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PHASE TRANSFORMATIONS, AND DIFFUSION

Scanning Tunneling Microscopy (STM) of Low-Dimensional NbO Structures on the Nb(110) Surface

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Abstract—Method of scanning tunneling microscopy (STM) has been used to investigate a clean Nb(110) face and low-dimensional quasi-periodic NbO structures on the Nb(110) face formed during high-temperature annealing of a single crystal in a vacuum. It is shown that the structures of the NbO type are present on the Nb(110) face in the form of linear rows (chains) consisting of 10 ± 1 atoms of niobium surrounded by oxygen atoms. The height of the NbO structures above the Nb(110) surface and the spacing between the adjacent chains have been determined to be $d \sim 1.2 \text{ \AA}$ and $L \sim 13 \text{ \AA}$, respectively. Two possible orientations of NbO structures in the directions $\langle 111 \rangle$ of the Nb(110) surface are demonstrated; the structures are mounted into domains. An atomic model of the NbO/Nb(110) surface is suggested.

Keywords: niobium, surface, scanning tunnel microscopy

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INTRODUCTION

Niobium and related alloys are used traditionally in high-tech devices as a superconductive material. They are employed in the elements which use the Josephson effect for tunneling electrons (SQUID magnetometer) [1], in superconductive resonators of particle accelerators [2], in the detectors of photons of infrared radiation [3], in memory elements on single-electron transistors [4], in the rapid single-flux quantum logic (RSFQ) [5], etc. The properties of niobium as a superconductor, especially in the case of thin Nb films, are negatively affected by oxide layers formed on the metal surface and by some other phases, which do not possess superconductive properties.

It is considered that for niobium, as for some other transition metals (Ti, Zr, etc.), “there is no vacuum”; i.e., even under the conditions of ultralow pressures on its surface there accumulate chemisorbed particles of residual gases [6]. The object of experiment in this work are oxide structures that are formed on the surface of niobium via an alternative method, namely, due to the segregation of impurity oxygen atoms from the volume of the crystal upon a high-temperature annealing in a vacuum. The chemical composition and the degree of niobium oxidation on such a surface were studied in our previous works by X-ray photoelectron spectroscopy (XPS) and photoelectron diffraction (XPD) [7–9], where there was made a conclusion about the formation of specific oxide structures close to the niobium monoxide on the surface. The average thickness of the NbO layer was evaluated to be 0.5 nm.

In this work, we studied the NbO/Nb(110) surface by the method of scanning tunneling microscopy (STM) with a purpose of the visualization of the atomic structure of the oxide that is formed on the Nb(110) face upon the high-temperature annealing of the crystal in a vacuum.

EXPERIMENTAL

The experimental studies were performed on a VT STM Omicron scanning tunneling microscope combined with an ESCALAB MkII electron spectrometer. The research complex consists of the chambers of the analyzer of the electron spectrometer and the STM microscope, and of the chamber for the preparation of samples; the residual vacuum in the system was maintained on the level of 5×10^{-9} Pa. Such a construction of the instrument makes it possible to prepare a clean Nb(110) surface, to create NbO structures on the Nb(110) surface, and to carry out in situ XPS, XPD, and STM studies in an ultrahigh vacuum (UHV). The composition of the single-crystal surface was controlled by the method of XPS [7] with the use of nonchromatized MgK_α radiation (1253.6 eV). The calibration of the energy scale of the spectrometer was conducted by the $\text{Au}4f_{7/2}$, $\text{Ag}3d_{5/2}$, and $\text{Cu}2p_{3/2}$ lines. The charging of the sample was evaluated based on the C1s band of the hydrocarbon contamination (284.5 eV). The STM measurements were carried out in the dc regime with the aid of an atomically sharp tungsten needle at room temperature.

The preparation of the (110) surface of single-crystal niobium (99.99%) included the following proce-

dures: (i) determination of the Nb-crystal orientation and preparation of a sample ($10 \times 10 \times 1$ mm) with a (110) surface; (ii) mechanical polishing; (iii) electrochemical polishing; (iv) ionic Ar^+ cleaning of the Nb(110) surface and a high-temperature annealing of the crystal in a vacuum. For the electrochemical polishing, we used a mixture of HF and H_2SO_4 acids in a ratio of 1 : 9 [10, 11]; the anodic dissolution of the surface layers of niobium was conducted at a potential difference of 9 V and a current of 0.03 A for 20 s. To prevent the damage of the Nb(110) surface by hydrogen bubbles, a polymeric tracking membrane was established between the cathode and the anode, which was resistant to the acids and ensured the free passage of the reaction products through the 4- μm pores. After such a treatment, the crystal was washed in distilled water and dried in a flow of high-pure argon (99.99%).

The XPS analysis of the Nb(110) surface after electrochemical polishing showed that the metal surface was oxidized to Nb_2O_5 and was covered with a layer of hydrocarbon contaminations. The removal of the oxides and hydrocarbons was carried out under UHV conditions with the aid of ionic bombardment (Ar^+ , 4 keV, 20 μA) of the Nb(110) surface at an angle of 20° with a continuous rotation of the sample about the axis normal to the surface. The rotation was used to ensure a uniform cleaning of the surface and a reduction in the "crater" effect from the Ar^+ beam. After ionic cleaning, the Nb sample was heated under UHV conditions to a temperature of ~ 2300 K by an electron beam using the *flash* method with a purpose to remove argon implanted into the surface layers and to form a defect-free structure of the Nb(110) surface. The procedure of the bombardment of the surface by argon ions and flash heating was repeated cyclically; the duration of each cycle was ~ 20 min. The criterion of the chemical purity of the surface was the absence of impurities on the Nb(110) surface. For obtaining a clean Nb(110) surface, the vacuum in the chambers of the spectrometer and STM microscope was maintained at a level of 5×10^{-9} Pa with the aid of additionally installed titanium sublimation pumps.

The niobium single crystal was fastened to a standard platelike holder made of tantalum with a rectangular opening of 4×6 mm, which made it possible to heat the Nb sample by the electron beam from the back side and to exclude the possibility of damage of the surface of the Nb single crystal. For conducting flash-heating of the Nb crystal to high temperatures (to 2300 K), in the preparation chamber of the ESCALAB MkII spectrometer there was installed an original system, which consisted of an electron source with a hot cathode and a table (holder) in the form of a pole, onto which the sample holder with the Nb crystal was mounted. The general view of the high-temperature cell is given in Fig. 1. All elements of the source of electrons and the polelike table (sample holder) are made of refractory materials (Ta) and are mounted on a ceramic base. As the source of electrons

(hot cathode), there was used a W wire with a thickness of 0.25 mm, a length of ~ 300 mm, and a resistances in the "cold" state of 0.5 Ω . The cathode is under the ground potential; across it, a small constant voltage is applied, which ensures a cathode filament current I_c to 8 A. At a current more than 6 A, the emission of electrons began. The hot cathode is surrounded by an electrically isolated screen made of tantalum. The distance from the cathode to the sample was $\sim 3\text{--}4$ mm. It is assumed that the larger part of the electrons that is emitted from the cathode is assembled on the sample and Ta holder, which are under a potential of +1200 V. The emission current between the cathode and the sample was varied in the range of 0–35 mA by changing the current of the cathode and potential on the sample. The temperature of the sample was controlled by an S-700.1 optical pyrometer. The working range of the pyrometer is from 1000 to 2500 K with a resolution of 1 K.

RESULTS AND DISCUSSION

Scanning Tunneling Microscopy of the Nb(110) surface

Figure 2 displays an STM image of the Nb(110) surface after electrochemical polishing and ionic Ar^+ cleaning in a vacuum. It is seen that the ionic cleaning has a negative effect on the microstructure of the surface. Although the XPS indicates the chemical purity of the surface, no traces of an atomic order characteristic of the Nb(110) face are observed, and a relief 10–15 nm high and traces of the mechanical polishing of the surface with a periodicity on the order of 200 nm are seen. The roughness measured by STM is approximately 10–15 \AA , i.e., approximately six Nb(110) interplanar spacings ($d_{110} = 2.33 \text{\AA}$). It can be supposed that during the ionic Ar^+ bombardment there occurs a nonuniform etching of the Nb(110) surface at the defects created at the stages of the preliminary preparation (mechanical and electrochemical polishing) of the surface, upon the natural oxidation of the crystal surface during the storage in air, and due to the action of the ion Ar^+ beam proper.

After ionic Ar^+ cleaning, the Nb crystal was heated in a vacuum to a temperature of ~ 2300 K by an electron beam, held under these conditions for 2 min, and sufficiently rapidly (in 10–15 min) cooled to a temperature close to room temperature. Note that the heating of the sample by the electron beam was conducted from the facial rather than from the back side. The STM image of the Nb(110) surface after this treatment is shown in Fig. 3. It is seen that due to the intense diffusion of niobium atoms at high temperatures there is formed a flat surface in the form of extended Nb(110) terraces separated by monolayer steps with faceted boundaries. The crystal surface can be called flat, since the area of the region shown in Fig. 3 is $2 \mu\text{m}^2$ and the total difference in the height is only 1.65 nm; the observed steps correspond to one or two Nb(110) monolayers. The average value of the

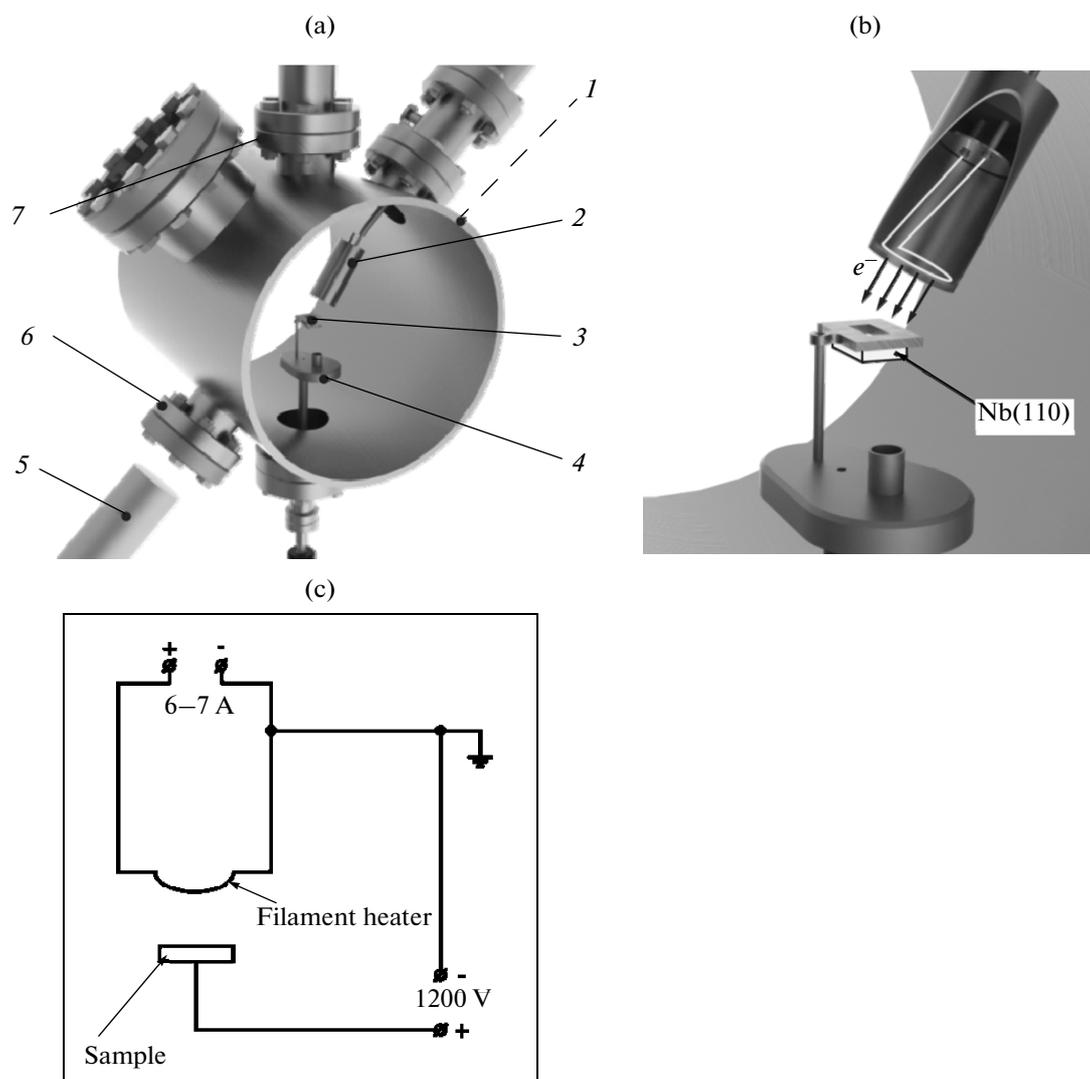


Fig. 1. High-temperature vacuum cell in the sample-preparation chamber of an ESCALAB MkII spectrometer: (a) general view; (b) source of electrons; (c) electrical circuit; (1) sample-preparation chamber; (2) source of electrons; (3) sample; (4) sample holder; (5) optical pyrometer; (6) window of the optical pyrometer; (7) equipment for growing epitaxial thin films.

height of one step is 2.3 \AA , which is close to the bulk value of the interplanar distance in pure bcc niobium in the direction $[110]$ ($d = 2.33 \text{ \AA}$). It can be assumed that at such high temperatures of annealing there can be created a clean Nb(110) surface without oxide structures on it (the XPS analysis shows an oxygen content on the surface on the level of several percent). Unfortunately, even under the conditions of ultrahigh vacuum $\sim 10^{-8} \text{ Pa}$ this surface is retained for only a short time (several tens of hours) and is gradually covered with oxide, apparently, amorphous structures.

Earlier, in [7–9, 12], where the results of an XPD analysis and quantum-chemical calculations of a clean surface of Nb(110) were discussed, the authors reported on the existence of an insignificant relaxation compression of surface Nb(110) layers, which does not exceed 4%, or approximately 0.1 \AA . The STM esti-

mates of the height of monatomic steps (Fig. 3c) also indicate the absence of significant relaxation effects on the Nb(110) surface. Only in one case, namely, for the upper monatomic step, there is recorded a small decrease in the interlayer spacing to a value of 2.2 \AA , i.e., by approximately 5%. However, the step itself is pronounced only weakly (represents a small protrusion in the profile $A-A$) and the accuracy of the determination of the step height is here only $\pm 0.05 \text{ \AA}$. Thus, it can be concluded that the STM analysis confirms the data of XPD and quantum-chemical calculations, which show up an insignificant amplitude of the relaxation effect (compression) of the surface layers of the close-packed face Nb(110).

In the STM image of the clean Nb(110) surface, linear defects, which are extended strictly along the directions $[111]$ (Fig. 3a) are seen. It can be supposed

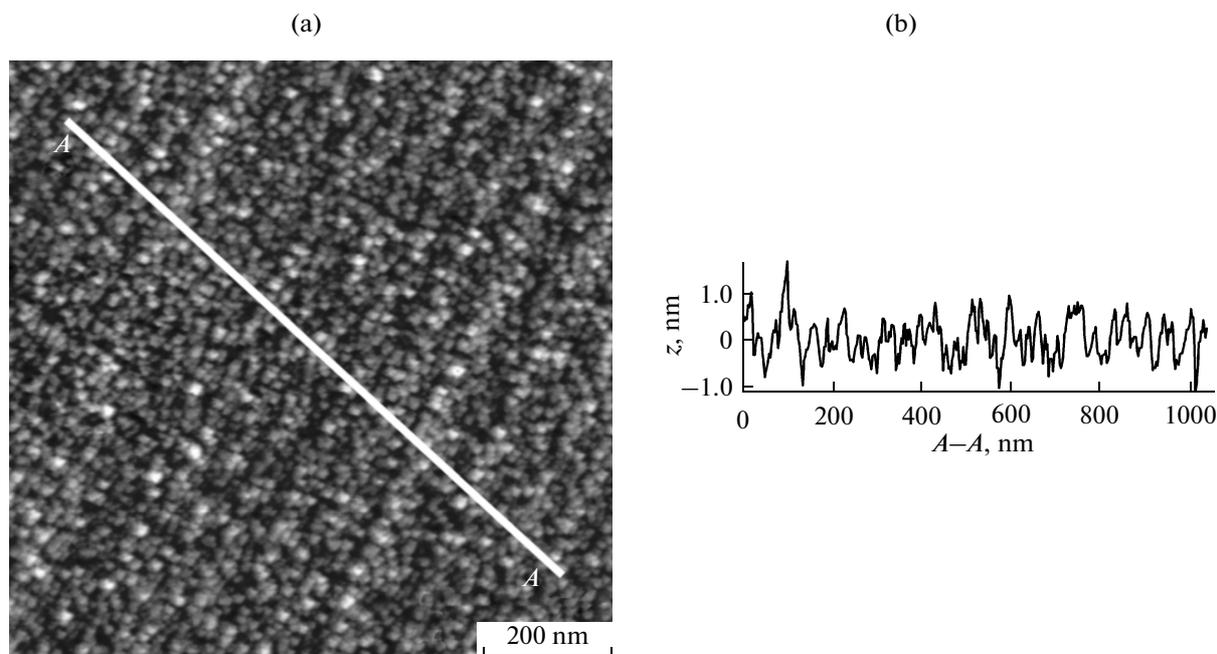


Fig. 2. STM image of the surface of an Nb(110) single crystal ($V = 0.1$ V, $I = 2.6$ nA) after the bombardment by Ar^+ ions; the area of the analysis, $1 \mu\text{m}$; the topological profile of the surface along the direction indicated on the STM image.

that these are nascent or, on the contrary, disappearing steps on the crystal surface. The steps themselves between the terraces are linear boundaries of the joining of three (110) crystal faces of bcc niobium: two planes make an angle of $\sim 110^\circ$ (between the faces of the step) and the third plane is arranged to them at an angle of 90° . Thus, the “stepped” structure of the Nb(110) surface, as could be expected, is formed by close-packed faces of the bcc lattice of Nb.

Scanning Tunneling Microscopy of NbO/Nb(110) Surfaces

Figure 4 depicts the STM images of the Nb(110) surface with regular NbO structures. These structures are formed on the Nb(110) surface upon heating a niobium single crystal to 1800–2200 K in a vacuum (bombardment by an electron beam from the back side of the sample) and rapid cooling down to room temperature. During this heating, the oxygen atoms dissolved in the volume of the metal diffuse to the surface, where oxide structures are formed. The higher oxides Nb_2O_5 and NbO_2 decompose at high temperatures and are desorbed into the vacuum. The lower oxide NbO or, more precisely, the low-dimensional structures on its basis, remains on the surface in the form of quasi-periodic surface structures; these structures are stable up to the temperature of 2273 K [13].

As is shown in Fig. 4a, the relief of the surface consists of terraces, on which there are formed linear nanostructures of the niobium oxide. The height of the steps between the terraces does not exceed one-two

monolayers. Figure 4b shows the profile along the direction $A-A$ (Fig. 4a) and the height of steps for two terraces is evaluated to be ~ 2.5 and ~ 4.9 Å. This value is multiple to the interlayer distances (1 and 2 monolayers) of the fcc lattice of NbO (2.43 Å); i.e., we deal here with steps corresponding to NbO structures with orientation (111) rather than with the single-layered steps of pure metal. The average width of single-layer terraces is 40–60 nm. The size of terraces is determined both by the deviation of the initial surface from the Nb(110) plane and by the roughness, which appears in the stages of the preparation of this plane. Based on the length of the terraces and the height of steps, we can estimate the deviation of the created surface from the (110) plane, which composes $\sim 0.24^\circ$ (according to the Laue X-ray diffraction data, the deviation does not exceed 1°).

Regular NbO structures on the Nb(110) surface are visualized by the STM method as linear arrays (chains) of Nb^* atoms assembled in groups of approximately 10 ± 1 atoms. The oxygen atoms, as was expected, are not detected by the STM method; however, according to the XPD data [9], they are located as inside the chains between and below the niobium atoms and also near the Nb chains. In the STM images of the surfaces of transition metals after exposure in oxygen, the atoms of metal are usually seen as bright protrusions, and the atoms of oxygen, as dark “lowlands” because of the lower local density of states near the Fermi level above the positions of oxygen and because of the strong electronegativity of oxygen [14]. Consequently, in the STM images of the $\text{NbO}_x/\text{Nb}(110)$ surface the

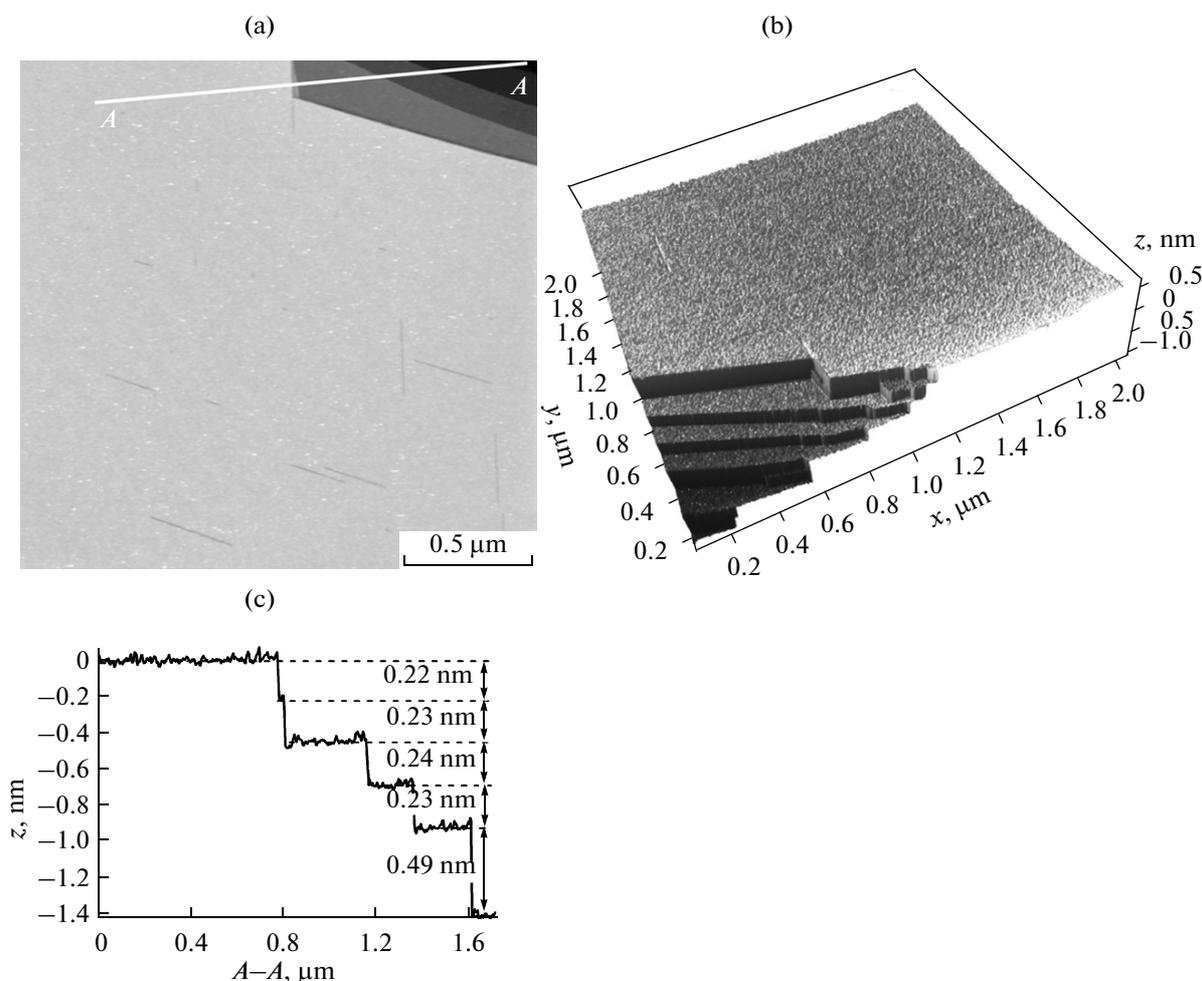


Fig. 3. STM image of the surface of an Nb(110) single crystal ($V = 0.1$ V, $I = 2.6$ nA) after bombardment by Ar^+ ions and thermal annealing in a vacuum of 10^{-8} Pa at $T > 2200$ K.

bright chains are ascribed to niobium atoms, and the dark rows, which separate adjacent short chains, correspond to oxygens.

From the STM- images (Figs. 4, 5), it is seen that there are two equally probable possible orientations of NbO structures on the Nb(110) surface that are ordered in directions $\langle 111 \rangle$, namely, $[1\bar{1}1]$ and $[\bar{1}11]$, of the Nb(110) plane. As a result, there are formed large regions (domains), in which the linear NbO structures are rotated relative to each other by approximately 60° . The domains coexist both within one common terrace and on adjacent terraces separated by monatomic steps.

The steps themselves form faceted boundaries, whose walls are oriented along the directions $[1\bar{1}1]$ and $[\bar{1}11]$ of the Nb(110) plane, and the size of the edge of a separate facet is determined by the length of NbO chains. In this case, different variants are possible. For example, in Fig. 4, there is shown a region of the surface, where near the monatomic steps there occurs a

competition between NbO structures of two different orientations and the prevailing orientation is formed at a certain distance from the edge of the step. In Fig. 5, on the contrary, it is distinctly seen that the NbO structures come to the boundaries of steps by their tips and no competition between the oxide structures of different orientations is observed. Apparently, this is connected with the height of steps, since in the second case a drop in the heights between the terraces composes 11.5 \AA , i.e., almost five monolayers.

Figure 5 demonstrates the results of “aging” of the NbO/Nb(110) surface, where after prolonged storage in a vacuum there are formed on the surface amorphous “clouds” of either higher oxides or adsorbates, for example, of hydrocarbons.

For an analysis of surface quasi-periodic structures of NbO on Nb(110), we used a Fourier analysis. Figure 6 depicts the result of STM scanning of some region of the surface and the Fourier transform of the image obtained. As could be expected, the NbO/Nb(110) surface exhibits a superlattice ordering. The niobium

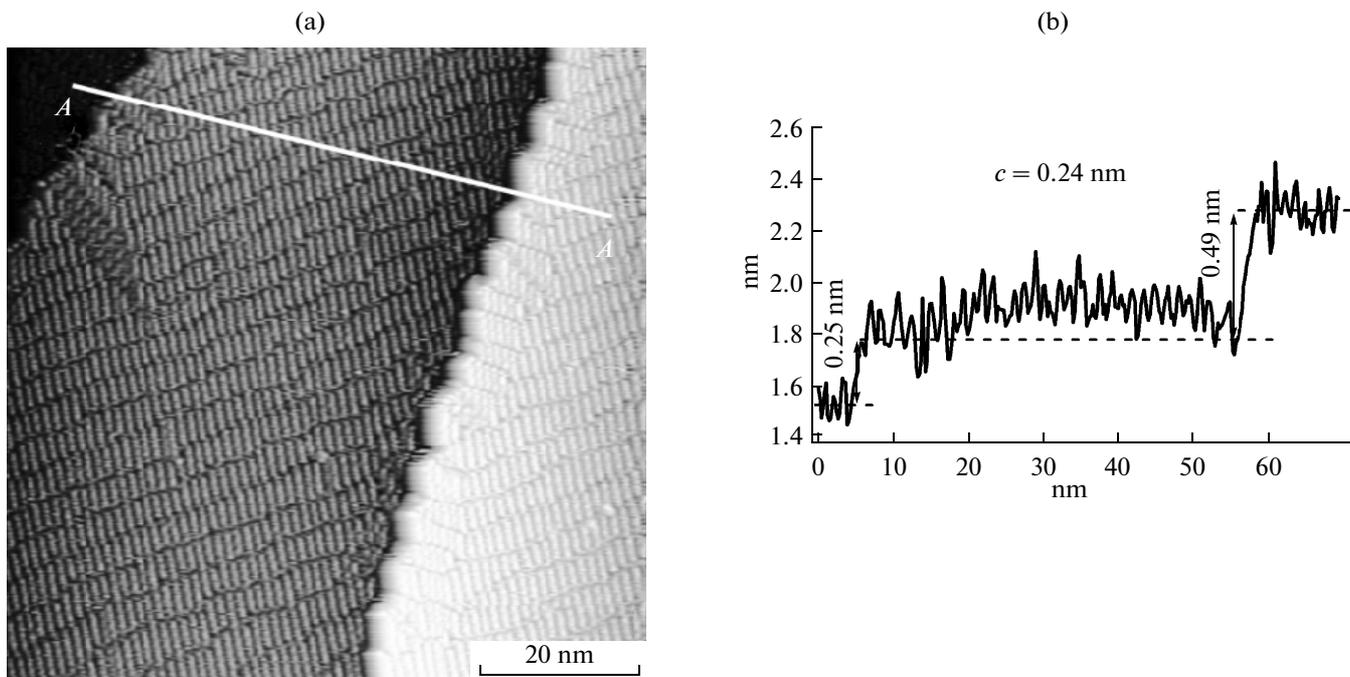


Fig. 4. STM image of the NbO/Nb(110) surface after a high-temperature annealing of the Nb(110) single crystal ($V = 0.25$ V, $I = 3$ nA) under UHV conditions to 1800–2200 K: (a) the image of a surface region (80×80 nm); and (b) profile along the direction A–A.

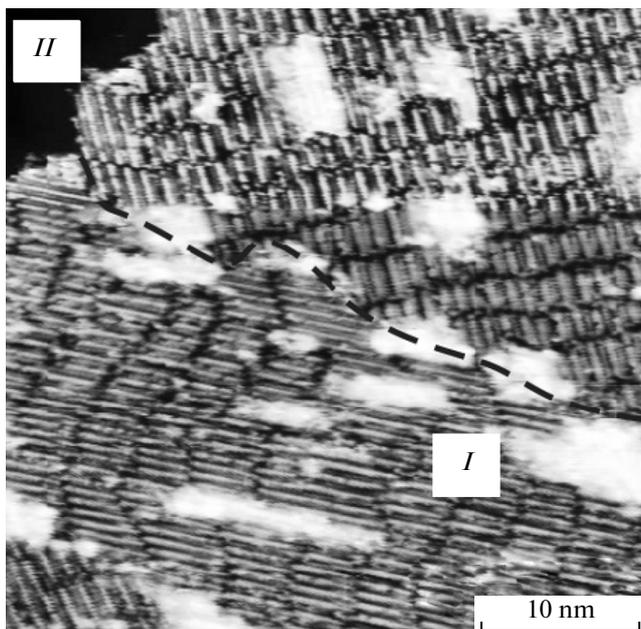


Fig. 5. STM image of a region (40×40 nm) of the NbO/Nb(110) surface ($V = 1$ V, $I = 3$ nA). Regions (domains) with two different orientations of the chains of NbO structures are seen. The dashed line corresponds to the boundary between the domains. Numbers I and II denote terraces that are located at the levels differing in height by 1.15 nm.

atoms on the surface are grouped into linear chains consisting of 10 ± 1 atoms. The interatomic spacing in the chains is 3.3 Å. The parameters of ordering along the directions a and b were determined as 12.7 and 34.7 Å, respectively. These parameters differ somewhat from the results obtained in [14], where the length of chains and the distance between them were reported to be approximately equal (~ 30 Å).

In our STM experiments there are also encountered regions (for example, one of the domains in Fig. 5) where the NbO structures are arranged sufficiently far from each other. However, in the majority of cases the length of Nb* chains is ~ 30 Å and the distance between the chains is ~ 12 – 13 Å. In this respect, our results completely coincide with the data of [15]. The reason is likely to be in the conditions of the formation of NbO structures on the surface of Nb: in [14], the structures were obtained at a temperature of ~ 1300 K, while in our studies and in experiments in [15] higher temperatures (1500–2200 K) were used. It can be supposed that at elevated temperatures the surface concentration of oxygen grows due to the diffusion from the volume and, as a result, the degree of coverage of the surface by NbO structures also grows.

In Refs. [9, 14, 15], there were discussed results of the angular dependence of XPS Nb3d and O1s spectra of the NbO/Nb(110) surface, which were used to extract information on the thickness of the oxide layer. It was shown [9] that within the framework of the island model, when the linear NbO structures cover

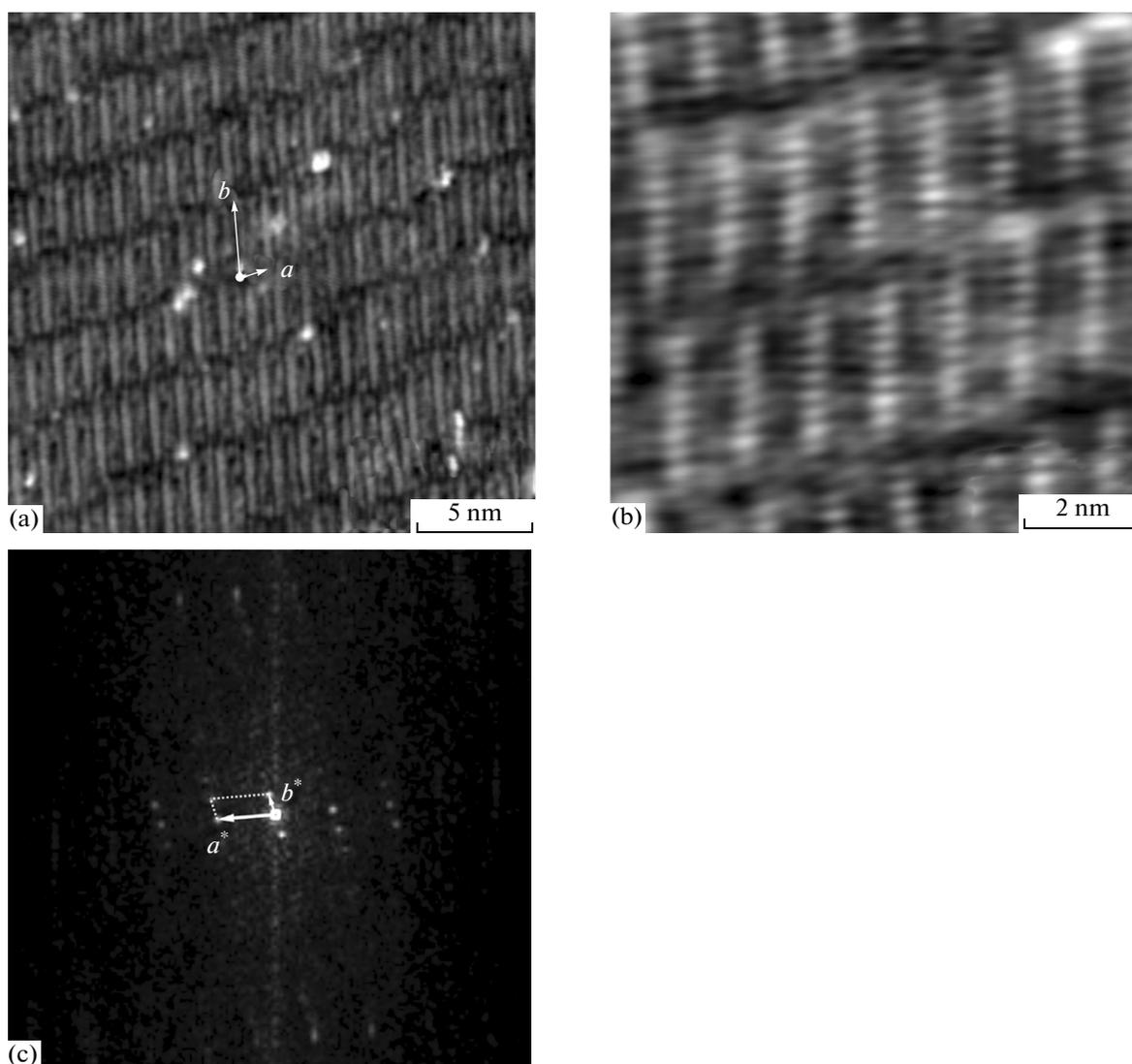


Fig. 6. Superlattice ordering on the NbO/Nb(110) surface after high-temperature annealing in a UHV: (a) STM image of a region 20×20 nm in size ($V = 0.08$ V, $I = 1.5$ nA); (b) STM image (10×10 nm); and (c) superlattice reflections on the Fourier transform.

only 50% of the metal surface, the thickness of the oxide layer is equal to ~ 5 Å, i.e., approximately two niobium atoms in the structure of the oxide. Below, we will try to estimate the height of NbO structures above the Nb(110) surface by the STM method.

Figure 7 depicts a three-dimensional STM image of the region of the NbO/Nb(110) surface corresponding in the usual two-dimensional view to the STM picture given in Fig. 6b. In the right-hand lower part of the figure, a topological profile of the surface along the direction $A-A$, which intersects a number of parallel Nb* chains, is shown. The height of Nb* chains relative to the metal surface and the distance between the linear NbO structures along the direction $\langle 001 \rangle$ on the Nb(110) surface found from these patterns are $d \sim 1.2$ Å and $L \sim 13$ Å, respectively. Similar STM experiments were conducted in [15], where the

height of Nb chains was estimated to be 0.8 ± 0.2 Å at the thickness of the oxide layer of 1.4 ± 0.3 monolayers; and in [14], where the height d was determined to be $\sim 0.8-1.0$ Å.

As is seen, the STM method gives a considerably smaller value of the height of Nb* chains than that estimated by XPS with angular resolution for the thickness of oxide layer. This difference can be explained sufficiently simply. The photoelectronic spectroscopy is characterized by a larger probing depth and “feels” the chemical states of niobium atoms under the surface, in particular, under the Nb* chains. Since the oxygen atoms are arranged in the structure of these chains (between the niobium atoms and below them), as well as on either side from them, the atoms of the metal of the first surface layer of Nb(110) are also chemically bound with oxygen and

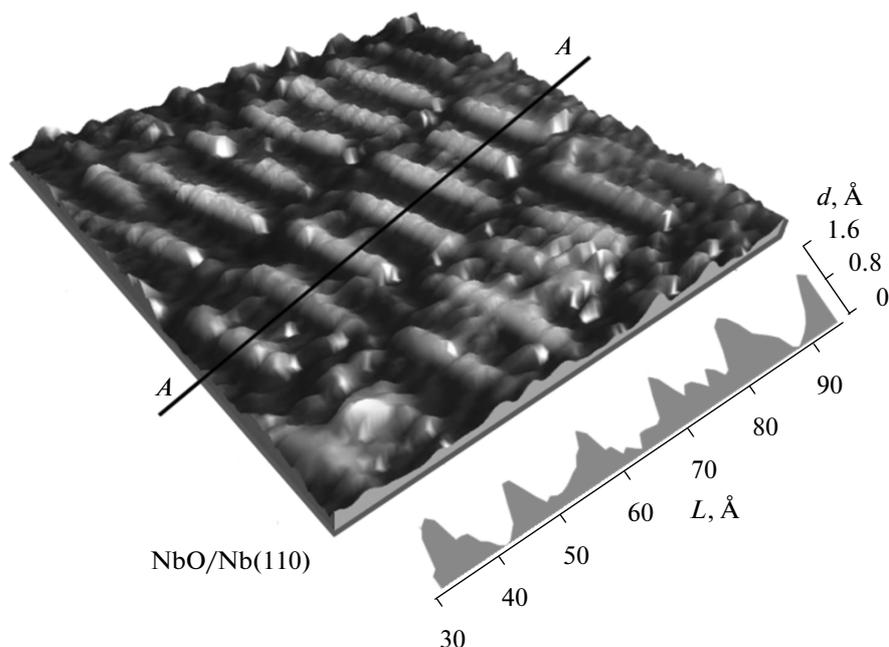


Fig. 7. Three-dimensional STM image of the NbO/Nb(110) surface, 6.5×6.5 nm ($V = 0.08$ V, $I = 1.5$ nA). The topological profile of the surface along the direction A–A.

are reasonably interpreted in terms of the XPS method as the components of the oxide NbO. The scanning tunneling microscopy, on the contrary, shows only the topology of the NbO structures relative to the surface of the metal, but does not determine the true thickness of the oxide layer.

Model of the Formation of the NbO/Nb(110) Surface

The oxide structures on the Nb(110) surface after heat treatment in a vacuum and/or adsorption of oxygen were previously investigated by several research groups [14–16]. All the authors agree that on the surface of the metal there is formed a layer of NbO. However, according to [15], this layer consists of periodically arranged NbO nanocrystals, whereas the authors of [14, 16] suggest the formation of surface superlattices, which are predecessors of the process of growth of an epitaxial NbO layer. Our XPS, XPD [7–9] and STM studies testify in favor of the last variant.

Figure 8 shows the unit cells of the bcc lattice of niobium and of the fcc lattice of NbO with the shaded planes Nb(110) and NbO(111) and the projections of the unit cells onto these planes. The niobium monoxide, as is known, has a defect structure of the NaCl type with 25% vacancies ordered over the metal and oxygen sublattices; therefore, in the center of the hexagonal cell in the NbO(111) plane there is located a vacancy. In the projection planes, the distances between the niobium atoms are indicated. These distances are sufficiently close, which favors a successful epitaxial growth of an NbO(111) layer on the Nb(110)

surface. For the interface matching between the bcc and fcc lattices, two basic orientation relationships (ORs) are known to be possible: Nishiyama–Wasserman (N–W) and Kurdjumov–Sachs (K–S), depending on the ratio $r = d_{\text{fcc}}/d_{\text{bcc}}$ of the distances between the nearest neighbors; these questions have well been studied and are characteristic of many metal–metal systems.

In the case of the NbO/Nb(110) surface, the low-energy electron diffraction (LEED) analysis [15] indicates an angular shift by $\sim 5^\circ$ between the atomic Nb* chains of the arising NbO structure (direction $[\bar{1}10]_{\text{fcc}}$) and the rows of the Nb(110) substrate (direction $[\bar{1}11]_{\text{bcc}}$). For this variant, it is the Kurdjumov–Sachs orientation relationship that is suitable better. Here, however, the $[\bar{1}\bar{1}0]_{\text{fcc}}$ rows must be arranged in parallel to $[\bar{1}\bar{1}1]_{\text{Obcc}}$ and the $[10\bar{1}]_{\text{fcc}}$ rows should be turned by 5.26° relative to $[001]_{\text{Obcc}}$. For the NbO(111) surface layer on Nb(110), the parameter $r = 1.042$ is somewhat lower than the ideal value of the K–S OR $r_{\text{KS}} = 1.0887$, but differs substantially from the optimum value of the alternative N–W OR. According to [14], the reasons for which the K–S OR is not entirely suitable for describing the NbO/Nb(110) interface lies in the method of the preparation of this surface. An epitaxial growth in a surface layer on a substrate with another symmetry is accompanied by the formation of a thin interface layer with misfit stresses and/or misfit dislocations. In our case the oxide NbO layer is formed due

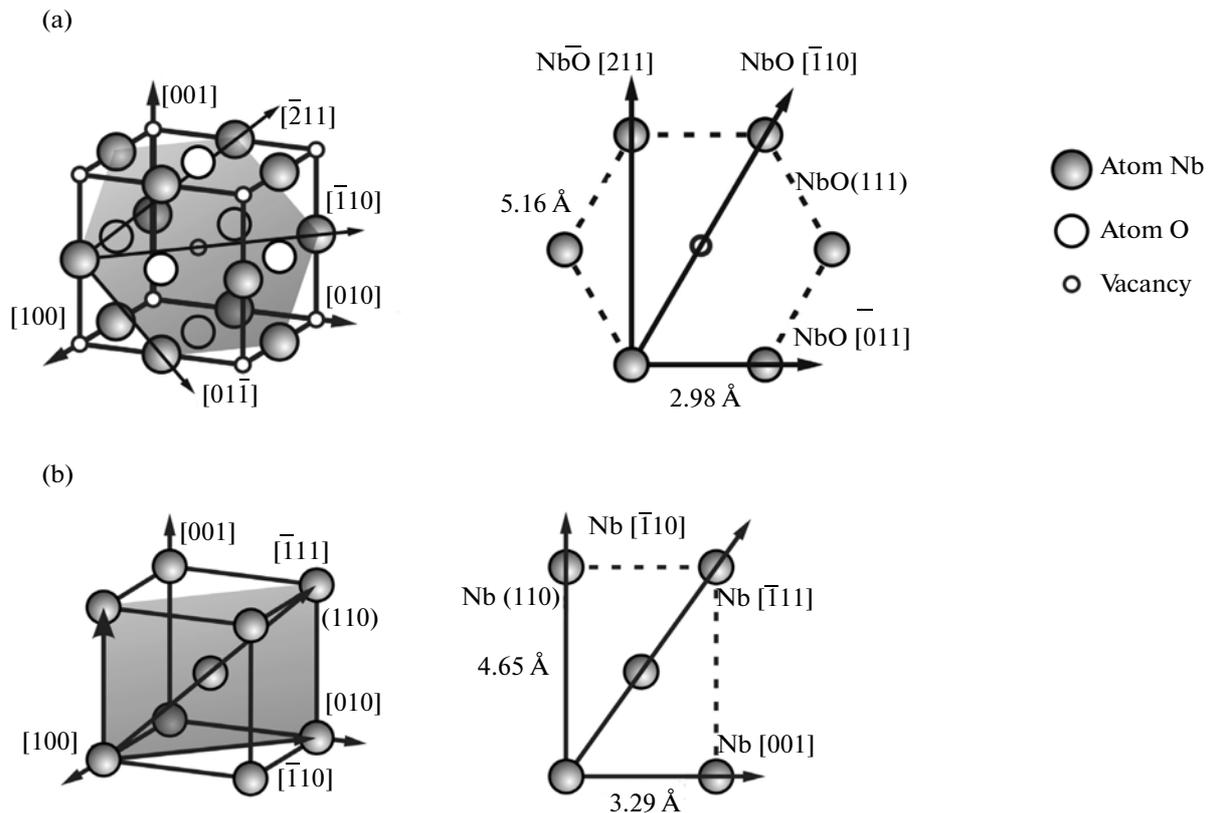


Fig. 8. Unit cells of (a) fcc NbO and (b) bcc Nb with shaded planes Nb(110) and NbO(111).

to the diffusion of oxygen from the volume of the crystal, which leads to a gradual change in the interatomic distances; i.e., there is a sufficiently extended interface transition from the “parent” bcc lattice of Nb to the fcc lattice of the oxide NbO.

Figure 9 schematically shows a model of the $NbO_x/Nb(110)$ surface constructed on the basis of our AR XPS, XPD, and STM experiments and theoretical calculations.

The difference of this model from the variants proposed by other authors [14–16] is in the fact that we for the first time revealed two chemically nonequivalent forms of oxygen (O_I and O_{II}) in the surface NbO layer [7–9], determined their exact ratio (2: 1), and established their structural positions on the surface. It was proved that both forms of oxygen are arranged approximately at the same height above the crystal surface. This contradicts the model suggested in [15], which implies the existence of two separate oxygen layers—one under the Nb surface and one above it—and on this basis a conclusion is made on the formation of a structure consisting of ordered NbO nanocrystals on the surface. We believe that a similar structure has not yet been formed on the NbO/Nb(110) surface. At the same time, in contrast to a number of other models [14], we admit the existence of an inter-

face niobium layer which is located on the Nb(110) surface, but has an fcc lattice of the NbO(111) layer, which agrees with our experiments on the photoelectron diffraction and with the theoretical XPD calculations.

As a result, the model (Fig. 9) we suggested here is an Nb(110) surface on which there is arranged an Nb layer with a structure of the fcc NbO(111) layer. In this layer there alternate rows with ordered vacancies in the positions of metal atoms. Then, there is located an oxygen layer, and, further, rows (chains) of niobium atoms along the NbO $[\bar{1}10]$ direction. Approximately one third of oxygen atoms are localized in the structure of Nb* chains; the oxygen atoms are arranged between the atoms of metal in the linear chains and are below the Nb* atoms. The remaining two thirds of oxygen atoms are localized directly near the Nb* chains, forming an ordered structure of the O sublattice close to that of the NbO_{fcc} structure.

Since we deal with the interface of two different—bcc and fcc—lattices, the structure of the surface still-not-completely-formed NbO_x layer is somewhat distorted: (i) the chains of niobium atoms have a finite length of 10 ± 1 atom, breaking at a critical shift of Nb* atoms in the chains from the optimum positions

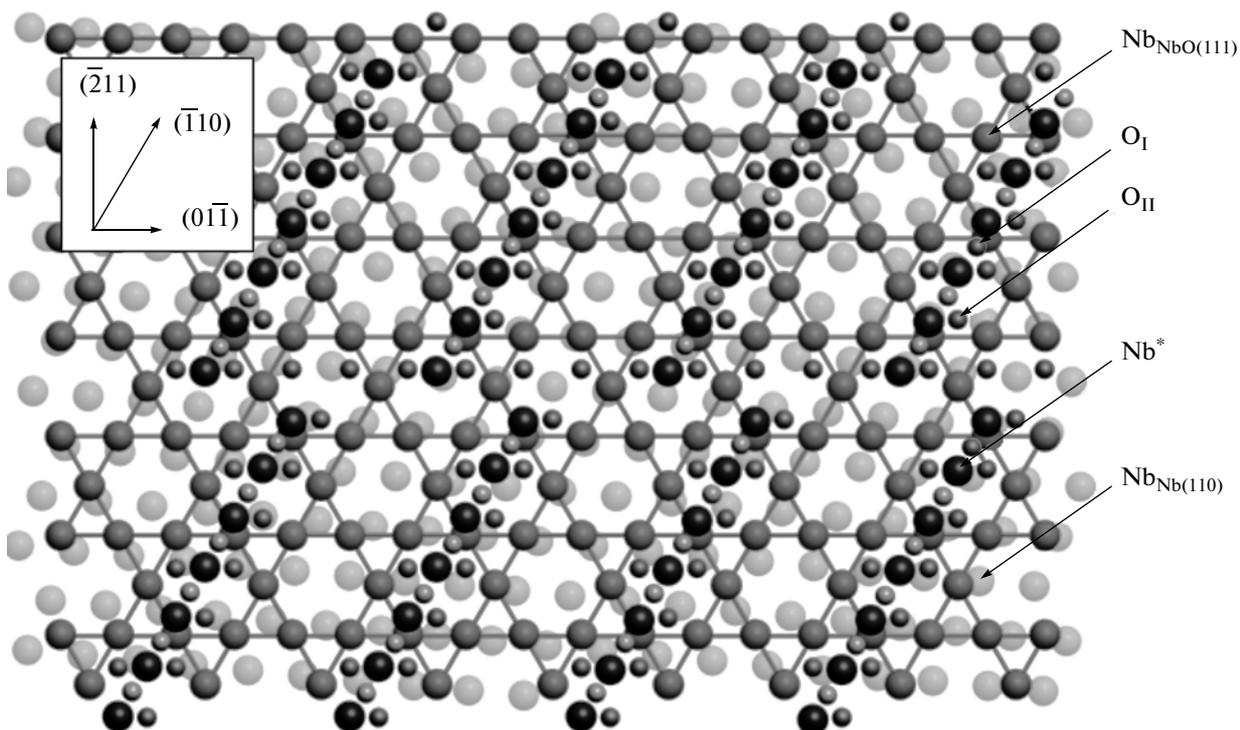


Fig. 9. Model of the NbO/Nb(110) surface: $\text{Nb}_{\text{Nb}(110)}$, Nb atoms in the upper layer of the substrate with an fcc packing of NbO(111) planes; O_I and O_{II} , positions of two types of oxygen atoms; Nb^* , niobium atoms in the chain structures on the surface; and $\text{Nb}_{\text{NbO}(111)}$, Nb atoms of the Nb(110) surface.

in the Nb(110) substrate because of the deviation of the directions $[\bar{1}10]_{\text{fcc}}$ and $[\bar{1}11]_{\text{bcc}}$; (ii) Nb^* chains are shifted along a direction of the $[\bar{1}10]_{\text{NbO}}$ so that each second Nb^* atom would be located between two O_I atoms in the plane $\text{NbO}(\bar{2}11)$; the remaining Nb^* atoms neighbor in this plane only with one atom O_I (Fig. 5.13); and, finally, (iii) half Nb^* atoms in the chains is “elevated” relative to the hexagonal Nb monolayer by $\sim 0.6 \pm 0.2 \text{ \AA}$; as a result, the Nb chains acquire a “sawtooth-like” form.

The last conclusion have been made on the basis of XPD experiments and calculations [9]. However, the STM data, in particular, the analysis of the topology of the surface (Fig. 7), do not confirm such a significant displacement of Nb atoms in the chains. At the same time, in a number of our STM experiments and in analogous experiments of other researchers [14] there was observed a distortion of Nb chains over the height by $\sim 0.5 \text{ \AA}$. In this case, the chains of Nb atoms acquired the form of bent bridges with the maximum amplitude of the displacement of atoms in the middle rather than in the form of a “saw,” where the successive Nb^* atoms are shifted alternately up and down.

Apparently, much depends on the procedure of the creation of the NbO/Nb(110) interface by thermal

annealing in a UHV, especially in the high-temperature range, above 2000 K, when it becomes difficult to reliably control the process (the temperature and the time of annealing, the pressure of residual gases, the rate of cooling, etc.). Figure 10 depicts an example of an untypical case, where the STM records a maximally close packing of NbO chains on the Nb(110) surface.

Such a surface is obtained upon a prolonged annealing of the crystal at temperatures above 2000 K in an insufficiently high vacuum. It is seen that in the case of such a close packing of NbO chains they become strongly deformed and the amplitude of the bending of chains of Nb atoms reaches 3 \AA . This proves that distortions of NbO structures on the Nb(110) surface do occur and the scale of these distortions depends on a number of factors, which include both the synthesis conditions and the mechanisms of the formation of the interface between the $\text{NbO}(111)_{\text{fcc}}$ and $\text{Nb}(110)_{\text{bcc}}$ lattices.

CONCLUSIONS

Thus, it can be concluded that the segregation of oxygen on the Nb(110) surface upon the annealing under UHV conditions at temperatures to 2200 K leads to the formation of oxygen-induced surface

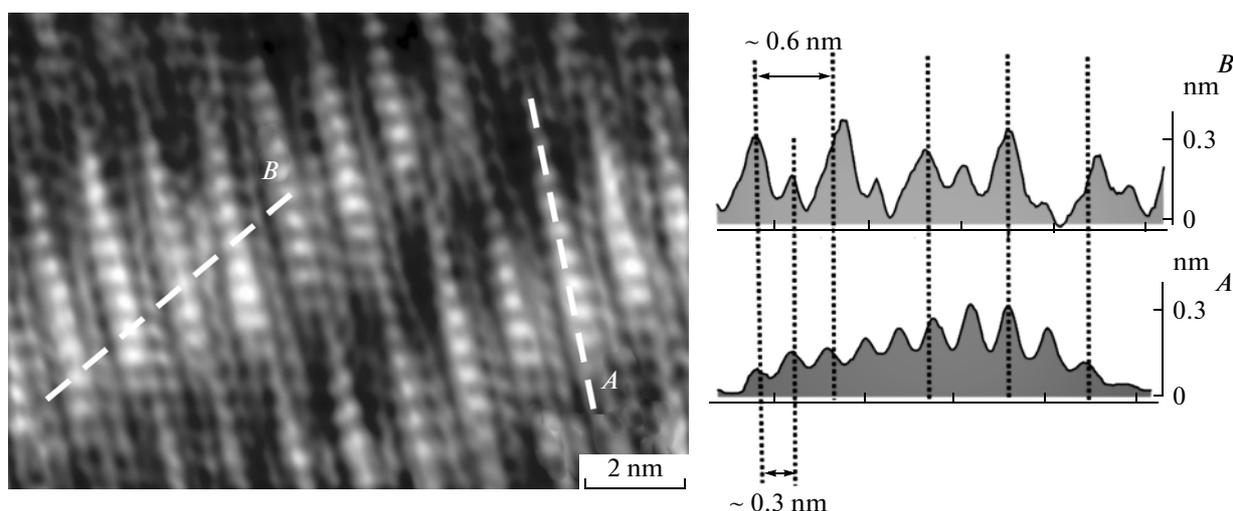


Fig. 10. STM image of the NbO/Nb(110) surface ($V = 0.02$ eV, $I = 10$ nA) prepared at $T > 2000$ K. The topological profiles of the atomic arrangements above the surface along the directions A–A and B–B.

structures in the form of linear chains turned by up to 5° counterclockwise relative to the directions $[\bar{1}11]$ of the Nb(110) surface. These structures can be defined as predecessors (precursors) of the process of epitaxial growth of an fcc layer of NbO(111) on the bcc Nb(110). The finite length of the chains (10 ± 1 Nb* atoms) and the superstructure observed appear as a result of anisotropic stresses arising between these two different types of lattices.

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REFERENCES

1. V. Corato, S. Rombetto, P. Silvestrini, et al., "Observation of Macroscopic Quantum Tunneling in a RF Superconducting Quantum Interference Device System," *Supercond. Sci. Technol.* **17**, 385–S388 (2004).
2. W. Singer, "Seamless/Bonded Niobium Cavities," *Physica C* **441** (1–2), 89–94 (2006).
3. G. N. Gol'tsman, O. Okunev, G. Chulkova, et al., "Picosecond Superconducting Single-Photon Optical Detector," *Appl. Phys. Lett.* **79**, 705–707 (2001).
4. J. Shirakashi, K. Matsumoto, N. Miura, and M. Konagai, "Room Temperature Nb-Based Single-Electron Transistors," *Jpn. J. Appl. Phys.* **37**, 1594–1598 (1998).
5. H. Töpfer, T. Harnisch, and F. H. Uhlmann, "Peculiarities of RSFQ Applications with High-Tc Superconductors—An Approach for Design," *J. Phys. IV* **6** (C3), 345–350 (1996).
6. M. V. Kuznetsov, E. V. Shalaeva, N. I. Medvedeva, and A. L. Ivanovskii, *Chemistry of the Titanium–Gas Interface: Experiment and Theory* (Ural. Otd. Ross. Akad. Nauk, Ekaterinburg, 1999) [in Russian].
7. A. S. Razinkin, E. V. Shalaeva, and M. V. Kuznetsov, "Photoelectron Spectroscopy and Diffraction of NbO_x/Nb(110) Surface," *Fiz. Met. Metalloved.* **106** (1), 59–69 (2008) [*Phys. Met. Metallogr.* **106** (1), 56–66 (2008)].
8. A. S. Razinkin, E. V. Shalaeva, and M. V. Kuznetsov, "Surface Quasi-Ordered NbO_x/Nb(110) Nanostructures: Study by Methods of Surface Analysis," *Izv. Ross. Akad. Nauk, Ser. Fiz.* **72** (10), 1395–1399 (2008).
9. M. V. Kuznetsov, A. S. Razinkin, and E. V. Shalaeva, "Photoelectron Spectroscopy and Diffraction of Surface Nanosized NbO_x/Nb(110) Structures," *Zh. Strukt. Khim.* **50** (3), 536–543 (2009).
10. K. Saito, "High Accelerating Gradients in Niobium L-Band Cavities," *Particle Accelerators* **60**, 193 (1997).
11. L. Lilje, A. Matheisen, D. Proch, et al., "Improved Surface Treatment of the Superconducting TESLA Cavities," *Nucl. Instrum. Meth. Phys. Res., Sect. A* **516** (2–3), 213–227 (2004).
12. K. I. Shein, I. R. Shein, N. I. Medvedeva, et al., "Effects of Atomic Relaxation and the Electronic Structure of Niobium (100) and (110) Surfaces," *Fiz. Met. Metalloved.* **102** (6), 604–610 (2006) [*Phys. Met. Metallogr.* **102** (6), 604–610 (2006)].
13. B. An and S. Fukuyama, "Surface Structures of Clean and Oxidized Nb(100) by LEED, AES, and STM," *Phys. Rev. B: Condens. Matter Mater. Phys.* **68**, 115423 (2003).
14. Ch. Surger and M. Schock, "Oxygen-Induced Surface Structure of Nb(110)," *Surf. Sci.* **471**, 209–218 (2001).
15. I. Arfaoui, J. Cousty, and C. Guillot, "A Model of the NbO_{x-1} Nanocrystals Tiling a Nb(110) Surface Annealed in UHV," *Surf. Sci.* **557**, 119–128 (2004).
16. F. Matsui and M. Fujikado, "Structural Analysis of Oxygen Segregated Nb(110) Surface by Photoelectron Diffraction," *Czech. J. Phys. No. 1*, 61–68 (2006).