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In Situ Study of Interaction of Oxygen with the Si(111) Surface by Ultrahigh-Vacuum Reflection Electron Microscopy

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Abstract—Reactions of gases with an atomically clean silicon surface were examined by ultrahigh-vacuum reflection electron microscopy. The initial stages of interaction of oxygen with the Si(111) surface were studied in the temperature range from 500 to 900°C. Motion of monatomic steps to the upper terraces during etching by oxygen at high temperatures was visualized. Conditions for the formation of surface vacancies were determined. A dependence of a step velocity on the width of adjacent terraces was measured. Oscillations of intensity of the electron beam reflected specularly from the Si surface were observed during the etching of silicon by molecular oxygen, which proceeded by a two-dimensional-island mechanism. The activation energy for diffusion of surface vacancies, which are formed owing to the interaction of oxygen with silicon, was estimated to be 1.35 ± 0.15 eV. *© 2001 MAIK "Nauka/Interperiodica".*

INTRODUCTION

Atomic processes on crystal surfaces can be described in the context of the behavior of such elementary defects as adsorbed atoms (adatoms) and surface vacancies, which are always present on a surface at temperatures above absolute zero. The migration and interaction of adatoms and vacancies with each other, monatomic steps, and superstructural domains determine structural processes on a real crystal surface. Structural investigations based on *in situ* observations of surface processes with a resolution on the order of one monolayer open up new possibilities for obtaining reliable information about properties of the surface. Of interest is also the *in situ* study of atomic processes proceeding during the interaction of an atomically clean silicon surface with a gas atmosphere, in particular, the interaction of oxygen with a reconstructed silicon surface. Such investigations are of practical importance, because oxidation of the silicon surface is a basic stage of the insulator-layer formation in the present-day micro- and nanodevice technology.

The interaction of the silicon surface with oxygen was examined with diffraction- and laser-related ellipsometric and other methods. However, all these methods provide integral data on the surface structure, which are averaged over a large area. Silicon–(silicon dioxide) interfaces can be investigated by electron-microscopic methods, which possess a fairly high spatial resolution. However, the *in situ* electron-microscopy study is of limited usefulness because of the necessity to obtain and maintain an atomically clean Si surface during the experiment, which requires ultrahigh-vacuum (UHV) conditions in the column of an electron microscope. Interesting results were obtained in UHV electron-microscopy studies of transformations of a clean Si surface during its oxidation and the initial stage of etching by oxygen [1–4]. The scanning tunneling microscopy (STM) is an efficient method for examining the atomic structure of a surface interacting with a gas ambience [5, 6]. However, STM observations of the silicon surface in an oxygen ambience are hampered by the formation of a silicon-dioxide layer, which decreases the tunnel current. This study was devoted to the development of a controlled gas-inlet system for admitting a gas into a column of ultrahigh-vacuum electron microscope and *in situ* investigations of the effect of oxygen adsorption on the structural transformations proceeding on the Si(111) surface at various temperatures and oxygen pressures. Much attention was concentrated on the analysis of transformations of the Si surface at rather low oxygen pressures, when etching rather than oxidation of the Si surface in an oxygen atmosphere took place.

EXPERIMENTAL

Structural reconstructions of the silicon surface were studied by ultrahigh-vacuum reflection electron microscopy (UHV REM), which was described in detail elsewhere [7]. The unique design of the differential cryogetter pumping system provides a residual pressure of $\approx 10^{-9}$ Torr, which makes it possible to prepare and maintain an atomically clean silicon surface during the experiment [8]. The UHV REM allows for

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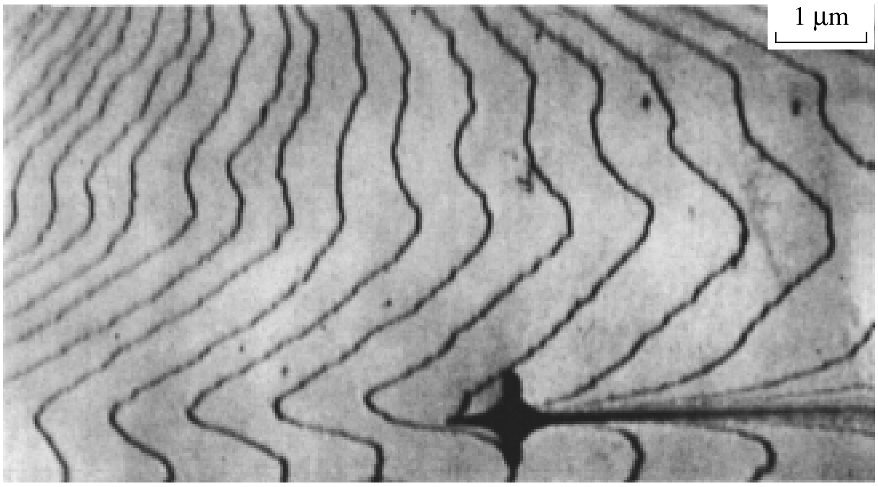

Fig. 1. REM image of the atomically clean Si(111) surface annealed at a high temperature. The surface contains a system of monatomic steps. An immobile particle acting as a step-pinning center (bottom of the photograph) serves as a reference. The terrace height increases from left to right.

the visualization of such elements of the surface relief as monatomic steps, which are 0.31 nm high on the Si(111) surface even at temperatures above 1200°C. After UHV REV studies, some samples were analyzed by atomic force microscopy (AFM) at atmospheric pressure (SOLVER P-47H NT-MDT).

Samples with dimensions of 8 × 1 × 0.3 mm were cut from a standard Si(111) wafer misoriented less than 1°. After conventional chemical cleaning, the sample was mounted on a holder with tantalum clamps. The sample was heating by a direct or alternating current. The holder with the attached sample was placed into the electron-microscope column. Then, the sample was heated to 1200°C in an ultrahigh vacuum by the alternating current. The sample temperature was calibrated against the current with the use of an optical pyrometer (at high temperatures) and a thermocouple (at low temperatures). The surface was considered to be atomically clean if its microdiffraction pattern contained no additional reflections, a reversible $(1 \times 1) \longrightarrow (7 \times 7)$ superstructural transition took place, and no centers pinning monatomic steps during sublimation were observed. REM images were taken on photographic plates or filmed with a special-purpose Gatan TV camera. The intensities of the diffraction reflections were measured with a semiconductor detector built into the microscope screen.

To analyze the reactions of gases with the crystal surface under study, we devised a gas-inlet system and connected it to the microscope column. This system consists of a high-pressure oxygen bottle connected to a ballast tank. The tank is linked to one of the channels of an electronic two-channel leak admitting the gas into a vacuum chamber of the differential cryogetter system through a built-in connecting pipe fitted with a diffuser made of a stainless-steel wire. Another ballast tank connected to an adsorption pump is coupled to the second channel of the leak. Closing the first channel of the two-channel leak while simultaneously opening the second channel during the gas admission, we minimized the additional exposure time of the sample to the gas atmosphere owing to the evacuation of the residual gas from connecting pipes through the second channel. Thus, the devised gas-inlet system equipped with the two-channel leak and the electronic control system allows us to let in the gas over a wide range of pressures with a high accuracy and a specified exposure time.

RESULTS AND DISCUSSION

Figure 1 shows a representative REM image of the Si(111) surface cleaned at the high temperature in the UHV chamber of the electron microscope. The twisting dark lines are images of monatomic steps 0.31 nm in height. The monatomic-step contrast is a superposition of diffraction and phase contrasts, which are caused by deformation fields near a monatomic step and a phase shift due to reflection of the electron beam from terraces adjacent to the step. REM images have different magnification scales along and perpendicular to the direction of incidence of the electron beam due to the small angle of incidence of the electron beam on the surface studied. This results in a uniaxial contraction of the REM images. In this study, the images are contracted in the vertical direction by a factor of about 40. During sublimation at temperatures above 850°C, movement of the monatomic steps to the upper terraces was observed. This is attributed to the fact that, during sublimation, adatoms are removed from terraces and the steps act as sources of adatoms. The positions of the monatomic steps on the Si surface were related to positions of immobile particles, most probably, of silicon carbide or a refractory metal, which were not removed from the surface by thermal annealing. Such particles

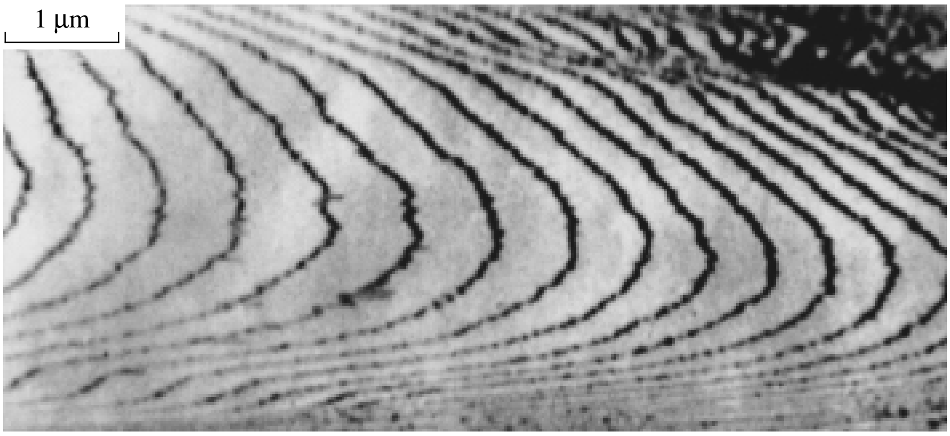

Fig. 2. Representative image of the stepped Si(111) surface exposed to the oxygen atmosphere at a pressure below P_{crit}. Monatomic steps moved from left to right.

are visible on the REM images owing to the shadow contrast (the dark spot at the bottom of Fig. 1). These particles do not migrate over the crystal surface at temperatures of up to the melting point. Their typical density is several particles per several square millimeters.

A step velocity depends on temperature and the separation between monatomic steps [9, 10]. A system of regular monatomic steps or a system of step bunches, which consists of bundles of monatomic steps and surface areas with a low step density, formed on the surface in certain temperature ranges, depending on the direction of the electric current heating the sample [11, 12]. Using the effect of a kinetic unstable system of monatomic steps induced by electromigration of Si adatoms, we controlled the interstep distance on local surface areas from several nanometers to dozens of micrometers in size. The distribution of the steps or step bunches formed at sublimation temperatures was unchanged on fast cooling of the crystal to temperatures below 800°C and did not alter during the characteristic observation time (several hours).

After oxygen was admitted into the UHV chamber of the electron microscope, no appreciable change in surface morphology was observed at oxygen pressures below P_{crit} (Fig. 2). At rather low pressures, oxygen had no noticeable effect on intensity of main and superstructural reflections in diffraction patterns. The REM contrast did not change, but the monatomic steps moved to higher terraces. As the oxygen pressure increased (remaining below P_{crit}), intensities of the superstructural reflections decreased slightly.

On exposure to molecular oxygen, the monatomic steps move apparently due to the etching of the silicon surface by oxygen at high temperatures [13]. It is well known that, at sufficiently high temperatures, an oxygen molecule on the silicon surface dissociates into two atoms O(ads), which remain in the adsorbed state on the silicon surface [14]. In turn, adsorbed oxygen interacts with silicon to form volatile silicon monoxide (SiO):

$$\mathrm{Si} + \mathrm{O}(ads) \longrightarrow \mathrm{SiO}(gas)\uparrow.$$

This reaction describes etching by oxygen at high temperatures, resulting in the removal of Si atoms from the surface. This phenomenon can explain the directional motion of the monatomic steps observed with the reflection electron microscope.

Indeed, if atoms are sequentially removed from a step, the step will move. On REM images, this process will appear as the motion of the monatomic step to upper terraces. Let us consider several possible mechanisms of the displacement of the monatomic steps during etching by oxygen. First, oxygen atoms may be adsorbed onto the silicon surface, migrate over the surface toward a monatomic step, and react with Si atoms on the step to form silicon monoxide. According to another mechanism, atomic oxygen reacts with Si atoms adsorbed on terraces, thus decreasing their concentration. The decrease in concentration of Si adatoms is compensated for by the generation of adatoms by the monatomic steps, which also leads to the upward motion of the steps. Finally, surface vacancies may form owing to the removal of Si atoms from terraces (as a result of the reaction with the formation of silicon monoxide). The flow of the vacancies toward a monatomic step will lead to the removal of atoms from the step owing to the annihilation of the vacancies and the atoms. We should take into account that the recombination of surface vacancies and Si adatoms on terraces may also result in the movement of monatomic steps to upper terraces. Consequently, analyzing the interaction of oxygen with the Si surface, we should take into account several atomic-scale mechanisms for the step motion, depending on experimental conditions.

As demonstrated above, ensembles of point defects and vacancies, which migrate over the terrace surfaces and interact both with monatomic steps and with each

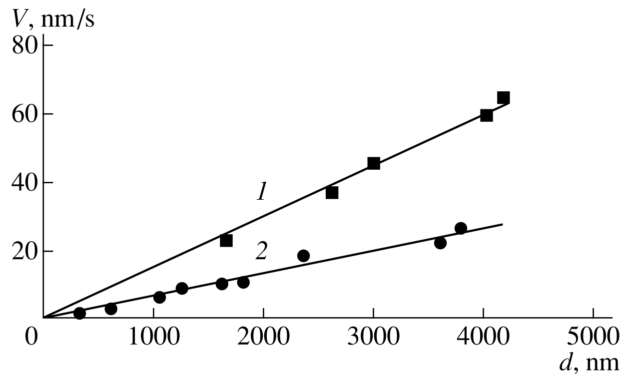

Fig. 3. Dependences of the velocity of a monatomic step on the distance to the neighboring step measured during exposure to the oxygen atmosphere at a pressure below P_{crit} and temperatures of (*1*) 870 and (*2*) 780°C.

other, may form during etching by oxygen at high temperatures. Let us consider specific features of the step-flow mechanism of etching of the Si(111) surface. This mechanism implies that there is no interaction between vacancies that result in their coalescence, i.e., in the formation of negative two-dimensional (2D) islands. According to the classical theory [15], the velocity of a monatomic step should depend on the width of adjacent terraces, all other factors being the same. This dependence should be linear if the diffusion length of surface vacancies exceeds the interstep spacing. If the terrace width is considerably greater than the vacancy-diffusion length, the velocity of the monatomic steps is independent of the width of adjacent terraces. Figure 3 shows dependences of the velocity of a monatomic step on the width of adjacent terraces for etching by oxygen at two temperatures. The wider the adjacent terraces, the higher the velocity of the monatomic steps. The linear dependence of the step velocity on the terrace width indicates that, at a given temperature and oxygen pressure, the length of migration of surface vacancies is greater than or equal to the interstep distance. The step velocity increases as temperature rises, since the vacancy mobility increases with temperature.

At an oxygen pressure above P_{crit}, an additional REM contrast was observed on wide terraces between the monatomic steps. This contrast was identified as negative islands of monatomic depth (Fig. 4). This finding is consistent with the results by Shimuzu *et al.* [16]. As in homoepitaxial growth [17], no negative islands were formed on terrace areas adjacent to the steps. Moreover, the negative islands were absent on surface areas with high density of the monatomic steps. Further exposure of the Si surface to the oxygen atmosphere led to an increase in island size. After a certain time, the growing negative islands came in contact with the monatomic steps. As a result, the islands disappeared and the step shape changed. The absence of an REM contrast at points of contact between the islands and the steps suggests that the depth of the negative islands is equal to the height of the monatomic steps, i.e., one interplane distance. As the steps moved further, they gradually recovered their original shape. It should be noted that, as the oxygen pressure exceeded a certain value, oxidation of the Si surface began, which manifested itself in appearing of homogeneous ripples on the REM images and termination of the step motion.

The formation of the negative 2D islands on terraces suggests that etching of the Si surface proceeds through the generation of surface vacancies, which coalesce to produce the negative 2D islands. The formation of similar negative islands on wide terraces was observed previously during high-temperature (>1200°C) sublimation [18] or a sharp change of the sublimation temperature, resulting in the decrease in diffusion length of adatoms [11]. However, in the case of etching of the Si surface by oxygen at high temperatures, these islands form at lower temperatures (500–900°C).

Based on these results, we may conclude that etching of the Si surface proceeds either by the step-flow

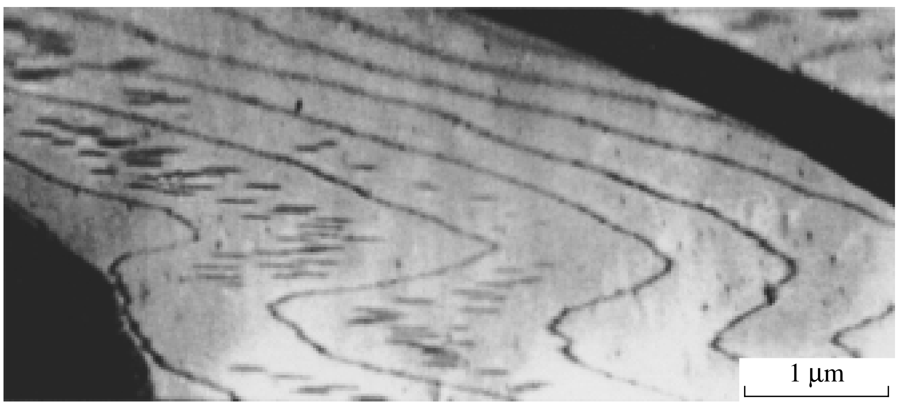

Fig. 4. Representative REM image of the Si surface containing negative 2D islands, which were formed during etching by oxygen at a pressure above P_{crit}.

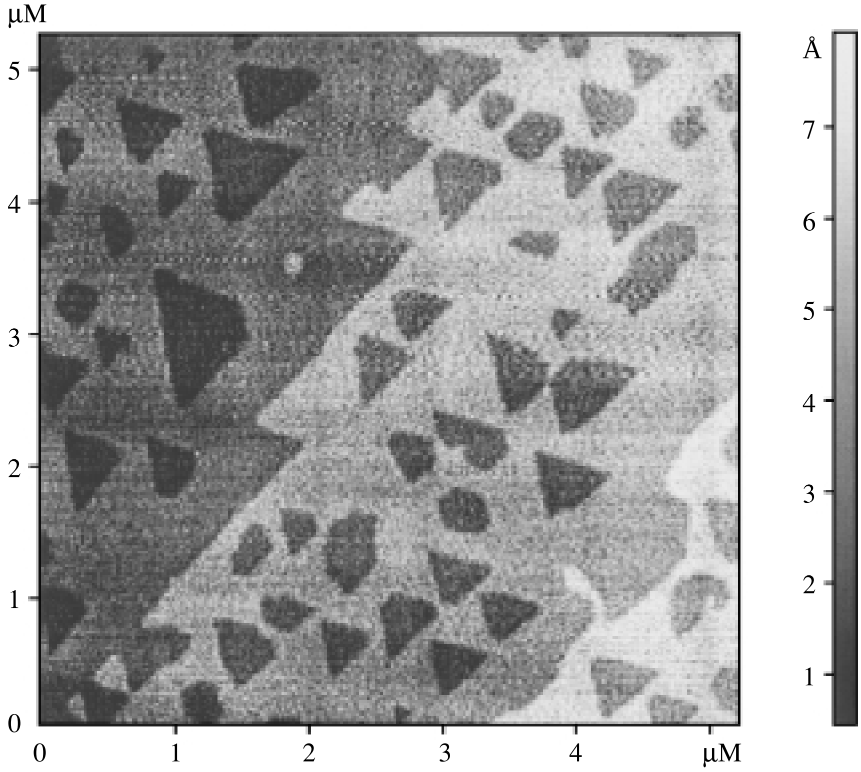

Fig. 5. An AFM image of the atomically clean Si(111) surface after exposure to the oxygen atmosphere. The oxygen pressure and the crystal temperature were chosen so that etching by oxygen proceeded via the formation of 2D islands.

mechanism or via nucleation of the 2D negative islands, depending on temperature and oxygen pressure. Displacement of the monatomic steps on exposure to the oxygen atmosphere is characteristic of the step-flow mechanism, which is effective at high temperatures or low oxygen pressures owing to the generation and migration of surface vacancies and their interaction with the steps. The 2D-island mechanism of etching operates at lower temperatures or higher oxygen pressures and is characterized by the formation of the 2D negative islands. Depending on the ratio of temperature to oxygen pressure, etching by the first or the second mechanism was observed, and sometimes these mechanisms operated concurrently. For example, both the formation of large islands and the step motion were observed at an oxygen pressure of $\approx 10^{-7}$ Torr and temperatures above 750°C, whereas only the step motion occurred at temperatures exceeding 860°C, and mainly origination of small 2D islands with high density took place at temperatures below 640°C. It should be noted that, at a given temperature and oxygen pressure, etching of the sample surface proceeds by the step-flow mechanism or through nucleation of the 2D islands, depending on the step density, i.e., the terrace width.

It is noteworthy that, on exposure of the Si(111) surface to the oxygen atmosphere, the shape of the monatomic steps on a microscopic scale changed from smooth to staggered (Figs. 1 and 2). Since microkinks on the steps are observed even during etching by the step-flow mechanism, they are apparently formed due to the interaction of vacancies with atoms on the steps rather than the interaction of the moving monatomic steps with the negative islands, as discussed above. A thorough analysis of the REM images taken from the same area at different azimuthal angles shows that the microkinks consist of linear portions oriented parallel to $\langle 110 \rangle$ crystallographic directions. A dependence of the length of the linear portions on the time of exposure to the oxygen atmosphere was measured at various temperatures and oxygen pressures. Analyzing the standard deviation of the step shape from the original shape, we find that, at the initial stages of the interaction of oxygen with silicon, the roughness of the steps initially increases with time and then tends to a constant value. The final step roughness and, consequently, the linear dimension of the step kinks increase as crystal temperature or oxygen pressure rises. However, the step roughness is found to decrease sharply near the temperature of the superstructural transition. Consequently, the superstructural reconstruction induces a "faceting" of the monatomic steps during etching of the Si surface at a low oxygen pressure. The appearance of similar kinks on monatomic steps, but with a lower amplitude, was observed on the Si(111) surface undergoing the $(1 \times 1) \longrightarrow (7 \times 7)$ reconstruction, which took place as temperature decreased to <830°C [19, 20]. The kink formation was attributed to the orientation of superstructural domains and the presence of antiphase boundaries between them.

The island shape was not reliably established because of the uniaxial contraction of the FEM images caused by the small angle of incidence of the electron beam. Therefore, the island shape was analyzed by AFM after the samples were removed from the UHV chamber of the electron microscope. Although a film of natural silicon oxide forms on exposure to the atmosphere, AFM allows reliable images of monatomic steps buried under the natural-oxide layer to be obtained. Figure 5 shows an AFM image of the Si(111) surface after exposure to the oxygen atmosphere under conditions of etching via the 2D-island mechanism. The brighter the contrast, the higher the corresponding surface area. We can see three terraces separated by two monatomic steps, whose height equals one interplane spacing in the ⟨111⟩ direction in Si with an accuracy of 0.1 nm. One can see also faceted triangular islands one interplane spacing deep, which is consistent with the UHV REM observations. Depending on the crystal temperature, the 2D islands varied in shape from regular triangles at low temperatures (<700°C) to perfect circles at high temperatures (>800°C). It should be noted that the monatomic steps contain rectilinear kinks oriented parallel to crystallographic directions (Fig. 5).

Figure 6 shows time dependences of the intensity of the specularly reflected electron beam, which were measured during etching of the Si surface by oxygen at high temperatures. In the case of epitaxial growth, the oscillations are generally attributed to variations in the surface roughness caused by nucleation and annihilation of 2D islands on the crystal surface [21]. A similar phenomenon takes place during etching of the Si surface by oxygen at high temperatures, with the only difference being that the cyclic change of the relief is caused by the formation of the negative islands. When etching proceeds via the island nucleation, vacancies formed in the central part of a terrace have no time to reach a monatomic step and be incorporated into it. As a result, vacancies coalesce to form a negative island. The islands increase in size due to the further generation of vacancies and their interaction with the islands. The further growth of the islands and their interaction lead to the complete removal of the upper Si layer. In the course of this process, the surface morphology changes from smooth (terraces are free from islands) to rough (islands occupy half the terrace area), which results in the intensity oscillations of the specularly reflected electron beam. Consequently, the period of the oscillations corresponds to the removal of one Si monolayer. At a given oxygen pressure, the period is constant in the temperature range from 540 to 825°C. This finding points to a low activation barrier for the interaction of oxygen with silicon as well as to the fact that etching of the Si surface by oxygen at high temperatures is controlled by the supply of oxygen molecules to the Si surface. An increase in the oxygen pressure in the vacuum chamber enhanced the surface-etching rate determined from the step velocity and reduced the period of the intensity oscillations. It should be noted that the oscillation period is determined by the oxygen pressure and the temperature range in which the intensity oscillations are observed depends on the oxygen pressure and the interstep distance.

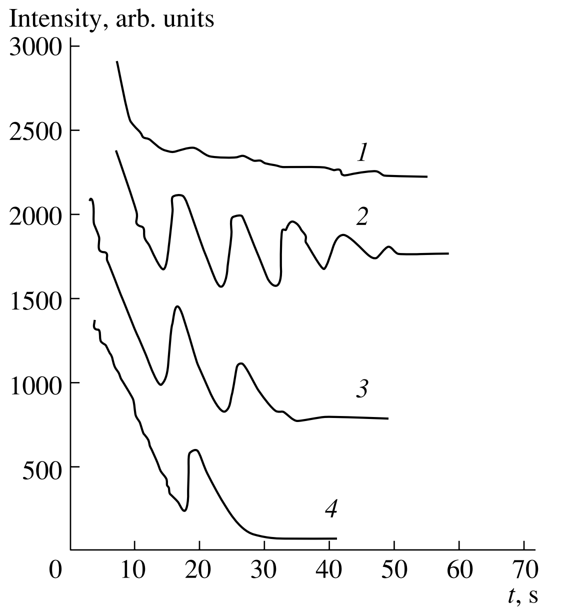

Fig. 6. Time dependences of intensity of the specularly reflected electron beam measured during etching of the Si surface at a constant oxygen pressure and temperatures of (*1*) 835, (*2*) 775, (*3*) 745, and (*4*) 730°C.

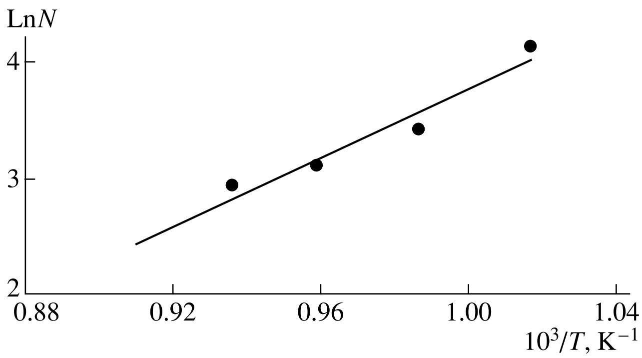

Fig. 7. Arrhenius plot of the number of the negative islands, *N*, nucleated over a given surface area at a constant oxygen pressure.

The density of the 2D islands on the crystal surface specifies an average interisland distance, which under certain conditions is proportional to the migration length of surface vacancies [22]. Direct measurements of the average interisland distance are hampered by two scales of magnification of the REM images caused by the low angle of view. For this reason, the average distance between the negative islands was determined from a number of islands formed over the same surface area at a constant oxygen pressure. To exclude the effect of the monatomic steps, we chose the surface area located in the central part of the widest terrace. Figure 7 show the Arrhenius plot of the number of the negative islands. Since, as demonstrated above, the rate of the reaction of the SiO formation remains unchanged in the temperature range from 500 to 900°C, the activation energy for migration of surface vacancies is 1.35 ± 0.15 eV. The same value was obtained from the temperature dependence of the width of the monatomic-step zone free from the 2D islands. This activation energy for migration of surface vacancies agrees with the values obtained by Shimuzu *et al.* [23] and, within the experimental error, is equal to the activation energy for surface diffusion of Si adatoms on the Si(111) surface [24].

CONCLUSION

Ultrahigh-vacuum reflection electron microscopy was used to study reactions of gases with the atomically clean silicon surface. The initial stages of the interaction of molecular oxygen with the Si(111) surface were studied. Vacancies were demonstrated to form on the Si surface during etching by oxygen at various temperatures and oxygen pressures. The motion of monatomic steps on exposure to the oxygen atmosphere was studied. The activation energy for migration of surface vacancies was estimated from the distribution of the negative 2D islands. Intensity oscillations of the electron beam reflected specularly from the Si surface were observed during etching by oxygen at high temperatures.

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