exceeds the height of the potential barrier on the Si-SiO_2 interface (3.2 eV). The charge captured in the adsorbate layer can reduce the electron affinity and raise the additional emission component of the current. The latter can be registered by the STM as a protrusion on the surface.

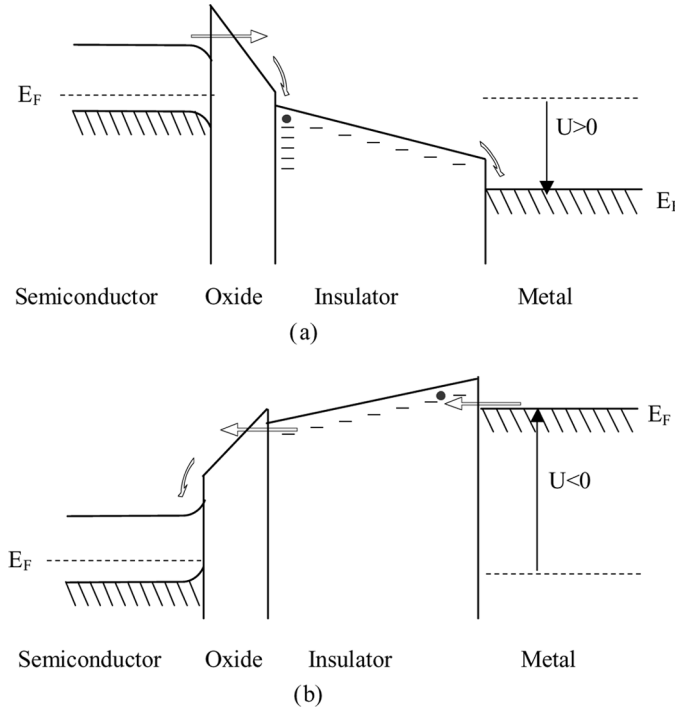

FIGURE 6 Energy diagrams of the experimental structure under different voltages. (a) a negative voltage applied to the sample, (b) a positive voltage applied to the sample. Arrows indicate a charge carrier movement. E_f is the Fermi level.

When the positive voltage is applied to the *p*-type semiconductor substrate, there is a bend of zones in the semiconductor, which leads to an increase in the number of majority carriers (holes) at the surface of the semiconductor (the mode of enrichment) (Fig. 6b). This can reduce the tunneling probability, which can be registered by the STM as a cavity.

4. CONCLUSIONS

In this work, we have shown that the character of modification depends on the polarity of the applied voltage (at the negative and positive polarities on a sample, protrusions and cavities are formed, respectively). The change of a surface morphology has the charging nature. The surface modification of a sample occurs under condition for the applied voltage to excess some threshold meaning ($U_{\text{thr}} = 3\,\text{V}$).

The suggested model of the modification of the interface charge state predicts the possibilities of writing, reading, erasing, and rewriting the information by means of the polarity change.

The electrochemical process of depassivation or oxidation alone can hardly explain the Si surface modification during the STM investigations. On the investigated surface, a structure of the insulator-oxide-semiconductor type forms with the adsorbate or polymer layer as an insulator. The charge carriers injected through the oxide layer are captured in the insulator layer. The STM methods allow one to stimulate the injection processes and to register the resulting redistribution of the charge near the Si-SiO_2 surface.

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