

Atomic reconstruction of niobium (111) surfaces



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ABSTRACT

The {111} surface of niobium single crystals has been investigated by ultra-high vacuum scanning tunneling microscopy. An atomic reconstruction has been experimentally observed and has been characterized by a lattice constant two times larger than that expected for a body-centered cubic structure. Moreover, an upper incipient structure is observed on these (2×2) surfaces. The upper unit cell is $2\sqrt{3}$ times larger than the bulk one and is also rotated by 30° with respect to the bulk structure. A model is proposed to explain the competition between a covering of the free surface by a non-dense atomic structure and an island formation of niobium atoms in the dense configuration. The experimental results are finally discussed with the help of *ab initio* calculations used to determine the surface energies of the associated atomic configurations.

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Niobium alloys are widely used in a large range of applications in aeronautic and aerospace, mainly due to their refractory properties and low density [1]. Superconducting properties are also of interest, for instance for planar waveguides and resonators [2–5], for superconducting electronics [6] or qubit fabrication [7]. It is now well-established that niobium crystals are reactive to inorganic elements, which may modify their intrinsic properties. For instance, the superconducting transition temperature is significantly affected by dissolved oxygen, about -1 K/at.%, due to the thin oxide layers that develop at the free surface [5]. As a consequence, the efficiency of radio frequency (RF) cavities may be strongly affected [8]. In this context, atomistic simulations have been performed in the past to determine the surface energy of several oriented Nb crystals [9–13]. The influence of crystallographic orientations on the growth of the oxide layers has been also studied. In particular, the {100} and {110} surfaces have been extensively investigated [14–22], mainly because the laminated polycrystals used for RF cavities are textured along {110} directions. No experimental investigations have been focused on the {111} surfaces and, to the best of the author's knowledge, only a study on the growth of Nb thin films on sapphire substrates has been reported [23]. In this paper, we have examined by ultra high vacuum scanning tunneling microscopy (UHV–STM) the associated atomic structure. *Ab initio* calculations have been performed and a continuum model has been proposed to discuss the experimental results.

Niobium single crystals of high purity (< 5 ppm, except for Ta, C and O given at 180, 25 and 15 ppm respectively) have been first mechanically polished. The specimens have been oriented along the [111] crystallographic direction with an accuracy better than 0.5° . The {111} surfaces have then been prepared using an original UHV experimental device that allows us to follow the evolution of sample surfaces under

stress by *in-situ* AFM–STM [24]. The surface preparation consists in successive Ar ion sputtering (1 kV at 6 μ A, for 5 min) and radiative annealing at 1250 K for approximately 10 min. Recent atomistic simulations have shown that the diffusion of Nb atoms at the {111} subsurface may be activated [25] at 1250 K, even if this temperature only corresponds to 44% of its melting point [1]. In Fig. 1 a characteristic UHV–STM investigation of the free surface is presented. A large overview of the surface (90 nm \times 90 nm for the scan size) is shown in Fig. 1a and b in topographical and signal error modes, respectively. Signal error mode does not allow calibration in the out-of-plane direction but presents a great visual interest due to fine detail enhancement. As expected, the Nb surface is composed of {111} terraces limited by atomic steps. A characteristic terrace width of a few nanometers is experimentally observed. The three-fold symmetry of the atomic structure is clearly distinguishable on each terrace (see Fig. 1c for enlargement). However, an atomic distance of approximately 1 nm is experimentally obtained along the $[0\bar{1}1]$ direction while the dense {111} body-centered cubic (bcc) atomic arrangement should lead to a theoretical value of $a\sqrt{2} = 0.47$ nm, for a lattice constant $a = 0.33$ nm [1]. Thus, the present STM investigations strongly suggest that the {111} Nb surface is associated with a specific atomic structure characterized by a lattice constant two times larger than the expected one. This (2×2) reconstruction is thus related to an atomic density reduced by 4. It is worth noting that chemical Auger electron investigations have been performed in the same UHV device. It was observed that the Nb surface does not exhibit a high level of oxygen, even if some traces can be detected together with some carbon contaminations. It can be concluded that the atomic structure considered here is not ascribed to an oxide layer; contrary to the observations usually reported in the literature for the {100} and {110} surfaces [14,17–19,15,20–22,16]. Note that such a (2×2) atomic structure on the {111} Nb surface has been already suggested in the 70s from X-ray diffraction experiments

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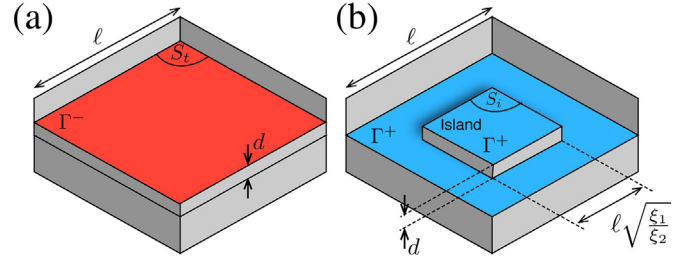
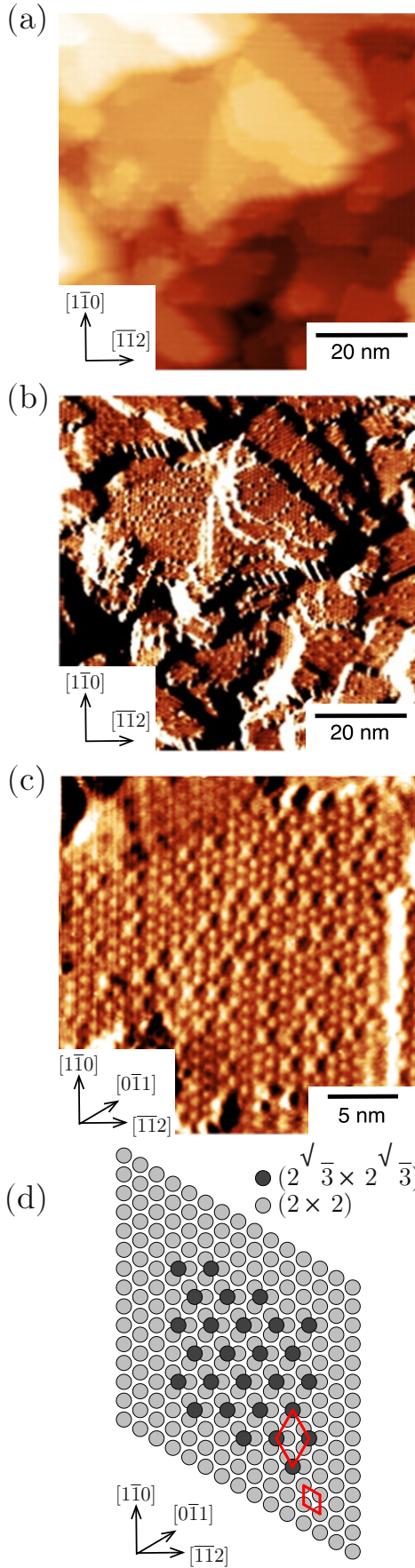


Fig. 2. Schematic of a diamond terrace (a) covered by Nb atoms in a non-dense configuration (Γ^- for the surface energy) and (b) associated with a dense island over a dense configuration (Γ^+ for the surface energy). ℓ and d correspond to the width of the terrace and the height of the island respectively. S_t and S_i are the area of the terrace and the island, respectively.

[15]. A fine investigation of the surface (see Fig. 1c) strongly suggests an upper incipient reconstruction on the (2×2) surface. This upper structure is characterized by atoms positioned in the middle of some triangular cells to form another non-dense atomic arrangement associated with an atomic density reduced by 12. The unit cell is now $2\sqrt{3}$ times larger than the bulk one and is also rotated by 30° with respect to the dense structure, two layers below. This structure is called $(2\sqrt{3} \times 2\sqrt{3})R30$ in the following. Note that the (1×1) structure is not visible in the STM image (Fig. 1c) since blurred by the (2×2) . Finally, a schematic of the Nb atom positions is presented in Fig. 1d.

The question which arises is to understand why the Nb atoms in excess cover the available surface with a non-dense structure, instead of forming a Nb single layer island with a dense structure. In the following, a dense diamond island of surface S_i is considered, according to the three-fold symmetry of the Nb (111) crystallographic structure (Fig. 2). It is assumed that a reference diamond surface S_t can be covered by the Nb atoms that form the dense island. The side ℓ of the reference surface can be assimilated to the terrace width experimentally observed. It leads to:

$$S_i = \delta \cdot S_t = \delta \frac{\sqrt{3}}{2} \ell^2, \quad (1)$$

with $0 < \delta < 1$, the ratio of the density of the non-dense structure to that of the dense one.

For the sake of simplicity, no crystallographic effect has been considered so that the line energy related to the step of the island is given by $\Gamma^+ d$ with Γ^+ , the surface energy of the dense configuration and d , the height of the island. It is assumed that the surface energy of the island is the same than that of the dense structure and that the line energy terms arising from the full covering of the reference surface compensate each other (see Fig. 2a). The energy balance between covering and island formation can consequently be written as:

$$\Gamma^- \cdot S_t = \Gamma^+ \cdot S_i + \Gamma^+ \cdot p \cdot d \quad (2)$$

with p , the perimeter of the dense island. Γ^+ and Γ^- correspond to the surface energies of the high and low density configurations, respectively. As $p = 4\ell\sqrt{\delta}$ and $d = a/(2\sqrt{3})$, this leads to a critical length:

$$\ell^* = \frac{4}{3} a \sqrt{\delta} \frac{\Gamma^+}{\Delta\Gamma} \quad (3)$$

with $\Delta\Gamma = \Gamma^- - \Gamma^+$.

It is emphasized that only the case of a single dense island is considered here. The assumption of several separated islands would lead to a higher energetic configuration due to the increase of p , that is a higher value of ℓ^* . Consequently, the value of ℓ^* given in Eq. (3) corresponds

Fig. 1. STM investigations of Nb $\{111\}$ single crystal surfaces. (a) Topographical mode image, (b) signal error mode image, (c) enlargement of (b) highlighting the atomic structure and (d) schematic of atom positions.

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