Fabrication of germanium and silicon nanostructures using a scanning tunneling microscope

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<u>Abstract.</u> The state of the art of research on the fabrication of semiconductor surface nanostructures using a scanning tunneling microscope (STM) is reviewed. The continuous atom transfer occurring due to directional surface diffusion initiated by the STM electric field and involving field-induced evaporation is analyzed. The effect of irradiation with an external electron beam on the tip-sample interaction is discussed, which consists in reducing the barrier for direct interatomic reactions and

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Received 22 February 2006 Uspekhi Fizicheskikh Nauk **176** (9) 913–930 (2006) Translated by S N Gorin; edited by A Radzig in changing the direction of the tip-sample atomic transfer. The possibilities of fabricating germanium and silicon nanostructures such as islands and lines and also making silicon windows on oxidized silicon surfaces are demonstrated.

1. Introduction

The wide interest in the investigation of nano-sized structures is due to the general tendency toward miniaturization of electronic devices. However, there also exists a fundamental reason related to the electronic properties of nanostructures, which differ from the properties of bulk materials by the presence of spatial quantization effects. The dependence of the energy-band structure of an object on its size can be used to substantially expand the region of application of materials in electronic and optical circuits. A change in the position of energy levels can be accompanied by changes in the conditions of electronic transitions and, consequently, can affect the efficiency of optical emission. Spatial quantization creates clearly pronounced discrete energy levels in structures whose size is about 10 nm or less. Such structures, which are called quantum dots, form the components for the fabrication of single-electron transistors, new photoelectron devices, and quantum computers [1-4].

Among the methods of fabrication of semiconductor nanostructures, the widest application has those that are based on the use of processes of self-organization occurring during relaxation of stressed heterostructures [2, 5-7], as well as those that modify the surface to alter the initial stages of

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growth [8-11]. The natural mechanisms used in these methods include spontaneous nucleation and growth, which permit one to vary the geometrical parameters of nanostructures only in certain limits. These methods are efficient for creating dense arrays of nanostructures. To fabricate single nanoobjects in given positions, a search for the methods of addressable modification of the surface morphology, using additional technical tools such as scanning of the surface with electron beams and microprobes, should be demanded.

Numerous investigations showed that the scanning tunneling microscope (STM) [12] is an efficient tool not only for the investigation of surface morphology and atomic structure of surfaces but also for the direct fabrication of nano-sized structures [13-15]. The unique possibilities of STMs have been demonstrated in the field of modification of metal surfaces, namely, in the fabrication of structures such as a 'quantum corral' [16, 17]. A specific feature of these experiments is the use of very low temperatures of the samples, on the order of 10 K. This is a result of high adatom mobility at higher temperatures. The transfer of atoms occurs both along the surface (lateral translation) and between the sample and the STM probe (vertical transfer). Both the experiments [18-20] and the theory [21, 22] concerning the lateral translation indicate the occurrence of an 'adjustment' of chemical bonds between the probe and adatoms, whereas in the case of the vertical transfer an important role is played by the excitation of vibrations of the adatom-substrate bonds due to inelastic electron tunneling [23-27].

Owing to covalent bonding, semiconductor surfaces are more stable thermally than metal surfaces, which makes it possible to modify them at room temperature. Pits or hills (islands) have been formed on the surface of semiconductor samples with the aid of an STM probe by applying a voltage pulse between the surface and the probe tip, usually of millisecond length [28, 29]. The pulses are applied at the moments when the STM tip approaches the sample surface to within a distance of a few angströms. Under the effect of a voltage pulse of about 3 V, the surface is modified due to the chemical and mechanical interaction of the atoms of the tip and the sample. When a higher voltage (4-6 V) is applied in the regime of a constant STM tunneling current (at a tip-tosample distance of about 0.6-0.8 nm), atoms are seen to remove from the surface of the silicon sample [30]. The removal occurs via the formation and transfer of positive or negative ions under the effect of a strong electric field from the STM [31]. This process has been used to create grooves several nanometers wide on the silicon surface [32]. Apart from the transfer of atoms between the sample and the STM probe, there occurs a displacement of atoms along the sample surface, following the movement of the probe [13, 14]. Such a displacement is due to the existence of an electric-field gradient and occurs in the direction toward the site where the field is higher, i.e., toward the center of interaction between the sample and the probe [31]. The modification of a sample surface with an STM probe can also be effected without application of voltage by bringing the probe tip toward the sample to a state close to mechanical contact [33]. An automated approach of the STM tip to within a short distance from the sample occurs in a regime of STM operation at a zero bias voltage and fixed large tunneling currents (up to 10 nA) [34]. The desired modification of the surface when using the latter methods occurs only with a certain restricted probability because of the possible change in the chemical composition and shape of the probe tip after

each act of interaction. The use of the STM probe as a tool for nanolithography has been considered by the example of various materials in a recent review by Tseng et al. [15].

In this review, we consider the process of a continuous transfer of surface atoms with the aid of an STM probe as applied to the fabrication of silicon and germanium nanostructures [35-37]. The continuous transfer of atoms occurs under the effect of a strong electric field from the STM upon the application of an enhanced stationary bias voltage between the sample and the probe. The result of the interaction between the sample and probe depends on the polarity of the applied voltage. With a negative voltage at the tip, the surface atoms of the sample move to the center of interaction, creating a three-dimensional island with dimensions of about 10 nm. Contrary to the methods based on the application of voltage pulses, in which a transfer of a small atomic cluster per pulse occurs, methods based on the use of enhanced stationary bias voltages ensure a process with a continuous transfer of atoms at a constant rate. The rate of atom transfer is determined by the magnitudes of both the tunneling current and applied voltage [37, 38]. By scanning the surface with an STM probe in the regime of a continuous transfer of atoms, lines can be produced on the sample surface [39]. The process of atom transfer can be described by a scaling relationship between the rate of transfer, the magnitude of the bias voltage, and the effective dipole moment of atoms at the surface [40]. This relationship permits one to estimate the magnitudes of effective dipole moments and the interaction energies between these dipole moments and the applied electric field [37, 40].

Additional information on the mechanism of atom transfer can be obtained by studying the interaction of the sample with the STM probe under various experimental conditions. An interesting effect shows itself upon irradiation of the region of interaction between the sample and the probe by an external electron beam. The irradiation causes the transfer of atoms from the sample onto the probe tip when the silicon surface is covered with a film of silicon oxide [41]. Not only the atoms of the layers deposited on the oxide, but also the atoms of the oxide itself as well as silicon atoms appeared after removing the oxide become involved in the transfer. This effect permits one to produce silicon windows in the silicon oxide layer with the aid of an STM probe interacting with the samples kept at room temperature.

The experimental data given in this review have been obtained using a unique ultra-high-vacuum setup whose molecular-beam-epitaxy chamber was equipped with an STM, an ultra-high-vacuum gun of a scanning reflection electron microscope (SREM), a secondary electron detector, and a high-energy electron diffraction (RHEED) detector. The disposition of the STM probe and electron gun allowed their use for simultaneously scanning the sample surface and observing (on the SREM monitor) the probe tip state and its manipulations over the sample surface.

2. Formation of silicon islands on a silicon surface

2.1 Conditions for island formation

The interaction of an Si(111) sample and STM probe in the regime of constant tunneling current (I_t) leads to a transfer of atoms of the sample material toward the center of interaction. The transfer occurs at an elevated negative bias voltage (5.5–

10 V) applied to the probe and relatively small tunneling currents (up to 1 nA) [36, 38, 40]. As a result of such a travel, a three-dimensional island is formed at the surface, whose size depends on the interaction time which is usually 1-60 s. After the island is formed, its shape and size are fixed by recording the image of the sample surface using the STM. Figure 1 displays some data for silicon islands grown at different bias voltages V. Each island has an individual shape which differs somewhat from the shape of other islands.

Although island formation was observed in a wide range of bias voltages (from 5.5 to 10 V), islands with wellreproduced sizes could be obtained only at higher voltages (7 to 10 V). As is seen from Fig. 1, the scatter of island heights was less than 20%. Islands grown at a bias of -9 V for 7 s had a height of about 3 nm and a base width of about 9 nm. Such parameters correspond to an aspect ratio (the ratio of the island height to the length of its base) of ~ 0.3 , a value approximately twice as high as in the case of silicon islands produced using a high-temperature STM. During the interaction between the probe and the Si(111) sample at elevated temperatures, an island in the form of an oblique pyramid with {311} lateral faces was formed [34]. Notice that a similar pyramidal shape of islands is also observed in the case of heteroepitaxial growth of germanium on an Si(111) surface, when the coverage with germanium exceeds that corresponding to a changeover from two-dimensional to three-dimensional growth [42, 43]. The large difference in the shape of the islands observed points to the different mechanisms of their formation on the samples held at room or elevated temperature.

Annealing of the sample at 700 °C for 5 min resulted in a decrease in the size of the islands (Fig. 1c). The islands became



Figure 1. (a) Silicon islands grown on an Si(111) surface at a constant tunneling current of 0.3 nA and three bias voltages applied to the probe, namely, -9.0, -9.5, and -10.0 V, for the rows shown from left to right, respectively. Each island was fabricated for 7 s. (b) An enlarged image of two islands from the left-hand row. (c) An image of the same region of the surface as in figure (a) after annealing the sample at 700 °C for 5 min. (d, e) Profiles of the surface along the white lines passing through the islands in Figs 1a and 1b, respectively.

completely spread out over the surface when the sample was annealed at 900 °C for 3 min.

2.2 Kinetics of island growth

Island size increases with increasing duration of the interaction between the sample and the STM probe. The island height reached 12 nm at an interaction time of 10³ s. Notice that to obtain an STM image of the island shape, the STM tip should be sharper than the island. The measurement of the island height is independent of the shape of the STM tip. Figure 2 displays islands obtained at relatively short interaction times. The STM images obtained with an atomic-scale resolution revealed that the surface around the islands has a disordered atomic structure in which a part of the atoms of the surface layer is absent (Fig. 2b). These data show that the silicon atoms used for the formation of islands are taken from a wide region around the islands; the absence of large changes in the surface morphology indicates that the transfer of silicon atoms occurs mainly in the form of single atoms.

The kinetics of island growth was studied using measurements of the dependence of the island height on the time of interaction of the STM tip with the sample at a negative bias voltage over a range from -6 to -10 V (Fig. 2d). To estimate the amount of silicon in an island, the island shape should be known. Since the height of the island is correctly measured by STM irrespective of the island shape, the island volume was calculated based on the assumption that all the islands have the same shape in the form of a cone with an aspect ratio of 0.3. Then the island volume is equal to $3H^3$, where H is the island height. On the other hand, at a constant rate of atom transfer into the island, we have for the island volume the following expression:

$$3H^3 = Rt, \qquad (1)$$

where *R* is the rate of growth, and *t* is the time of growth of the island. The rate of growth of islands in the initial growth period was determined by fitting Eqn (1) to experimental data obtained for islands with heights less than 4 nm (Fig. 2d); in this case, the magnitude of *R* was used as an adjustable parameter. Figure 2e shows the magnitudes of *R* that were determined as a result of fitting depending on the bias voltage (the parameters *s* and α are determined below, in Sections 2.4 and 2.5, respectively).

2.3 Effect of the tunneling current on island formation

The growth of silicon islands under the effect of an STM tip depends on the magnitude of the tunneling current. The wellreproduced growth is observed at relatively small tunneling currents (less than 0.5 nA). At greater currents, the island height increases on average with increasing duration of the interaction between the sample and the tip, but this increase is by no means monotonic. This manifests itself in the spread of data in the dependence of the island height on the interaction time, which exceeds the accuracy of measurements of the island height (Fig. 3a). To analyze the experimental data, the process of island growth was divided into an initial and a later stage. The growth rates were determined by fitting expression (1) to experimental data obtained at the corresponding growth stages. The growth rate at the initial stage proved to be much higher than that at the later stage; in the case, the dependence of the rate on the tunneling current had a maximum at 0.3 nA (Fig. 3b).

The spread of island heights increases with increasing tunneling current, and the process of growth of the island is



Figure 2. (a) STM image of a surface region with silicon islands grown at $I_t = 0.3$ nA and V = -10.0 V applied to the STM probe for 1, 3, 6, 11, 17, 27, and 47 s (from the top down). (b) Enlarged image of a region with small islands, marked in Fig. 2a by a white rectangle. (c) Surface profile along the white line in Fig. 1a. (d) Height of silicon islands depending on the growth time. The data are given for islands grown at bias voltages V = -6, -8, and -10 V, and tunneling current $I_t = 0.3$ nA. Solid lines correspond to the process of island growth at a constant rate of atom transfer into the island according to formula (1). (e) Growth rate of silicon islands at the initial stage as a function of the negative bias voltage applied to the probe and $I_t = 0.3$ nA.

accompanied by spontaneous fluctuations of the tunneling current. The fluctuations become stronger at the bias voltage of -10 V and tunneling current of 1.2 nA or greater; their amplitude can reach 500 nA. As a result of fluctuations, pits instead of islands can arise on the sample surface or near the islands (Fig. 4). This finding can be explained as follows. A feedback inherent in the STM operation is directed to support a constant tunneling current via a change in the distance between the tip and the sample. Because of the presence of this feedback, the emergence of fluctuations of the tunneling current causes the appearance of mechanical vibrations of the STM tip along the direction toward the sample surface. Such vibrations were observed with the aid of a scanning electron microscope. The vibrations can lead to a mechanical contact between the tip and the sample. The formation of a pit at the sample surface is likely to be a result of such a contact. It should be emphasized that the transfer of material upon mechanical contact has been considered in several works [31, 44, 45] to explain the appearance of hills and pits on the sample surface after the application of voltage pulses between a probe made of gold and the silicon sample.

2.4 Mechanism of atom transfer to islands

Figure 5 displays images of the surface regions obtained after the interaction of the probe tip and sample at different polarities of the bias voltage. In the case of a negative bias applied to the probe tip, we observed the formation of an island on the sample's surface, as described above, whereas at a positive bias, a small depression appears at the surface. Heike et al. [35] showed that in this case an island was formed at the tip of the probe. This indicates that the depression in the sample appears as a result of atom transfer from the sample to the probe tip. These findings permit one to discriminate the role of such processes as the evaporation of atoms in the form of ions and surface diffusion directed toward the interaction center. Aono and colleagues [30, 32] have determined that on the Si(111) surface the rates of the processes of evaporation of positive and negative ions of silicon are virtually equal. Thus, at a negative bias voltage applied to the probe, the electric field transfers atoms from the sample to the probe in the form of positive ions. This process is accompanied by a reevaporation of negative ions from the probe to the sample.

However, the transfer of positive and negative ions is by no means completely balanced. The formation of an island on



Figure 3. (a) Island height depending on the duration of the interaction between the sample and the STM probe at $I_t = 1.2$ nA and V = -10 V. The accuracy of measurements of the island height (within 10%) is significantly higher than the scatter of experimental data. (b) Growth rates of islands at the initial and later growth stages depending on the tunneling current I_t at V = -10 V. The accuracy of measurements of the growth rate at the initial stage ranges 15-20%. The horizontal arrow in the right-hand part of the figure shows the region of tunneling currents at which the growth of experimental data by formula (1) for the case of island growth at a constant rate, which was assumed to be different at the initial and later stages. The inset shows the initial growth rate depending on I_t at V = -8 V.

the sample surface at a negative bias voltage applied to the probe, as well as the growth of a needle at the surface of the probe tip at a positive bias, indicate that the balance in the ion transfer in both cases is shifted toward the electrode having a positive polarity. In other words, the rate of transfer of negative ions is greater than that of positive ions. Eigler et al. [23] revealed a similar phenomenon when studying the behavior of xenon atoms in the electric field of an STM; in their case, the direction of the flux of electrons between the sample and the probe. It should be noted that the formation of nanostructures under the effect of an STM tip when using gases such as silane and germane occurs stably at negative bias voltages applied to the probe [46–49].

Another result of the evaporation of sample atoms consists in the formation of an incompleted surface structure. In such a structure, the remaining atoms are bound with each other less strongly and, therefore, are more subject to



Figure 4. (a, b) STM images of an Si(111) surface obtained as a result of the interaction of a sample and an STM probe at V = -10 V and (a) $I_t = 0.3$, 0.7, 1.3, and 3.0 nA (from top down, respectively) for 22 s at each point, and (b) for 25 s at the magnitudes of I_t indicated in the figure. (c, d) Surface profiles between the arrows drawn in figures (a) and (b), respectively. The structures such as the pit near the island in figure (a), and the large pit in figure (b) were fabricated at $I_t = 0.3$ nA.

directional diffusion under the effect of the electric field set up by the STM. Since the tip of the probe is located directly over the top of the island (under the condition that the tunneling current is kept constant), the distance between the probe tip and the region of the sample surface around the island increases with increasing island size. At a constant bias voltage, this increase leads to a weakening of the electric field around the island, which, in the case of silicon, leads to a decrease in the rate of its growth (see Fig. 3). When successively recording several STM images of the Si(111) surface obtained after the formation of islands, it was revealed that the arrangement of atoms in the incompleted surface structure somewhat differs in these images. The difference is due to a displacement of surface atoms and indicates that they possess mobility even under the effect of the relatively weak electric field (-2.0 V) that is used when recording the images.

The evaporation of atoms under the effect of an electric field does not induce their transfer along the surface, which is required for the island to grow. The lateral displacement of atoms can occur as a result of directional surface diffusion caused by the existence of a gradient of the electric field at the sample surface. The potential energy for surface diffusion changes under the effect of an electric field as follows [14, 18, 50]:

$$E_F = E_0 - \mathbf{p} \cdot \mathbf{F_r} - \frac{1}{2} \ \alpha F_r^2 \,, \tag{2}$$

where E_0 is the activation energy in the absence of an electric field, p and α are the static dipole moment and the polarizability tensor of atoms at the surface, respectively, and F_r is the electric field strength at the sample surface, which decreases with increasing distance r from the center of the region of interaction between the sample and the STM tip. Similarly to the description of electromigration of adatoms over an Si(111) surface [51], the positive charge can be ascribed in our case to silicon atoms located in the incom-



Figure 5. STM images of the regions of an Si(111) surface, obtained after the application of (a) a negative, and (b) a positive bias voltage of 10 V to the STM probe for 6 s at $I_t = 0.5$ nA. The image contrast in figure (a) was significantly enhanced for clearness. (c, d) STM images of the same region of a germanium layer having a thickness of 2.7 bilayer deposited onto an Si(111) substrate at 450 °C. The images were obtained (c) before, and (d) after the application of a positive bias voltage (8 V) to the STM probe for 30 s at $I_t = 0.3$ nA.

pleted surface structure. This charge, and the corresponding mirror charge in the surface layer of the substrate, produce a static dipole moment. According to the second term of formula (2), the interaction between the electric field and the dipole can either decrease or increase (depending on the polarity of the bias voltage) the height of the potential barrier for the diffusion of atoms toward the center of interaction. The effect of the third term in formula (2), which describes the interaction of the electric field with the induced dipole moment, is always directed toward decreasing the barrier height for directional diffusion to the center of interaction irrespective of the bias polarity. The fact that at both polarities the transfer of atoms occurs to the center of interaction between the sample and the STM tip, namely, the fact that either an island grows at the sample surface or a needle arises at the tip of the STM probe, means that the second term in formula (2) is less than the third one. Consequently, the effect of the induced dipole moment is stronger than the effect of the static dipole moment. Therefore, below we neglect the second term in formula (2) when describing the growth of islands on the Si(111) surface. The diffusion under the action of an electric-field gradient can occur both on the sample surface and on the probe tip. The observation of changes in the arrangement of atoms during the recording of STM images shows that the diffusion of atoms at the sample surface under the action of an STM electric field indeed takes place. However, we have no experimental data which would indicate where diffusion

occurs more efficiently — at the surface of the probe tip or at the sample surface. In the model that is considered in the next section, we assume that the diffusion mainly occurs on the sample surface, although the scaling relationship obtained is independent of this assumption.

The dependence of the initial growth rate on the tunneling current I_t has the shape of a curve with a maximum (Fig. 3b) [38]. The magnitude of I_t is related to the separation s between the probe and the sample as follows: $I_{\rm t} \sim V \exp(-1.1s\phi^{1/2})$, where V is the bias voltage, ϕ is the effective height of the tunneling barrier in volts, and the distance s is expressed in angströms [52, 53]. According to this formula, the greater tunneling current corresponds to a smaller separation s and, consequently, to a stronger gradient of the electric field at the sample surface, which should correspond to a greater growth rate of the island. However, the dependence displayed in Fig. 3b shows that the initial growth rate increases with increasing current only at small currents (up to 0.3 nA) and then decreases. In our case, at the negative bias voltage applied to the probe, the diffusive flux of atoms on the sample surface is directed toward the center of interaction, whereas the flux of tunneling electrons is spread from the center. This direction of the movement of atoms is opposed by the electron 'wind' known from the electromigration effect [51, 54]. Thus, the action of the electron flux on the direction of the transfer of atoms is opposite to the decreasing potential barrier effect for diffusion under the action of the electricfield gradient. In the presence of two forces acting in opposite

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directions, the dependence with a maximum seen in Fig. 3b can be a result of their competition. At tunneling currents above 0.3 nA, a decrease in the initial growth rate can occur due to the predominant action of the electron 'wind' force. However, the real cause for the decrease in the growth rate is likely to be related to a simpler effect, namely, to the increasing mechanical vibration of the probe at larger tunneling currents.

The kinetic data of Fig. 3b display a substantial difference in the growth rates of silicon islands at the initial and the later stages of growth. With increasing island height, there automatically occurs an increase in the separation between the probe and the region of the surface located around the island. It is natural to suppose that the decrease in the growth rate in the case of high islands is due to a weakening of the electric field associated with an increase in this distance.

2.5 Model of atom transfer

When the tip of the STM probe has the form of a cone, the electric field at the sample surface around an island can be described (in the first approximation in *r*) as $F_r = V/S_r$, where $S_r = s + H + \beta r$, with *s* being the separation between the probe tip and the sample, which is automatically kept fixed in the regime of constant tunneling current of the STM, and β being a parameter which depends on the geometry of the probe tip. For atoms located at the point *r*, the probability *G* of overcoming the potential barrier at the point r - a/2 in the presence of an electric field under a negative bias voltage applied to the probe is given by the expression [40]

$$G_{r-a/2} = v \exp\left(-\frac{E_0 - (1/2) \,\alpha F_{r-a/2}^2}{kT}\right),\tag{3}$$

where *a* is the length of atom diffusion hops, and *v* is the frequency of atomic vibrations. The diffusive flux in the direction toward the center of interaction between the sample and the probe, which is created due to the difference in the heights of the potential-energy barriers, is proportional to $\Delta G(S_r) = G_{r-a/2} - G_{r+a/2}$ or

$$\Delta G(S_r) \approx \frac{G_0 \,\beta \,a\alpha V^2}{2S_r^3 kT} \exp\left(\frac{\alpha V^2}{2S_r^2 kT}\right),\tag{4}$$

where $G_0 = v \exp(-E_0/kT)$, and the ratio a/S_r was used as the parameter of smallness. The spatial distribution of the density θ of mobile atoms around a growing island is determined by the evaporation and re-evaporation of atoms as well as by the diffusion flow of atoms. Assuming that the evaporation processes are dominating in producing a given density θ at the initial stage of growth of the island, the magnitude of θ can be considered constant. With allowance for Eqn (4), the rate of atom transfer toward the center of interaction is written down as

$$R \approx A\theta \Delta G(s) \,. \tag{5}$$

The factor A describes here the result of integrating the diffusive flux around the island. A formula analogous to Eqn (4) can also be obtained for the case where the third term in Eqn (2) can be neglected in comparison with the second term. Then, for the initial growth rate of the island we obtain

$$R \approx \frac{A\theta G_0 \beta \, ap V}{s^2 k T} \exp\left(\frac{p V}{s k T}\right). \tag{6}$$

As will be shown below, this case corresponds to the growth of a germanium island under the effect of an STM tip at the surface of a wetting layer of Ge on Si. In practice, formulas (5) and (6) can be used as scaling relationships between the initial growth rate R of an island, the magnitude of the bias voltage V, and the effective dipole moment p. Using these scaling relationships and the experimentally obtained dependences of the initial rate of island growth on the bias voltage, we can estimate the magnitudes of the effective dipole moments and the interaction energies between these dipole moments and the electric field. In these estimations, the weak dependence of the separation s on the bias voltage V ($s \sim \ln V$), which takes place at small tunneling currents [53], can be neglected.

2.6 Estimation of the parameters of interaction of the STM electric field with silicon surface atoms

The description of the initial growth rate of islands as a function of the bias voltage applied to the probe was performed using the approximate expression (4) taken in the form $R = c_1 V^2 \exp(c_2 V^2)$, where c_1 and c_2 were used as adjusting parameters. The fitting of this formula to experimental data is illustrated by the solid curve in Fig. 2e with the parameters $c_1 \approx 0.016$ and $c_2 = \alpha/2s^2kT \approx 0.024$. The quantity c_2 was used for the estimation of the induced dipole moment $\alpha F = \alpha V/s \approx 2 \times 10^{-28}$ C cm at the following values of the parameters: V = 10 V, s = 1 nm, and T = 300 K. The corresponding interaction energy between the induced dipole moment and the electric field, $\alpha F^2/2 = m_2 V^2 kT$, lies between 0.02 and 0.06 eV for bias voltages from 6 to 10 V. Earlier, the estimation of the energy of interaction between the dipole and the STM field was performed for caesium atoms on the GaAs(110) surface [55]. In this estimate, a value of 1.6×10^{-27} C cm, which was obtained from the change in the work function per adsorption of a single Cs atom [56], was utilized for the static dipole moment. For this value, the interaction energy was calculated to be about 0.1 eV [55]. It is important to note that the above method permits one to estimate either the static or induced dipole moment, as well as the corresponding magnitude of the interaction energy between the dipole and the electric field, using experimental data obtained only by scanning tunneling microscopy.

At a negative bias voltage across the STM probe, the induced dipole moment is formed by a positive charge qinduced on surface atoms and the mirror negative charge in the surface layer. The induced dipole moment can be expressed as $\alpha F = ql$, where *l* is the separation between these charges. For a covalent material such as silicon, the mirror charge is located on nearest atoms. For the dipole moment obtained above, at l = 0.3 nm we find q = 0.04e, where e is the electron charge. Ab initio calculations performed when analyzing the electromigration effect showed that there are two different positions of adatoms on the Si(111) surface, which are characterized by different charge densities. It was then found that the jumps by adatoms in the presence of an electric field directed along the surface occur predominantly from one such position to another, thereby creating a diffusion flow. The effective force acting on the diffusing atoms can be expressed in the form of the interaction force between the electric field and the effective positive charge whose magnitude is about 0.05e [51]. The effective charge responsible for the surface electromigration was also determined using the mesoscopic theory which gave for this charge an estimate $\leq 0.01e$ [54]. These theoretical investigations give the value of the static charge. Although the mechanism of directional diffusion in the electric field of an STM differs from the electromigration mechanism, the fact that the estimated values of the charges are comparable is expected, since in both cases the directional atom transfer has an electrostatic origin.

3. Formation of germanium islands

3.1 Specific features of the formation of germanium islands

Growing germanium islands with the aid of an STM probe has been studied on two-dimensional germanium layers at Si(111) surfaces. The formation of germanium islands occurs reproducibly at negative bias voltages across the STM probe in a range from -7 to -10 V. At the same duration of interaction between the sample and the probe, the island size was larger at greater bias voltages (Fig. 6). The aspect ratio of germanium islands is about 0.2. This value is approximately twofold greater than the aspect ratio of three-dimensional germanium islands that are formed upon heteroepitaxial growth of germanium on the Si(111) surface at germanium coverages greater than the coverage sufficient for the transition from two-dimensional to three-dimensional growth [42, 43]. A significant difference in the shape of the islands indicates that their formation likely occurs by the same mechanism as in the case of silicon, rather than is a result of relaxation of a strained epitaxial layer of germanium on the Si(111) surface under the effect of the electric field set up by the STM. This is also confirmed by some other experimental data which will be considered below.

Figure 7 demonstrates that the size of the islands increases with increasing duration of the interaction between the sample and the probe. The island height grew to 15 nm, when the interaction duration increased to 10^3 s. It is seen from Fig. 8 that the formation of an island occurred due to the removal of a large number of germanium atoms from the surface layer in a region located around the island. This means that, as in the case of a silicon surface, the transfer of



Figure 6. STM image of germanium islands on a germanium layer 2.9 bilayers thick grown on an Si(111) substrate at 450 °C. The three rows of islands were fabricated using the STM probe at the same tunneling current $I_t = 0.3$ nA but different negative bias voltages applied to the probe, indicated in the figure for each row. When fabricating each island, the duration of the interaction between the sample and the probe was 7 s. The inset shows the surface profile between the white arrows drawn in the STM image.



Figure 7. (a) STM image of germanium islands on a germanium layer 2.3 bilayers thick deposited onto an Si(111) substrate at 450 °C. The islands were grown at $I_t = 0.3$ nA and V = -10 V. The growth time is indicated near each island. (b) The germanium island height depending on the growth time. The islands were grown at V = -9 V applied to the STM probe at $I_t = 0.3$ nA. The solid line corresponds to the island growth model for a constant rate of germanium transfer to the island. The inset shows data for the initial stage of island growth. The scatter in the data obtained in different experimental series exceeded the accuracy of measurements of the island height, which was within 10%.

germanium atoms to the island proceeds by displacement of single atoms. However, some differences were also observed between germanium and silicon. As is known, the Ge(111) and Si(111) surfaces are comprised of a bilayer, i.e., double atomic layers. In the case of silicon, atoms of both sublayers of such a surface bilayer were involved in the process of atom transfer (Fig. 9), whereas the STM image of the germanium surface shows (see Fig. 8) that atoms of only the uppermost sublayer are absent at the surface around the island being formed. This STM image was obtained using a smaller tunneling current as compared to its optimum value that gives the best atomic resolution. Experiments with a successive recording of several STM images showed that even at smaller tunneling currents, which correspond to smaller values of the electric field strength at the sample surface, the germanium atoms in the incompleted surface layer could displace easily along the surface during scanning by the STM probe. This points to the high mobility of these atoms under the action of the STM electric field.

3.2 Interaction between the STM electric field and germanium surface atoms

One more difference between germanium and silicon was observed when utilizing a positive bias voltage applied to the STM probe. In this case, a disordered surface structure (Figs 5c, 5d) forms, which means the absence of a directional transfer of atoms, whereas at a negative bias voltage, an



Figure 8. (a) STM image of a germanium island on a germanium layer 2.7 bilayers thick deposited onto an Si(111) substrate at 450 °C. The island was grown on an atomic step at $I_t = 0.3$ nA and V = -10 V applied to the STM probe for 5 s. The contrast of the image was significantly enhanced to reveal the atomic structure of the surface around the island. (b) Surface profile between black arrows drawn in Fig. 8a.



Figure 9. Initial stages of growth of germanium and silicon islands depending on the magnitude of a negative bias voltage applied to the probe at $I_t = 0.3$ nA. The data for silicon are the same as in Fig. 2e (here, they are given for comparison with germanium). The solid lines represent the approximation of the experimental data by formula (8).

island in the central region of interaction grows, as described in the previous section. Notice that a similar dependence on the field polarity was observed by Lyubinetsky et al. [48] in the case of vapor-phase deposition stimulated by an electric field and the tunneling current of the STM. Such a dependence on the polarity of the bias voltage means that the second and third terms in formula (2) have opposite signs and are approximately equal in magnitude. This dependence also shows that the germanium surface atoms have a positive static charge. Below, when estimating the interaction force between the probe and the surface atoms of the sample at a negative bias voltage applied to the probe, we shall introduce a parameter such as the effective dipole moment written in the form $p^* = p + \alpha F_r/2$. This permits us to unite the second and third terms in formula (2), which now can be written as $-p^*F_r$. We will use p^* as a quantity that is independent of the bias voltage. Such an approximation yields an error of about 20% in the determination of the quantity p^* in the range of bias voltages from -6 to -10 V.

3.3 Comparison of the formation processes of germanium and silicon islands

The parameters of interaction of the electric field set up by the STM probe with germanium surface atoms can be determined from the kinetics of island growth. As in the case of silicon, the growth kinetics were studied by measuring the island height depending on the interaction time (Fig. 7b). Assuming that all islands have the same conical shape with the ratio of the island height to its base equal to 0.2, for the amount of germanium transferred to the island we obtain $6.5H^3$. At the same time, we have

$$6.5 H^3 = R (t - t_0) \tag{7}$$

for islands growing with a constant rate *R* for a time *t*. The parameter t_0 is added to account for the uncertainty in the determination of the instant of the onset of island growth; this parameter (ranged ± 1 s) is related to the time of the automated approach of the probe tip to the sample surface when creating the next island. We analyzed only the initial stage of island growth. The solid line in Fig. 7b demonstrates the kinetics of growth at a constant rate *R* whose magnitude was determined by fitting formula (7) to experimental data for interaction times between 0 and 30 s. To estimate the effective dipole moment, the magnitude of *R* was obtained as a function of the bias voltage in the range from -6 to -10 V (see Fig. 9). The description of these data by formula (6) taken in the form

$$R \sim DV \exp\left(\frac{p^* V}{skT}\right) \tag{8}$$

yields a value of the adjusting parameter equal to $p^*/skT \approx 0.2$. As in the case of silicon, we here also neglect the weak logarithmic dependence $s \sim \ln V$ [53]. The results of fitting are shown in Fig. 9 by a solid line. The effective dipole moment was estimated equal to $p^* \approx 0.2 skT$, which at s = 1 nm and T = 300 K gives $p^* \approx 8 \times 10^{-29}$ C cm. The corresponding interaction energy between the effective dipole moment and electric field *F*, i.e., $p^*F \approx 0.2VkT$, lies in the range 0.03 to 0.05 eV at bias voltages from -6 to -10 V.

To directly compare the parameters that characterize the transfer of germanium and silicon atoms, the experimental data for silicon were also approximated using formula (8), which gave a fitted value of $p^*/skT \approx 0.6$. The results of this fitting are displayed in Fig. 9. Since the magnitude of p^*/skT for silicon is three times that for germanium, the corresponding dipole moment and the energy of interaction of the dipole with the electric field is also greater by a factor of three. However, the growth rate for silicon is smaller by approximately a factor of five (depending on the bias voltage) than that for germanium. The fact that the weaker interaction



Figure 10. STM image of the same region of germanium lines on a germanium layer 2.5 bilayers thick deposited onto an Si(111) substrate at 450 °C. The germanium lines were fabricated at $I_t = 0.3$ nA, a recording rate of 0.8 nm s⁻¹, and V = -9 V. The images were obtained (a) before, and (b) after annealing of the sample at 550 °C for 10 min. The inset to the center of the figure shows the image of a region with dimensions 356×356 nm containing the entire structure with lines grown after their annealing. The region shown in the images (a) and (b) is delineated in the inset with white lines.

between the dipole and electric field yields, nevertheless, a greater rate of transfer of atoms is likely to be due to the fact that the activation energy for processes occurring at the germanium surface is much smaller than that at the silicon surface. This is also consistent with the observation indicating that it is only atoms of the uppermost sublayer of the double surface layer that have been involved in the process of atom transfer by the electric field at the germanium surface, whereas atoms of both sublayers were involved in this process in the case of silicon. It should be noted that in earlier studies Becker et al. [57] observed a modification of the germanium surface at relatively low bias voltages applied to the probe, such as -4 V, at a constant tunneling current, whereas it is known that for the modification of silicon surface the bias voltages above -5 V are required [30, 32].

4. Fabrication of lines of germanium atoms

4.1 Continuous transfer of germanium atoms using an STM probe

As was shown above, at fixed values of the bias voltage and tunneling current the initial stage of island formation is described well by a model with a constant rate of atom transfer by the electric field of the STM probe into the central region of the interaction between the probe and the sample. Under conditions of a continuous atom transfer, the movement of the probe along the sample surface produces a linear protrusion whose height is determined by the speed of motion of the probe tip along the surface, i.e., by the 'recording rate'. It was revealed that for each bias voltage in the range from -7to -10 V there existed an optimum recording speed at which the arising lines were uniform along their length. For example, at a bias voltage of -9 V this speed was about 0.9 ± 0.1 nm s⁻¹. Under such conditions, the average values of the height and width of the line were about 2 and 5 nm, respectively (Fig. 10a). At greater recording speeds, the rate of atom transfer was insufficient for the formation of a continuous line, i.e., a line without breaks, whereas at lower recording speeds, a large differential in the height along the line was observed.

4.2 Effect of annealing on the shape of germanium lines

As distinct from the behavior of silicon islands at a silicon surface, which became spread out during sample annealing, the height of germanium lines, on the contrary, increased (see Fig. 10). This difference is related to the distinct mechanism of growth of germanium islands on the Si(111) surface, which includes a decrease in the thickness of the wetting layer of germanium after the formation of three-dimensional structures. The decrease in the thickness of this layer is related to the generation of germanium adatoms whose diffusion ensures the growth of three-dimensional structures even in the absence of an external flux of germanium atoms to the surface [58]. The inset to Fig. 10 demonstrates that segments of lines located on the perimeter of the region they occupy increase in size much more greatly than the segments lying within the central part of this region. It is obvious that this phenomenon is observed due to the fact that the peripheral segments of the lines are supplied with adatoms from a larger area of the surface than the line segments located at the central part of the line region. The STM images show that annealing leads to a lateral growth of the lines, whereas the height maximum of line segments remains unchanged. Thus, under the effect of annealing the lines become more uniform in height but wider than before annealing.

The structure of the lines was determined with the RHEED detector using the electron beam of the SREM focused to a diameter of a few nanometers on the sample



Figure 11. (a, b) SREM images obtained with the direction of incidence of the primary electron beam (a) perpendicular, and (b) parallel to germanium lines on the sample surface. The images were obtained (a) for lines shown in Fig. 10a, and (b) for five lines fabricated under the same conditions as for the lines shown in Fig. 10. RHEED patterns obtained (c) from a surface region located far from the lines, and (d) for the case shown in Fig. 11a, at an electron beam focused on the lines after the sample was annealed.

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surface. Figures 11a and 11b display SREM images of some surface regions containing germanium lines. When the beam is incident parallel to the lines (Fig. 11b), the lines look like dots because of the use of the glancing angle of the incident primary electron beam in the reflection electron microscopy. When the beam impinges perpendicular to the lines, ten germanium lines look like a single line (Fig. 11a).

The RHEED patterns from surface regions located far from the lines indicate the existence of a 5×5 reconstruction at the surface (Fig. 11a), which is typical of a wetting layer of germanium on the Si(111) surface. The lines grow by a mechanism that includes electric-field-induced evaporation of atoms between the sample and the probe, as well as fieldinduced directional surface diffusion that transfers atoms to the center of interaction between the probe and the sample. Therefore, the growth of the line due to diffusion is accompanied by its bombardment with ions having an energy that is determined by the bias voltage. Since these processes proceed at room temperature, it can be expected that the structure of the lines in the bulk should not be crystalline. The RHEED patterns obtained for both directions of electron-beam incidence with respect to a line direction show that the structure of the lines is not epitaxial. Nor do the lines become epitaxial after annealing (Fig. 11d). The STM images indicate that after annealing the lines possess a polycrystalline structure with crystallite sizes of a few nanometers.

4.3 Intersection of germanium lines

Figure 12 displays an STM image obtained from a surface region containing intersecting germanium lines. The lines going in the x direction were grown first, i.e., earlier than the lines lying in the y direction. Two differences can be noted between the lines going in these directions. The amount of germanium accumulated in the x lines was much greater than that in the y lines. Since each line was produced as a result of atom transfer from surrounding regions of the surface due to directional surface diffusion induced by the STM electric field, the amount of germanium transferred into the line is proportional to the area of the region from which the atoms have been transferred. Therefore, the difference between the x and y lines is likely to reflect the fact that the areas of regions that supplied the y lines with atoms were restricted by the previously grown x lines. The second difference resides in the fact that the y lines were more uniform along their length than the x lines. Based on the experience of line fabrication with the aid of an STM probe, we can suppose that this difference is related to the shape of the probe tip. The uniform lines and continuous line intersections are usually formed when the probe tip is sharp and has a symmetrical shape. However, when the tip has a relatively flat shape, the lines generated consist of chains of islands, in which some neighboring islands do not even touch each other. Therefore, the difference in the uniformity of the x and y lines, seen in Fig. 12, is likely to be the result of an asymmetry of the tip shape at which the tip profile in the plane that is perpendicular to the x line was sharper than that in the plane perpendicular to the *y* line.

The results obtained reveal that there exist materials, such as germanium, which are characterized by a relatively high rate of atom transfer when using an STM probe and thereby permit one to create nanostructures on substrates at room temperature. When fabricating grooves on the silicon surface with the aid of an STM probe, backward deposition of silicon



Figure 12. Germanium lines fabricated using an STM probe on a germanium layer 2.5 bilayers thick deposited onto an Si(111) substrate at 450 °C. The rate of recording lines was 0.8 nm s⁻¹ at $I_t = 0.3$ nA and V = -9 V. The STM image was obtained after the sample was annealed at 450 °C for 10 min.

from the tip of the probe onto the sample can be seen from the appearance of islands along the grooves [32, 59]. However, no formation of nanostructures of the continuous-line type similar to germanium lines has been observed on the silicon surface. This appears to be due to the fact that the rate of atom transfer over the silicon surface is lower by approximately a factor of five than that over the germanium surface. Although the rate of transfer increases sharply with increasing bias voltage, the use of too large a bias voltage (greater than -10 V) at a constant tunneling current seems to be quite problematic. This is related to the simultaneous increase in the rates of the processes of evaporation and re-evaporation of atoms between the probe and the sample, which can lead to a change in the shape of the probe tip, making it flat. Based on the results obtained by Ichimiya et al. [34], we can suppose that the rate of silicon transfer using an STM probe increases significantly with increasing sample temperature and, probably, can reach magnitudes sufficient for the reproducible creation of lines. Notice that, unlike the method based on the use of an STM probe for desorption of hydrogen from a hydrogen-passivated silicon surface, where the passivation and stimulated desorption are utilized as intermediate stages, the continuous atom transfer considered above is a direct method of creating nanostructures.

5. Effect of irradiation with an external electron beam on the interaction between the sample and the STM probe

The capabilities of the STM probe in the modification of surfaces of wide-band dielectrics has proved to be rather limited as compared to metals and semiconductors. Thus, a thin SiO₂ film can be removed from a silicon surface from a region with dimensions of 10-50 nm under the action of an electron flux from the STM probe onto the sample at a sample temperature above $450 \,^{\circ}\text{C}$ [60-62]. The mechanism of the film removal is related to the fact that the formation of volatile SiO molecules in the SiO₂ film after its irradiation with an electron beam begins at lower temperatures [63]. In this section, we consider a method in which the transfer of atoms from an oxidized silicon surface to the STM probe is achieved by direct interaction between the sample and the probe. The method permits one to remove both the material

deposited on the surface of the silicon oxide and the oxide itself from a sample at room temperature. For accomplishing the stability of the transfer process, both the chemical composition of the probe tip and external conditions (namely, the irradiation of the sample-probe interaction region with an external electron beam) are of significance.

5.1 Removal of atoms from a germanium layer deposited on an oxidized silicon surface

It was shown in Sections 3 and 4 that germanium atoms preliminarily deposited on a silicon surface could be built up into islands or lines under the action of the electric field set up by an STM at enhanced negative bias voltages applied to the STM probe. However, when applying this method to an oxidized silicon surface (both covered with a germanium layer and without a coating), the transfer of atoms of the sample into the central region of interaction between the sample and the probe does not occur even at large bias voltages such as -10 V. Instead, there is observed an atom transfer from the oxidized silicon surface to the probe. This process is neither a stable nor easily reproducible with respect to the tunneling current and bias voltage. We can only note that the process of atom transfer occurs more efficiently at small separations between the probe and the sample, which are reached at relatively large tunneling currents (several nanoamperes) and small negative bias voltages (2-3 V)applied to the probe. The transfer process was analogous to the manipulation of silver clusters on a passivated silicon surface [64].

In experiments with an oxidized silicon surface, the silicon oxide film is prepared as follows. A silicon sample is heated to a temperature of $620 \,^{\circ}$ C in an oxygen atmosphere at a pressure of 2×10^{-4} Pa for several minutes. As a result, a silicon oxide film about 0.5 nm thick is formed on its surface [65, 66]. Then, if required, the sample is covered by a germanium layer two-three bilayers thick at a temperature of about 400 °C. The germanium deposited on the oxidized silicon surface forms a layer of hemispherical islands (Fig. 13a) [10, 67]. At low substrate temperatures, let's say 400 °C, the germanium islands are crystalline, but are not epitaxial with respect to the silicon substrate because of the presence of a film of silicon oxide.

Unlike the pure silicon and germanium surfaces, in the case of an oxidized silicon surface the interaction between the STM probe and the sample was strongly affected by irradiation with the external electron beam of the SREM. The result of the interaction depended on the chemical composition of the probe tip. The effect of the probe on the sample was more efficient after the initial tungsten probe was modified as follows. The probe was moved out to the silicon sample over a distance of about 100 nm, which was controlled with the aid of an SREM. Then the silicon sample was heated to a temperature of about 1000 °C by passing electric current through it. The resulting thermal expansion led to mechanical and electrical contact between the sample and the probe tip, which was accompanied by the melting of the silicon at the site of contact, and the probe tip was probably covered with silicon. It should be emphasized that the use of a mechanical contact between a sample and the probe (embedding the probe into the sample) under an applied bias voltage is a usual method of changing the shape and chemical composition of the probe tip in the case of metal samples [68]. As distinct from metallic samples, mechanical contact with a silicon sample at room temperature leads to a flattening of the



Figure 13. (a) STM image of germanium islands formed on an oxidized silicon surface after the deposition of two bilayers of germanium at 420 °C. The Debye rings in the RHEED pattern in the inset point to the fact that the islands are crystalline but not epitaxial with respect to the Si(111) substrate. (b, c) STM images of the same region of the surface (b) before, and (c) after interaction of the sample with the probe irradiated with an external electron beam of 2 nA. The germanium removal in figure (c) occurred as a result of a 200-s scanning of the region 46 × 46 nm² in area with an STM probe at V = -4 V and $I_t = 0.3$ nA. The region of scanning is delineated with black lines in figure (b).

probe tip. The edge of the probe tip can become sharp if melting and subsequent crystallization of the tip occur during contact.

When employing an STM probe with a tip made of silicon and under irradiation of the region of interaction between the sample and the probe with a beam of electrons produced in an SREM there occurred an effective and reproducible removal of material from the surface of the sample (Figs 13b, 13c) and its transfer to the probe tip, which was observed with the help of an SREM. It was revealed that the efficiency of transfer depends on the intensity of irradiation and the magnitudes of the bias voltage and tunneling current. The investigation of this phenomenon was carried out for the case of fixed irradiation conditions. The current of the electron beam focused to a diameter of a few nanometers was chosen to be 1 or 2 nA (the magnitude of the current was measured using the STM probe) and the mode of scanning for obtaining an SREM image with a magnification of 20,000 in the region of interaction between the probe and the sample was established.

Figure 14a shows lines fabricated by removing germanium from a layer of germanium islands depending on the bias voltage (at a tunneling current of 0.3 nA) for the case



Figure 14. STM images of surface regions after interaction between a sample and an STM probe under irradiation with an electron beam (1 nA) of an SREM. The lines on the surface of the silicon oxide were obtained by removing germanium from the oxidized silicon surface under various experimental conditions: (a) $I_t = 0.3$ nA, recording rate 6 nm s⁻¹, and various negative bias voltages from -3.0 to -5.0 V applied to the tip and indicated near each line; (b) -4 V, 6 nm s⁻¹, and various I_t between 0.3 and 4.8 nA (indicated alongside the lines); (c) -4.0 V, 3.0 nA, and various recording rates between 30 and 600 nm s⁻¹. The scale of the level of contrast in figure (a) is approximately the same as for figures (b) and (c).



Figure 15. A series of STM images of a surface region after several processes of interaction between a sample and an STM probe lasting 200 s each at $I_t = 0.3$ nA and V = -3.0 V under irradiation with an electron beam of an SREM. The pit in the center of the image in figure (a) was formed after the first interaction process. The images in figures (b-d) portray the results of subsequent interaction processes. Germanium islands which decrease in size or vanish after each subsequent interaction process are indicated with arrows. The size of the region shown is 40×40 nm².

where the probe was moved along the sample surface with a constant speed. The removal of germanium atoms occurs stably at a negative bias voltage in the range from -3.5 to -4 V applied to the probe. The efficiency of the removal decreases substantially at lower voltages; at greater bias voltages, the process becomes unstable. Figure 14b shows that the efficiency of germanium removal increases with increasing tunneling current. The depth of the line of removed germanium approximately corresponds to the level of the surface of the silicon oxide film. The efficiency of germanium removal speeds of the probe movement along the surface, i.e., for various



Figure 16. (a-c) A series of SREM images of the region of interaction between a sample and the probe, obtained after subsequent processes of removing germanium from a layer of germanium islands on an oxidized silicon surface. The removal of germanium proceeded at V = -4.0 V and $I_t = 3.0$ nA under irradiation with an SREM electron beam during scanning of a surface region $400 \times 400 \text{ nm}^2$ in area with the STM probe. The region with a removed germanium come into view in the SREM image in the form of a white line. The upper black region in these images represents the profile of the probe tip; the lower region represents the shadow of the probe. (d - f) SREM images of the probe tip after germanium transfer from the sample to the probe tip under irradiation with an electron beam of an SREM under the following conditions: (d) a relatively high rate of germanium removal achieved at V = -4.0 V and $I_t = 3.0$ nA; (e) the average rate of germanium removal at V = -4.0 V and $I_t = 0.3$ nA, and (f) after growing a needle at the probe tip at an average rate of germanium removal and subsequent growth of the probe tip at a low rate of germanium removal at V = -3.0 V and $I_t = 0.3$ nA.

recording rates (Fig. 14c). The efficiency remained sufficiently high (sufficient to ensure the complete removal of germanium from the surface of silicon oxide) even at high recording rates such as $0.6 \ \mu m \ s^{-1}$. It should be noted that such recording rates are also used in the case of depassivation of a silicon surface covered with hydrogen [69, 70].

In the regime characterized by a low rate of germanium removal from the sample surface, the possibility of removing isolated germanium islands has been checked. Figure 15 represents a series of STM images of a surface region after a 200-s interaction between the probe and the sample at a bias voltage of -3 V, and a tunneling current of 0.3 nA. The images obtained demonstrate that after each interaction one or two germanium islands were removed either partly or

completely. The fact that the germanium islands could decrease in size gradually means that the process of germanium removal proceeds by breaking away small clusters or individual germanium atoms.

5.2 Atom transfer from the sample to the STM probe

The removal of germanium atoms from the sample surface is accompanied by the growth of a needle at the tip of the STM probe. The region at the sample surface with dimensions $400 \times 400 \text{ nm}^2$, where germanium islands were removed, appeared as a bright line in the images of the surface in the SREM which registered a specularly reflected electron beam; at the tip of the probe, a needle grew in this case (Figs 16a-16c). The shape of the needle depended on the bias voltage and magnitude of the tunneling current. At a bias voltage of -4 V and tunneling current of 1.0 nA (these conditions correspond to a high rate of germanium removal from the sample surface), the growing needle had a relatively large diameter (about 30 nm at the base, see Fig. 16a). At a medium rate of germanium removal, which was achieved under the conditions of -4 V and 0.3 nA, the needle diameter ranged 10-15 nm (Fig. 16e). A sharp tip of a needle could be grown at a low rate of germanium removal with a bias voltage of -3 V and a current of 0.3 nA (Fig. 16f). The conditions surrounding the appearance of the needle indicate that it is comprised of germanium. This also agrees with the fact that the estimate of the amount of germanium removed from the surface corresponds to the amount of germanium calculated from the size of the needle grown. It should be noted that the STM images presented in this section were obtained with the aid of a probe whose tip represented a germanium needle grown at a low rate of germanium removal from the sample surface.

5.3 Fabrication of silicon windows on an oxidized silicon surface

After removal of germanium islands from an oxidized silicon surface, the subsequent interaction between the sample and the STM probe leads to a removal of the silicon oxide as well (Fig. 17a). To produce the structure represented in Fig. 17a, germanium islands were removed from a relatively large surface area ($60 \times 60 \text{ nm}^2$). Then, the process of interaction was continued on a small central part of this area. The surface profile (Fig. 17d) shows that this interaction leads to a subsequent removal of material from the sample surface. This means that the capability of a probe to attach atoms does not change substantially after an attachment of some amount of silicon oxide and silicon. Figure 17b exemplifies another structure which was fabricated by, first, removing germanium islands from a band 16 nm wide by successively removing the islands from square areas with dimensions of $16 \times 16 \text{ nm}^2$ under the same experimental conditions as in the case of the structure depicted in Fig. 13c. About a 1-min STM-probe scanning was required to remove germanium from one such area. After the fabrication of a surface band without germanium islands, the subsequent interaction of the STM probe with the sample in the regime of germanium removal was conducted at the left-hand end of the line for 5 min. This resulted in the formation of a pit with a depth of about 2 nm, which indicated the complete removal of the silicon oxide film (whose thickness was 0.5 nm) also from this area of the surface.

The formation of windows in silicon oxide occurs even when no germanium islands are located at the edges of the region from which silicon oxide was removed. However, without a germanium layer on the surface of silicon oxide the capability of the STM probe with a silicon tip to the



Figure 17. (a, b) STM images of structures fabricated by atom transfer from a sample to an STM-probe tip. The process of atomic transfer was stimulated by the irradiation of the region of interaction between the sample and the probe with an electron beam. (c) An STM image of the surface after an attempt to remove the oxide from the oxidized silicon surface without using a coating of the surface with germanium islands. The oxide from the central part of the region shown has been removed incompletely. (d, e) Profiles of the surface between the arrows drawn in Figs 17a and 17b, respectively.



Figure 18. STM images of an oxidized silicon surface covered with germanium islands (a) after germanium transfer from the sample to the probe at a negative bias voltage applied to the probe under the same conditions as in Fig. 13c, and (b) after the backward transfer (redeposition) of germanium from the probe to the sample at a positive bias voltage applied to the probe. The backward transfer occurred upon the interaction of the probe with the sample at a fixed point *1* for V = 4 V, and at point 2 for V = 7 V.

attachment of silicon oxide atoms is limited and does not ensure the creation of even a single window with completely removed silicon oxide (Fig. 17c).

In order to characterize the effect of irradiation using an external electron beam, the dependence of the tunneling current on the bias voltage was measured both with and without irradiation in the regime when the feedback in the STM, which maintains the tunneling current constant, was switched off. The measurements showed that the irradiation produces fluctuations in the tunneling current, which reached several nanoamperes. These fluctuations can be initiated by both primary and secondary electrons produced by the scattering of the external electron beam. When the system of STM feedback is tuned to maintain the tunneling current at a constant level, these current fluctuations cause vibrations of the STM probe in the direction toward the sample surface. The amplitude of these vibrations can become so large that the vibrations can be visible in the SREM images of the sample and the probe during their interaction [38].

When the polarity of the bias voltage changes, the direction of the atom transfer between the sample and the probe is reversed. Germanium that is accumulated at the probe tip in the case of a negative bias voltage is transferred back to the sample at a positive bias voltage applied to the probe (Fig. 18). The backward transfer occurs at a high rate even when the region of interaction between the sample and the probe is not irradiated with an external electron beam. The use of irradiation significantly accelerates the process of the backward transfer and makes it poorly controllable.

5.4 Mechanism of atom transfer from the sample to the STM probe under irradiation with an external electron beam

Transfer of material from an oxidized silicon surface to an STM probe is by no means a process that is triggered by only the electric field of the STM; it differs from such a process in several aspects. In spite of the weakening of the electric field by the dielectric layer of silicon oxide, germanium transfer occurs even at low bias voltages such as 4 V, which is lower than the threshold for the evaporation of atoms with an electric field on clean germanium and silicon surfaces [32, 36, 37]. Another dissimilarity from the processes induced by an electric field consists in the direction of atom transfer. The

atoms evaporate from the surface under the action of an electric field in the form of positive or negative ions [31, 71]. In the case of clean germanium and silicon surfaces, the atom transfer between the sample and the probe follows the same direction as the flow of tunneling electrons, which indicates that the flux of negative ions dominates over the flux of positive ions [40]. This transfer direction is opposite to the direction of atom transfer from the oxidized silicon surface, where the transfer occurs to the STM probe that is under a negative potential with respect to the sample. Apart from these distinctions, note that the processes induced by only an electric field, such as evaporation and directional surface diffusion [14, 31, 71], involve atoms from a wide area (about 100 nm in size [37, 40]) around the center of interaction between the sample and the STM probe, whereas the process of germanium removal from an oxidized silicon surface is local, occurring in an area several nanometers in size.

The atom transfer from the sample to the STM probe is stable under two conditions: the probe has a silicon tip, and the probe vibrates in the direction toward the sample surface under the effect of irradiation of the interaction region with an external electron beam. During vibrations, the probe approaches the sample surface to a distance of a few angströms, at which, according to a theoretical analysis [31, 33, 71 - 74], there occurs a significant reduction in the height of potential barrier between the atoms for their transfer assisted by an electric field. The mechanism of such a transfer can be characterized as electric-field-assisted evaporation in combination with a chemical interaction. Both experimental [23, 25, 27] and theoretical [24, 26] works emphasize the importance of a vibrational excitation of the atomic bonds with the surface, induced by the tunneling current and bias voltage, in this process. In such a case, the atom transfer is local, since it involves only atoms of the sample that are at a distance of a few angströms from the atoms of the probe tip. This mechanism explains characteristics of the process such as the sufficiency of relatively low bias voltages and the small area of the surface region subject to atom removal. The experimental results obtained indicate that the direction of atom transfer as a function of the polarity of the applied voltage upon evaporation by electric field with the participation of a chemical interaction is opposite to electric-fieldassisted evaporation without chemical interaction. This indicates that with decreasing distance between the atoms of the sample and the probe, not only does a decrease in the potential barrier between these atoms occur, but also the configuration of this barrier changes, thus leading to a change in the direction of atom transfer.

The difference in the direction of atom transfer obtained agrees with the results of experiments on the interaction of a silicon sample and probe at high bias voltages (-10 V) and large tunneling currents (~ 3 nA) leading to the formation of pits at the silicon surface [38]. Under these rather extreme conditions of STM operation, the atom transfer between the sample and probe becomes unstable and leads to fluctuations in the tunneling current and, consequently, to a mechanical vibration of the probe. During vibrations, as in the case of the use of an external electron beam, the atom transfer mechanism changes due to the involvement of chemical interaction between the atoms of the sample and the probe. This results in the formation of a pit at the silicon surface instead of the growth of an island.

The distinction in the effect of a silicon tip as compared to a tungsten tip can be due to the different reactivities of their surfaces. The reactivity of atoms of a silicon surface to the attachment of germanium atoms is likely to be higher than that of the tungsten surface. A stable formation of silicon windows in a film of silicon oxide is observed when the silicon oxide is covered with a germanium layer. This means that the atoms of the oxide and of the silicon substrate are removed from the sample surface after the removal of the germanium layer which covers the tip of the probe. Thus, the presence of a germanium layer is required for coating the silicon tip of an STM probe to improve its capability of attaching atoms of the silicon oxide. An important role also belongs to the strength of the atomic bonds with the sample surface, which manifests itself in a significant difference between the rates of transfer of germanium atoms from the oxidized silicon surface and of silicon oxide atoms, since it is obvious that the atoms of the deposited germanium are bound with the silicon oxide more weakly than the atoms in the oxide itself.

The known methods of fabrication of nano-sized silicon windows on the surface of oxidized silicon are based on the thermal decomposition of the oxide at high temperatures (900 °C). The thermal decomposition of very thin films of silicon oxide occurs through the formation of pores with a density of 10^9 to 10^{10} cm⁻² rather than by proceeding uniformly over the surface [75, 76]. The irradiation of the oxide film with an electron beam at room temperature reduces the temperature of its subsequent decomposition to 720-750°C [63, 77]. This reduction occurs due to the decomposition of SiO₂ into SiO and oxygen upon irradiation. The irradiation effect was used for the fabrication of silicon windows on an oxidized silicon surface. To this end, irradiation with an electron beam focused to a diameter of a few nanometers and subsequent thermal decomposition of the oxide in only irradiated regions of the surface were utilized [63, 77, 78]. As a source of electrons, a flux of electrons produced by field emission from an STM probe can also be employed. In this case, the formation of silicon windows happens in the process of irradiation of the sample heated to a temperature of 450-630 °C [60-62]. Notice that the technique we described above does not rely on processes of thermal decomposition and permits one to fabricate silicon windows on an oxidized silicon surface directly with the aid of an STM probe at room temperature [79].

6. Conclusions

The modification of surfaces with the use of an STM probe can be effected by several methods. In this review, we considered the method of a continuous transfer of atoms at elevated bias voltages between the probe and the sample. This method permits one to transfer material at a constant rate to the central region of interaction between the probe and the sample and to fabricate, as a result of such a transfer, threedimensional structures like islands and lines on the sample surface. The transfer of atoms is effected by directional surface diffusion arising in the presence of a gradient of the STM electric field and occurs as a result of the interaction of the field with the effective dipole moments of surface atoms. A model of the process has been considered, which establishes a relationship between the rate of atom transfer, bias voltage, and magnitude of the effective dipole moment induced by surface atoms. This relationship permits estimating the magnitudes of the effective dipole moments, and the energies of interaction between the dipoles and the electric field by

measuring dependences of the rate of atom transfer on the bias voltage.

The result of interaction of the probe with the sample depends on the chemical composition of the probe tip and on the external action, for example, irradiation of the region of sample-probe interaction with an external electron beam. Upon irradiation, there is observed a transfer of atoms from the sample surface to the STM probe via the mechanism of field-induced evaporation with the participation of a chemical interaction between the atoms of the sample and the probe tip. Such a mechanism is effected at atomic spacings as small as a few angströms. In the case of silicon samples with an oxidized surface, other important conditions for atom transfer are the use of a silicon probe tip and coating the sample's oxidized surface with a germanium layer. The germanium atom transfer from this layer occurs with a high efficiency, which leads to coverage of the probe with germanium. The probe tip coated with germanium, in turn, becomes effective for the transfer of atoms of the silicon oxide film and atoms of the silicon substrate. Under such experimental conditions, silicon windows at an oxidized silicon surface can be fabricated directly by the STM probe even at room temperature. Interestingly, the atom transfer between the sample and the STM probe upon the realization of the mechanism of field-induced evaporation with the participation of a chemical interaction has a direction that is opposite to the atom transfer realized without a chemical interaction.

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