

Evidence for a large enrichment of interstitial oxygen atoms in the nanometer-thick metal layer at the NbO/Nb (110) interface

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The oxide/metal interface induced by surface segregation of oxygen during the annealing of a Nb single crystal in UHV has been studied by photoemission spectroscopy with synchrotron radiation. With 260 and 350 eV photons, four well-resolved peaks *A*, *B*, *C*, *D* are found in spectra within the 200–210 eV range of binding energy. One couple of peaks (*A* and *C*) is associated with $3d^{5/2}$ and $3d^{3/2}$ core levels of Nb atoms in the metal while the other one (*B* and *D*), shifted by 1.4 eV when compared to *A* and *C*, corresponds to $3d$ levels of oxidized Nb atoms. The metal peak *A* at 202.3 eV is formed by three $3d^{5/2}$ components: a peak due to a metallic state (202.1 eV) and two components shifted by 0.2 and 0.5 eV, which are attributed to Nb₆O and Nb₄O compounds due to interstitial atoms of oxygen, respectively. The estimated concentration of the interstitial oxygen atoms in the nanometer-thick metal skin underlying the NbO/Nb interface corresponds to a large enrichment when compared to the one in the Nb bulk. © 2002 American Institute of Physics. [DOI: 10.1063/1.1473699]

I. INTRODUCTION

It is well known that impurities located in crystalline materials induce changes in many of their properties. For example, mechanical properties of several bcc metals suffer drastic modifications in the presence of hydrogen atoms in interstitial sites since they become brittle.¹ The temperature of the normal/superconductor transition also depends on the impurity concentration.² On the other hand, thermal treatment of these materials often provokes a redistribution of impurities within the sample. In particular, some impurities in interstitial positions migrate at relatively low temperatures ($T \sim 0.2 T_m$ with T_m the melting temperature of bulk) and segregate into one-dimensional or two-dimensional defects as dislocations, surfaces and grain boundaries.³ For niobium, several studies have shown that a single crystal annealed at 1200–1800 K in UHV presents a surface covered by a thin overlayer of oxide due to segregation of the oxygen contained in the bulk.^{4–8} Recently, Hellwig has studied the oxidation of a thick Nb layer (200–500 nm) heated at 450–600 K in air.⁹ During the oxidation process, the thickness of the Nb₂O₅ overlayer increases while the underlying metal becomes thinner. This metal was found to contain a high density of interstitial oxygen atoms.

Photoemission spectroscopy through measurements of the binding energy shift of core levels has proven to be an excellent tool for studying the chemical state of atoms near metal surfaces. This core level shift (CLS) was used to probe the modifications of the electronic density of atoms within the surface layer due to the presence of the surface^{10,11} as well as the one induced by adsorbed impurities.¹² For niobium, the CLS induced by the surface was studied on Nb (001) and Nb (110) faces by using high resolution photoemission with synchrotron radiation.^{13,14} For a clean (110) Nb surface, the shift towards higher binding energies attains 180 ± 15 meV.¹⁴ For oxygen adsorption on Nb surface and thin overlayers of Nb oxides, few studies were reported using Al $K\alpha$ radiation.⁶ In contrast, Nb $3d$ CLSs for several kinds of bulk oxides were investigated mainly by using 1486 eV photon (Al $K\alpha$ radiation).^{15–18} These studies demonstrate that the energy shift of $3d$ levels of Nb atoms involved in oxides with different stoichiometries varies linearly with the Nb valence.¹⁹

In this article, we present results of photoemission spectroscopy with synchrotron radiation, which give evidence of the presence of interstitial oxygen atoms near the NbO/Nb interface. The oxygen concentration is also estimated.

II. EXPERIMENT

Measurements were performed in the photoemission chamber (base pressure of $1-2 \times 10^{-10}$ mb), which is con-

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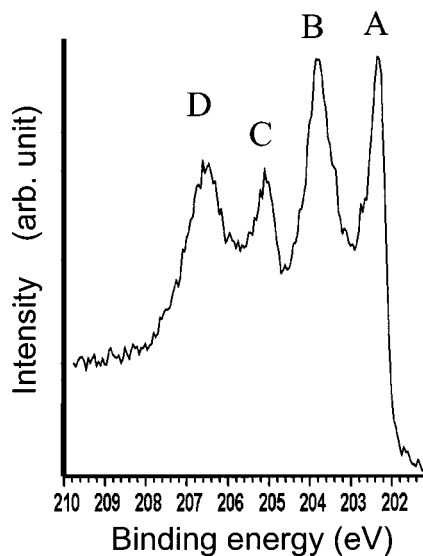


FIG. 1. Typical spectrum of $3d$ Nb levels from an annealed Nb (110) surface with 260 eV photons at normal collection of photoelectrons. Peaks A (202.3 eV) and C (205.1 eV) correspond to $3d^{5/2}$ and $3d^{3/2}$ levels of Nb atoms in the metal. Peaks B (203.7 eV) and D (206.5 eV), shifted by 1.4 eV from peaks A and C, are attributed to $3d$ levels of Nb atoms in the oxide overlayer.

nected to line SA 73 at Lure (Orsay). The sample (a 2-mm-thick disk with 6 mm in diameter) was cut in a single crystal of Nb (Goodfellow). Then, it was mechanically polished and chemically etched. The surface orientation was checked by x-ray back diffraction ($\pm 0.5^\circ$). Estimation of the crystal purity by resistivity measurements²⁰ gives an overall concentration of impurities of 300–400 ppm (mainly oxygen). After etching in a mixture of acids (HF:1,HNO₃:1,H₂PO₄:2), the crystal was rinsed with de-ionized water and dried under a flux of pure nitrogen before being mounted on the sample holder. In vacuum, the surfaces were further cleaned by many cycles of Ar⁺ sputtering (1 keV) and annealing at temperatures in the 1200–1500 K range (typical duration 20–30 min).

Photoelectrons are analyzed with a hemispherical analyzer (WSW 125). As the analyzer is fixed, a variation of the angle of photoelectron collection induces change in the incidence angle of photons. The overall resolution of the experimental setup is 200 ± 20 meV including the dispersion in the Fermi level positions. Analysis of $3d$ Nb peaks was performed from eight photoemission spectra taken with 260 and 350 eV photons and at 90° and 45° emission angles. All these spectra were fitted with line profiles having a constant $3d^{5/2}/3d^{3/2}$ splitting (2.75 eV), a constant branching ratio $3d^{3/2}/3d^{5/2}$ equal to 0.5 and an asymmetry factor for each profile (0.04).

III. RESULTS AND DISCUSSION

Figure 1 presents a typical photoemission spectrum of the Nb $3d$ levels of a Nb (110) sample annealed at 1400 K for ~ 20 min with 260 eV photons. This spectrum exhibits four peaks A, B, C, D at the following binding energies: 202.3, 203.7, 205.1, and 206.5 eV, respectively. Peaks A and C, separated by 2.8 eV, are associated with the $3d^{5/2}$ and

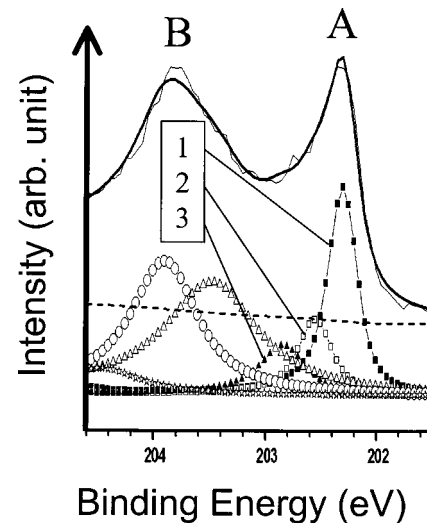


FIG. 2. Decomposition of peaks A and B due to different Nb $3d^{5/2}$ levels originating from atoms in the underlying metal and in the oxide, respectively. At least three components are required to fit the peak A.

$3d^{3/2}$ states of Nb atoms in the metal, respectively. Peaks B and D, also separated by 2.8 eV, appear shifted in energy by 1.4 eV from metal peaks. As a consequence, peaks B and D are attributed to $3d$ levels of Nb atoms in the oxide layer with a stoichiometry close to NbO since for a bulk NbO compound this shift attains 1.8 eV.^{16,19} We point out that the very low mean free path of photoelectrons with a kinetic energy equal to ~ 55 eV for 260 eV photon minimizes the contribution of photoelectrons from bulk Nb atoms.²⁵ As the resolution of our experimental setup (typically 200 meV) is similar to the one used by Strisland *et al.*,¹⁴ we expected a 180–220 meV width for the $3d^{5/2}$ level from a Nb crystal since they have a measured 180 meV width for the bulk component. As peak A exhibits a 600 meV width, we infer that several components shifted in energy are present. Several attempts to get a consistent analysis of the full set of $3d$ Nb spectra were made with an increasing number of components. In these conditions, the Nb $3d$ set is decomposed in, at least, seven couples of different Nb $3d^{5/2}$ and $3d^{3/2}$ components. Figure 2 gives the components associated with A and B peaks. We check that this analysis is valid for all the spectra obtained with 260 eV photons at 90° and 45° takeoff angles and for the spectra taken at 350 eV (90°). Focusing on the $3d^{5/2}$ level, we found that, at least, three peaks are required for fitting peak A. Binding energies and widths of these three peaks are gathered in Table I. Peak (B) originating from Nb oxides will be discussed elsewhere.²¹ In this

TABLE I. Binding energy and width of the Nb $3d^{5/2}$ levels composing peak A. This decomposition also fits several photoemission spectra taken with 260 and 350 eV photons. [Binding energies of Peak C ($3d^{3/2}$ levels) are not reported since they are deduced by a rigid shift of the binding energy from $3d^{5/2}$ levels.]

Nb $3d^{5/2}$	Peak 1	Peak 2	Peak 3
Binding energy (eV)	202.3 ± 0.1	202.5 ± 0.1	202.8 ± 0.1
Width (meV)	200 ± 20	300 ± 30	500 ± 50

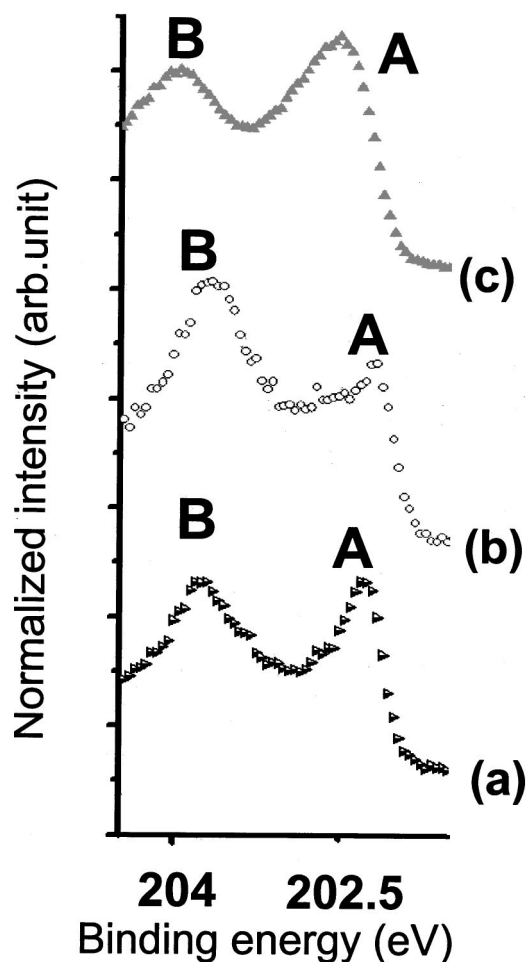


FIG. 3. Variations of the intensity of peaks A and B upon changes in the angle of collection and energy of photons. (a) Collection angle 90°, photon energy 260 eV; (b) 45°, 260 eV; (c) 90°, 350 eV.

spectra analysis, peak 1 corresponds well to the bulk Nb peak obtained by Strisland *et al.*,¹⁴ while peaks 2 and 3 are shifted by 0.2 and 0.5 eV towards higher binding energy from peak 1 and present a larger width than peak 1. On the other hand, relative variations of intensity of peaks A and B when angle θ and photon energy change, give information on the stratification of the NbO/Nb system. For example, the intensity of peak B increases upon increasing θ when compared to that of A, which demonstrates that this peak originates from Nb atoms located near the surface sample (Fig. 3). Consequently, we deduce that the oxide layer covers the metal in agreement with scanning tunneling microscopy (STM) observations.^{21,22} As the oxide layer covers the metal surface, peaks 2 and 3 cannot be related to surface core level shifts of Nb atoms as observed on clean Nb (110).¹⁴ Therefore, they originate from Nb atoms in the bulk metal. The shifts of peaks 2 and 3 when compared to peak 1 are then caused by the presence of impurities within the bulk. Taking into account the oxygen segregation, we will consider that these chemical shifts are related to the presence of oxygen in the metal as supported by both our Auger spectroscopy data²² and previous measurements.⁴⁻⁸

Several photoemission studies on bulk Nb oxides have clearly established that the 3d CLS presents a linear depen-

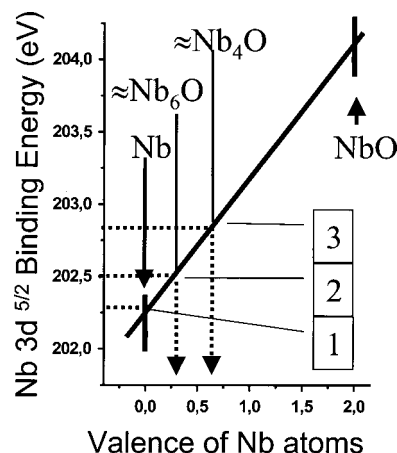


FIG. 4. Variation of the binding energy of the Nb 3d^{5/2} level as a function of the valence of Nb atoms. Valence states of Nb atoms corresponding to peaks 2 and 3 are deduced.

dence with the valence of Nb atoms.¹⁵⁻¹⁸ Using this linear variation as an abacus (Fig. 4), we deduce from the binding energies of peaks 2 and 3, the corresponding valence state of Nb atoms in the metal. Taking in account the dispersion of published studies, the deduced valence state of Nb atoms in the metal corresponds to Nb_xO compounds with $x = 7 \pm 2$ and 4 ± 1 , respectively. As oxygen atoms occupy interstitial sites in the bcc Nb lattice,²³ we infer that the shifted Nb 3d levels in peak A could correspond to Nb₆O and Nb₄O compounds associated with the octahedral and tetrahedral sites, respectively (Fig. 5). Therefore, our analysis of photoemission spectra shows that oxygen dissolved in a Nb single crystal segregates during annealing in UHV and forms a NbO-like overlayer covering a thin Nb metal layer enriched with interstitial oxygen atoms. The presence of these niobium/oxygen compounds in thick samples oxidized in air was proposed from x-ray measurements.²⁴ Recently, Nb₆O phase has also been detected in strongly oxidized thin Nb films deposited on sapphire.⁹

Furthermore, the high intensity of peaks 2 and 3 when compared to the one of peak 1 due to Nb atoms in the bulk suggests that the interstitial concentration could be high. As the metal is covered by a thin oxide film, we roughly estimate this concentration from calculations based on the relative attenuation of peaks 1, 2 and 3 when both takeoff angle θ and photon energy vary (Fig. 6). So, the intensity of photoemission signal associated with one kind of Nb atom situated in the *i*th plane from the reference, *I*, is given by the well known relation

$$I^i = I_{\text{ref}} \exp(-(d \cdot i) / \lambda \sin \theta) \tag{1}$$

with I_{ref} the intensity of photoemission signal of the reference surface, d the interplanar distance [$(d \cdot i)$ corresponds then to the depth of emitting Nb atoms from this reference], λ , the mean free path of photoelectron, and θ the angle of collection. In absence of clean Nb (110) surface, we take as a reference the interface between the oxide layer and the metal.²¹ For 260 eV photons, λ is equal to 0.4 nm as calculated from relations given by Ref. 25. For convenience, we consider that the metal contains two kinds of Nb atoms:

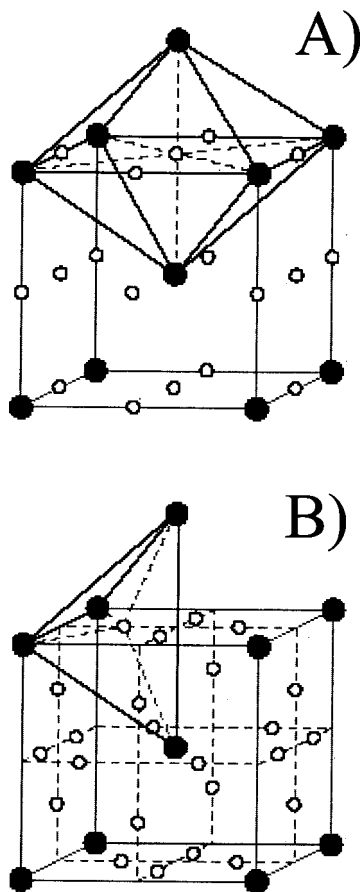


FIG. 5. Geometric models showing the octahedral (a) and tetrahedral (b) interstitial sites in bcc crystal. Empty circles are for the interstitial sites.

those close to an interstitial atom of oxygen labeled Nb_{int} , and those surrounded by Nb atoms, Nb_{Nb} . In a layer by layer description of the metal, the intensity of emission from Nb atoms located in the plane i , is given by

$$I^i = xI_{int}^i + (1-x)I_{Nb}^i. \quad (2)$$

In this equation, x is the fraction of Nb atoms influenced by an interstitial within the plane, I_{int}^i corresponds to the emission intensity of $3d$ levels of Nb atoms influenced by an interstitial in the plane i and I_{Nb}^i the one of Nb atoms with only Nb as first neighbors (Fig. 6). As the distance between neighboring (110) planes in Nb is equal to 0.258 nm, the probed Nb layers present a limited thickness ~ 1 nm because of the small value of λ . By combining relations (1) and (2) with the area of peaks 1, 2, and 3 for different angles of collection with 260 eV photons, we obtain $x = 0.5 \pm 0.1$. Considering that one interstitial atom of oxygen perturbs about five neighboring Nb atoms (mean value between Nb_6O and Nb_4O), the atomic concentration of oxygen in the metal layer near the NbO/Nb surface reaches $\sim 10\%$. We point out that this value measured in a nanometer-thick metal layer at the NbO/Nb interface is at least 200 times the oxygen concentration in bulk. Such an oxygen enrichment in the thin skin of the metal could be favored by the stress due to the misfit between the NbO (111) lattice (fcc) and Nb (110) (bcc) as illustrated by local changes in the nanostructure of the thin NbO overlayer observed by STM.²²

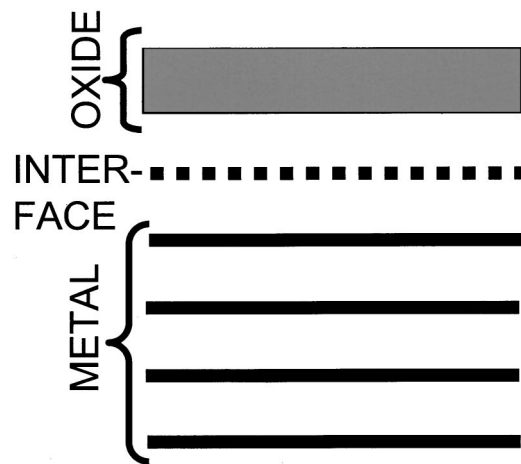


FIG. 6. Schematic model for calculation of the O concentration in the thin metallic skin below the NbO/Nb interface. The sample is formed by a stacking of Nb planes. Photoelectrons from the $3d^{5/2}$ level of Nb atoms in the metal, which present an electronic structure perturbed or not by oxygen interstitial atoms, are attenuated by the oxide overlayer (peak A). The $3d^{5/2}$ level of Nb atoms in the interface layer and in the oxide films gives the shifted peak B.

Finally, free surfaces are often considered as models for internal interfaces between grains in a polycrystalline sample. From these results, we infer that long annealing at low temperatures (~ 500 K) of Nb plates containing a few interstitial oxygen atoms provokes their segregation towards boundaries between grains and surfaces. As large amounts of oxygen can be accumulated in these defects, local modifications of many Nb properties are expected. In particular, the superconductivity/normal transition temperature, which depends drastically on the impurity concentration,²⁶ could decrease. In some cases, superconductivity could vanish out near grain boundaries in the bulk and just below the NbO/Nb interface. As a consequence, the oxygen segregation at metal surfaces and grain boundaries would degrade performances of Nb devices as Josephson junctions²⁷ or high frequency superconducting cells.²⁶

IV. CONCLUSION

In conclusion, we have presented an investigation of Nb $3d$ level shifts at the interface between niobium oxide and Nb (110) by using photoemission spectroscopy with synchrotron radiation. Analysis of these core level shifts reveals the presence of oxygen atoms located in interstitial sites in a nanometer-thick Nb layer located below the metal/oxide interface. The estimated oxygen concentration reaches 10%. The origin and some consequences of this large enrichment in interstitial oxygen atoms near the NbO/Nb interface are discussed. In particular, such a high concentration of oxygen near interfaces induced by annealing at very low temperature (about 0.2 Nb melting temperature) could explain some limited performances of devices made in polycrystalline niobium.

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