

Ordered oxygen phases in epitaxial Nb(110) layers

O. Hellwig,^{1,*} H. W. Becker,^{1,2} and H. Zabel¹

¹*Institut für Experimentalphysik/Festkörperphysik, Ruhr-Universität Bochum, D44780 Bochum, Germany*

²*Institut für Experimentalphysik/Ionenstrahlphysik, Ruhr-Universität Bochum, D44780 Bochum, Germany*

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Synchrotron x-ray diffraction studies during the atmospheric oxidation of epitaxial Nb(110) thin films at elevated temperature reveal the formation of highly ordered oxygen phases within the Nb(110) lattice. The oxygen is stored on interstitial lattice sites leading to an out-of-plane expansion of up to 4.3% without destroying the basic structure of the Nb host lattice. During a complete oxidation process of a 5000 Å Nb layer we observe the formation of a nonordered lattice gas phase succeeded by a well defined sequence of oxygen superstructures until finally the whole film is transformed into amorphous Nb₂O₅.

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Understanding the oxidation behavior of thin metal films is an important issue, not only to prevent oxidation, where it is not desired, but also to control it for tailoring specific sample designs.¹ One central goal is to influence and modify the properties of oxygen/metal compounds in order to create new materials for future applications. To this end it is important to understand the evolution of the oxidation process especially in thin films. The oxidation of Nb has been studied in the past because of its technological importance as a superconducting material^{2–4} and as a tunnel barrier in nano-electronic devices.^{5,6}

It is well known that oxygen forms a surface reconstruction on Nb(110), which has been characterized in detail by Sürgers and Löhneysen^{7,8} via low energy electron diffraction (LEED). Also the presence of oxygen in the Nb matrix as a non-ordered lattice gas is well established.^{2,3} However, ordered phases of oxygen within the Nb lattice have not been observed, in either bulk or thin film samples. Here we reveal the formation of highly ordered oxygen phases forming during the atmospheric oxidation of epitaxially grown Nb(110) films using synchrotron x-ray diffraction (XRD) techniques. We find a succession of distinct ordered oxygen structures, which modulate the Nb host lattice without destroying it.

Our earlier studies have shown that oxidation under normal atmospheric conditions at room temperature (RT) leads to the formation of an amorphous, passivating Nb₂O₅ layer with a thickness of ≈ 50 Å. Reflectivity studies reveal that the interface between the oxide and the metal film is very sharp. At elevated temperatures above 100 °C the Nb oxidation is reactivated.⁹ In contrast to the RT experiments we observe a dissolution of oxygen in the remaining Nb(110) layer as a lattice gas, leading to an uni-directional lattice expansion of up to $\Delta_{\text{max}} = 4.3\%$ in out-of-plane direction. In-plane the Nb film is pinned to the sapphire substrate with no lattice parameter change. Above a certain concentration the oxygen is ordering within the Nb matrix resulting in well defined XRD superstructure patterns. After the Nb lattice is saturated with oxygen we finally observe an unlimited growth of the amorphous Nb₂O₅ layer. In this communication we focus on the ordered oxygen phases that evolve from the random lattice gas phase with increasing oxygen concentration.

The Nb films were grown on *a*-plane sapphire substrates by molecular beam epitaxy (MBE) at 900 °C with a rate of 0.5 Å/s. Subsequent annealing of 20 min at 950 °C provides additional smoothening of the surface and the interface. *In situ* reflection high energy electron diffraction (RHEED), LEED and scanning tunneling microscopy (STM), as well as *ex situ* XRD confirm the high quality of the Nb films with a surface and interface roughness of less than 10 Å, a surface miscut of about 0.7° and a mosaicity between 0.02–0.2° depending on the Nb film thickness.¹⁰ After growth the Nb films were exposed to air to form the initial surface oxide layer. Subsequent oxidation at elevated temperatures (100–500 °C) in air leads to the formation of the ordered oxygen phases within the Nb. In order to monitor the oxidation process in detail, the films were oxidized in small time intervals and subsequently cooled to RT to stop any further oxidation during the x-ray characterization. The x-ray data were taken at the W1 beamline of the HASYLAB at DESY (Germany).

We found that Nb thicknesses of a few hundred nanometers and oxidation temperatures of ≈ 300 °C are good parameters to observe, control, and separate the ordered oxygen phases during the oxidation process. ¹H(¹⁵N, $\alpha\gamma$)¹²C nuclear resonance reaction profiling excludes the presence of any hydrogen in the Nb or Nb oxide films,¹¹ and RBS and XPS studies observe the presence of only Nb and oxygen within the system at any stage of the oxidation process.

For all investigated samples we observe the formation of a nonordered oxygen lattice gas phase as a first stage after reactivating oxidation at elevated temperature. The nonordered phase can be identified by a continuous shift of the Nb(110) Bragg reflection to lower angles reflecting a lattice expansion of up to $\Delta = 1.5\%$. In a second stage the Nb(110) reflection splits into two phases. In addition to the nonordered lattice gas phase we observe the appearance of a second phase with a fixed lattice expansion of $\Delta = 3\%$. Parallel to the splitting of the Nb Bragg reflection a characteristic superstructure pattern develops with additional Bragg reflections at $\pm 1/2$ with respect to the Nb(110) position as shown in Fig. 1. The corresponding real space structure is illustrated below the Bragg scan in a one-dimensional model, where a row of oxygen is added in between every other Nb lattice plane. This oxygen superstructure is commensurate

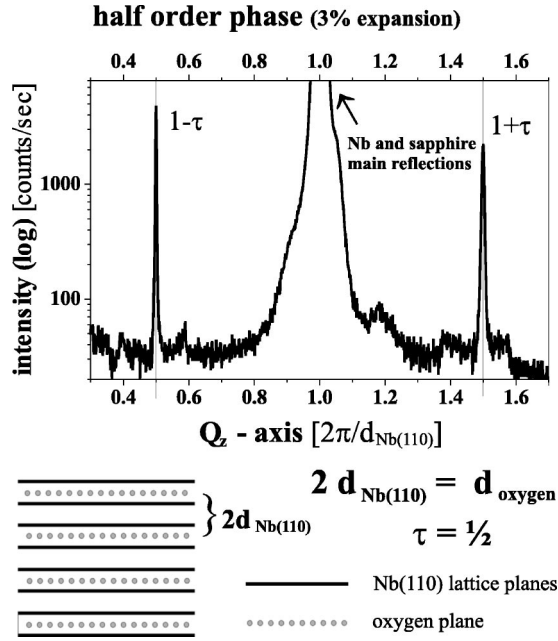


FIG. 1. Top: Bragg scan of the half order phase of a 4000 Å thick Nb layer after 5 h of oxidation at 290 °C in air. Bottom: Corresponding real space oxygen modulation in a one-dimensional model.

with the Nb lattice. The oxygen modulation period is twice as long as the Nb(110) lattice spacing and gives rise to an out-of-plane lattice expansion of $\Delta=3\%$.

Further oxidation at elevated temperature leads to a coexistence of less stable and more complex ordered phases (we will come back to those later) until a saturated state with a characteristic out-of-plane lattice expansion of $\Delta=4.3\%$ is reached. The diffraction pattern of the saturation phase is shown in Fig. 2. It consists of six different superstructure reflections, four symmetric and two asymmetric ones. The symmetric peaks appear at the positions $Q=(2\pi/d_{(110)})(0+\tau)$, $Q=(2\pi/d_{(110)})(1\pm\tau)$, and $Q=(2\pi/d_{(110)})(2-\tau)$ with $\tau=3/5$. The asymmetric peaks are closer to the Nb reflection, namely, at the positions 0.933 and 1.2 in units of $Q=2\pi/d_{(110)}$, corresponding to $\tau=-1/15$ and $\tau=+1/5$, respectively.

Starting from the half order phase, the system has to incorporate more oxygen into the Nb lattice without destroying the long range order of the oxygen up until saturation is reached. This requires a regular reduction of the separation between the oxygen planes. In the saturation phase six instead of five equally spaced oxygen planes are integrated in between ten Nb(110) lattice planes as shown in Fig. 2 below the Bragg scan. This modulation results in superstructure reflections at $\tau=3/5$, which are indeed observed as sharp peaks in Fig. 2. The exact origin and asymmetry of the two additional broader reflections closer to the Nb(110) peak are not well understood as yet. In contrast to the half order phase, the real space one-dimensional model of the saturation phase incorporates oxygen planes not only symmetrically in the center position between two Nb planes, but also in less symmetric positions close to the Nb. As a result the equilibrium position of the oxygen and also Nb planes could be

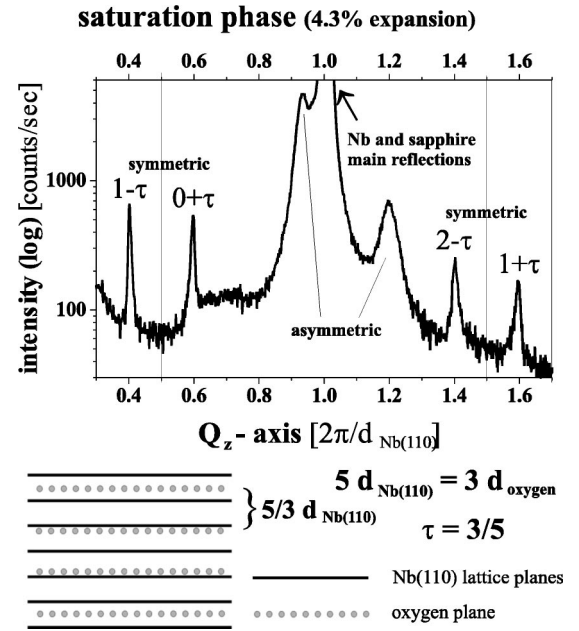


FIG. 2. Top: Bragg scan of the saturation phase of a 4000 Å thick Nb layer after 16 h of oxidation at 360 °C in air. Bottom: First approach of a simple one-dimensional real space model.

slightly disturbed. Such perturbations might lead to the additional observed asymmetric reflections.

Having reached the saturation phase, further oxidation causes no more changes of the superstructure pattern, but reduces the intensity of the saturation phase superstructure peaks. The intensity loss is due to the Nb_2O_5 growth front which steadily pushes itself forward towards the sapphire interface, thereby reducing the scattering volume of the remaining ordered oxygen structure.

Usually we observe a superposition of different ordered oxygen states due to an oxygen concentration gradient within the Nb film. The presence of each phase depends not only on the oxidation time, but also on oxidation temperature and film thickness. For some samples we could observe three separated Nb(110) reflections corresponding to the three distinct phases; the nonordered lattice-gas phase, half order phase, and saturation phase, which are present at different depth within the Nb layer due to the finite oxygen diffusion velocity. In addition, intermediate states with an oxygen spacing in between $2d_{\text{Nb}(110)}$ and $5/3d_{\text{Nb}(110)}$ have been observed. An example is shown in Fig. 3. We observe both the two half order and the six saturation phase reflections (marked by arrows). In addition we observe a continuous intensity distribution with sharp cutoffs starting at the symmetric saturation phase superstructure peaks and reaching half way to the half order reflections (these areas are dotted at the bottom scale of Fig. 3). The sharp intensity cut-offs at $\tau=\pm 3/5=12/20$ and $11/20$ indicates that at an intermediate stage all oxygen periods in between $20/11$ and $20/12d_{\text{Nb}(110)}$ are possible. Thus we obtain the following sequence of oxygen states within the Nb lattice: random oxygen lattice gas formation ($\Delta=0-1.5\%$), half order phase ($\Delta=3\%$, $\tau=1/2=10/20$), continuous phase ($\Delta=3-4.3\%$, $\tau=11/20-12/20$), and saturation phase ($\Delta=4.3\%$, $\tau=3/5=12/20$).

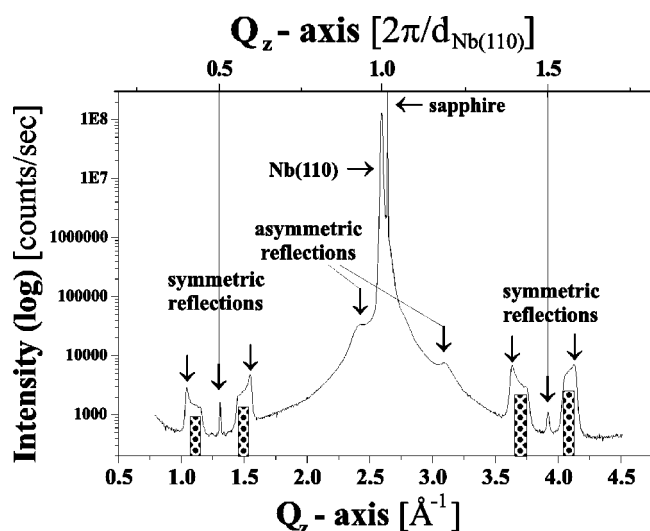


FIG. 3. Specular Bragg scan along the *out-of-plane* specular rod of a 5000 Å thick Nb film after 4 h of oxidation at 370 °C in air. Around the half order position superstructure reflections of both half order and saturation phase are visible (arrows). In addition two regions of continuous intensity with sharp cutoffs appear. They are marked by a dot pattern at the bottom scale.

Finally we want to prove that the observed lattice expansion and diffraction pattern are due to the ordering of the oxygen in the Nb(110) lattice only. Figure 4 shows 0.5° off-specular Bragg scans of a 5000 Å thick Nb film before and after different heating cycles at high temperatures. The as prepared sample exhibits only the Nb(110) reflection, while the sapphire peak intensity is faded out because of its narrow mosaicity due to off-specular scanning. After 4 h of oxidation at 370 °C, the Nb(110) reflection has shifted to the low Q side of the sapphire peak position and the characteristic superstructure pattern appears. After 6 h of oxidation the superstructure is still present. In the final step we heated the sample for 8 min at 500 °C, which leads to a complete oxidation of the remaining Nb film. With the Nb(110) reflection the complete superstructure disappears as well and only the sapphire substrate reflection remains visible. This provides evidence that the superstructure neither originates from the sapphire substrate nor from the capping Nb₂O₅ film. As a consequence the observed reflections can only be caused by the oxygen within the Nb(110) layer.

In conclusion we have shown, that the thermally reactivated oxidation process in epitaxially grown Nb(110) thin films exhibits new features compared to Nb single crystals or polycrystalline/amorphous thin films. We could identify ordered oxygen superstructures within the Nb layer. The discovery of these phases provides a new viewpoint concerning oxidation processes in thin epitaxial films. In a first stage oxygen is incorporated into the Nb lattice on random inter-

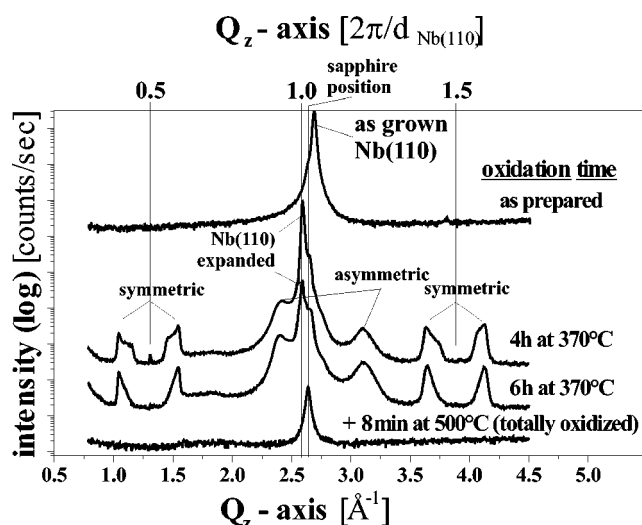


FIG. 4. Oxidation of a 5000 Å thick Nb(110) film. Off-specular Bragg scans with a 0.5° tilt (quicker scanning possible) before, during and after complete oxidation of the Nb layer. The different scans are vertically shifted with respect to each other for better comparison.

stitial lattice sites. Occupying more and more of these sites, the oxygen begins to form a characteristic sequence of systematically ordered oxygen configurations. The Nb-Nb bonds remain stable in these states and the oxygen possesses a certain mobility. At some critical oxygen concentration the Nb(110) lattice is saturated. Additional oxygen supply breaks the Nb-Nb bonds and destroys the bct(110) lattice. This is the final step of the oxidation process, resulting in the formation of amorphous Nb₂O₅. In this step the Nb-Nb interaction is being transformed from a metallic into a Nb-O ionic bound state. Additional experiments show that oxidation and subsequent UHV annealing allows one to prepare single phase materials with one selected and particular oxygen superstructure as shown in Figs. 1 and 2. These oxygen superstructures might lead to novel classes of materials with unique properties, which can be precisely tailored via their oxygen content.

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*Present address: IBM Almaden Research Center, San Jose, CA 95120. Email address: olav@us.ibm.com

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