Catalytic Oxidation of Niobium

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In situ x-ray photoelectron spectroscopy was used to study the oxidation of niobium films covered by some monolayers of cerium. Significant amounts of Nb_2O_5 are formed at pressures as low as 6.6×10^{-6} Pa, promoted by the cerium overlayer. This catalytic activity is related to the trivalent-to-tetravalent valence change of the cerium during oxidation. The kinetics of Nb_2O_5 formation beneath the oxidized cerium shows two stages; the first is fast growth limited by ion diffusion, the second is slow growth by electron tunneling.

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In recent years, there has been considerable interest in the room-temperature oxidation of polycrystalline niobium because of its application as tunnel-barrier material in superconductive Josephson junctions. The prime concern was to find direct evidence for the existence of suboxides which are thought to be the cause of large excess currents. Ultraviolet photoelectron spectroscopy[1] and x-ray photoelectron spectroscopy (XPS)[2-4] studies showed that the oxidation of niobium is characterized by an initial fast oxygen sorption, then the formation of a thin layer of NbO and NbO_2 followed by the formation of Nb_2O_5 on the surface. Sanz and Hofmann[4] determined the kinetics of Nb_2O_5 formation, which under ultrahigh-vacuum (UHV) conditions in dry oxygen followed a logarithmic growth law, attaining a thickness of 0.2 nm after an oxygen exposure of 10^4 L ($1\mathrm{L}=10^{-6}$ Torr sec). Further XPS studies showed that the air oxidation of niobium could be suppressed by the use of thin aluminum,[5] thin yttrium,[6] or Mg, Y, or Er overlayers.[7] In this work we report that, by contrast, a thin overlayer of cerium on niobium *enhances* the oxidation: For example, after only 200 L of oxygen exposure, 4.5 nm of Nb_2O_5 forms underneath the oxidized cerium and no lower oxides are detected. We believe that this is the first observation of the catalytic oxidation of a solid. In addition to the possibility of altering the quality of thin oxides, this work will bring new insight into oxidation mechanisms.

Niobium films and cerium overlayers were evaporated, oxidized at 300 K, and analyzed *in situ* with XPS. The experiments were carried out in a two-chamber UHV system. Details of the experimental setup can be found in Ref. 6. XPS was performed with Mg $K\alpha$ excitation (1253.6 eV), the direction of observation being nearly perpendicular to the surface.

First we evaporated about 25 nm of Nb; its XPS spectrum shows only the electron levels of the clean metal. A plot of the Nb $3d_{5/2}$ peak at 202.3 eV and the $3d_{3/2}$ peak at 205.1-eV binding energies is given in Fig. 1, curve *a*. After a 20-min exposure to 6.6×10^{-6} Pa of pure oxygen the Nb $3d$ levels show only the formation of a small amount of lower Nb oxides as seen in Fig. 1, curve *b*. In a first catalysis experiment, we evaporated 25 nm of Nb, and on top of it, 0.6 nm of Ce. Figure 2, curve *a*, shows the Nb $3d$ levels at this point. After an exposure to 6.6×10^{-6} Pa of pure oxygen for 20 min, a significant amount of niobium oxide was formed beneath the cerium, as shown in Fig. 2, curve *b*. The resulting oxide is characterized by a 5.1-eV chemical shift of the Nb $3d$ levels. This binding energy at 207.4 eV[8] for Nb $3d_{5/2}$ and at 210.2 eV[4] for Nb $3d_{3/2}$ is characteristic of Nb_2O_5. The thickness of the oxide, t_{ox}, can be estimated by

$$t_{\mathrm{ox}}=\lambda_{\mathrm{ox}}\sin\theta\ln\left(\frac{I_{\mathrm{ox}}n_m\lambda_m}{I_m n_{\mathrm{ox}}\lambda_{\mathrm{ox}}}+1\right), \qquad (1)$$

where λ_{ox} and λ_m are electron mean free paths, I_{ox} and I_m are integrated intensities, n_{ox} and n_m are Nb atom densities in the oxide and the metal, respectively, and θ is the detection angle from the sample plane. The electron mean free paths employed in calculating the oxide thickness were 1.4 nm for niobium, 2.4 nm for Nb_2O_5[9]; $n_m/n_{\mathrm{ox}}=2.69$. According to Eq. (1) the thickness of the Nb_2O_5 layer due to 20-min oxidation at 6.6×10^{-6} Pa is 3.5 nm. Different thicknesses of the cerium overlayer (0.5,

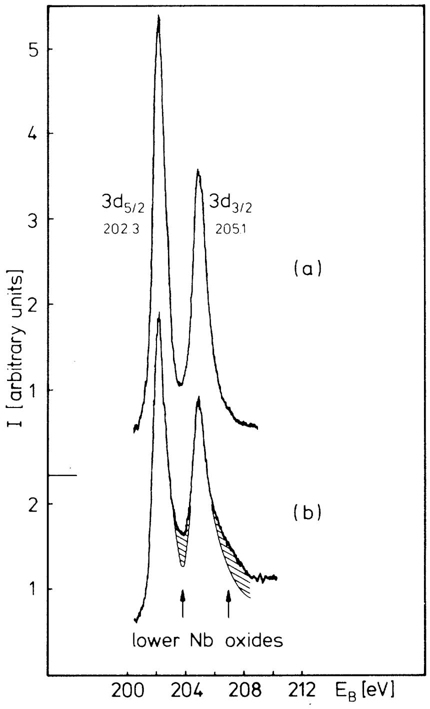

FIG. 1. XPS spectrum of (curve *a*) 25 nm of freshly evaporated niobium showing only the electron levels of the clean metal, the Nb$3d_{5/2}$ peak at 202.3-eV and the $3d_{3/2}$ peak at 205.1-eV binding energies. Curve *b*: After a 20-min exposure to 6.6×10^{-6} Pa of pure oxygen at 300 K the Nb $3d$ levels show only the formation of a small amount of lower Nb oxides.

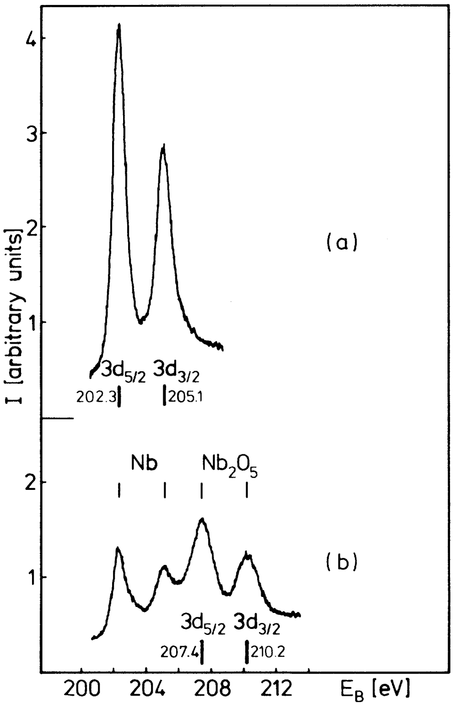

FIG. 2. XPS spectrum of 25 nm of freshly evaporated niobium covered by 0.6 nm cerium. Curve *a*: The Nb $3d$ levels before exposure to oxygen. Curve *b*: The Nb $3d$ levels after an exposure to 6.6×10^{-6} Pa of oxygen for 20 min at 300 K, showing a significant amount of Nb_2O_5 formation characterized by a 5.1-eV chemical shift of the Nb $3d$ levels.

1, and 2 nm) exposed to the same oxidation treatment produced identical amounts of Nb_2O_5. Thus we conclude that the catalytic action of cerium is independent of its thickness in the range 0.5–2 nm.

XPS[10] and core-level electron-energy-loss-spectroscopy[11] studies of the oxidation of cerium suggested the initial formation of Ce_2O_3 which, at larger exposures, was followed by the formation of a thin layer of CeO_2 on the surface. In agreement with Koel *et al.*,[12] Strasser and Netzer[11] found that only trivalent oxide is formed upon oxidation with water vapor. Because of the thinness (0.5–0.8 nm) of the cerium overlayer, in our experiments the formation of both Ce_2O_3 and CeO_2 took place at smaller oxygen exposures than in thicker films[11] or in cerium foils.[10] Figure 3 shows the Ce $4d$ levels of the overlayer as deposited and after 20-min exposure to 6.6×10^{-6} Pa (60 L) of oxygen. While the as-deposited cerium is trivalent, the Ce after oxygen exposure shows both trivalent and tetravalent species (compare Baer and Zürcher[13]). The Ce^{4+} does not disappear if the oxygen is pumped off ($p < 10^{-8}$ Pa). When we exposed 25 nm of niobium covered by 0.5 nm of cerium for 20 min to 6.6×10^{-6} Pa H_2O vapor instead of oxygen, we found no evidence of tetravalent cerium in the Ce $4d$ spectrum, and the niobium did not oxidize underneath the cerium. It seems then that the catalytic action of cerium is related to the trivalent-to-tetravalent change during surface oxidation. CeO_2 is known to have high catalytic activity in oxidation reactions, such as in the oxidation of hydrocarbons, where both the ease of the trivalent-to-tetravalent valence change and the high oxygen mobility in CeO_2 are well reflected.[14] CeO_2 is an oxygen-ion conductor, possibly more so in the amorphous than in the crystalline state.[15]

It is known that oxide films formed at low temperatures tend to be amorphous; some of these such as Nb_2O_5 form network structures, where a large oxygen ion can move more easily through the channels of the network than a tightly bound, though smaller, cation; therefore, these oxide films grow by oxygen-ion diffusion.[16]

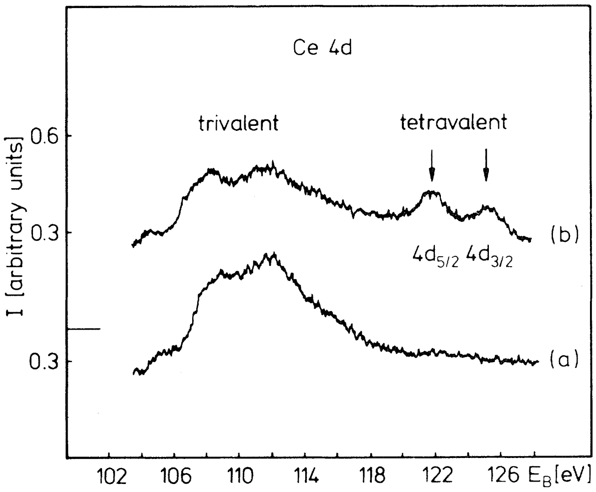

FIG. 3. Curve *a*: XPS spectrum of the cerium overlayer as deposited. Curve *b*: After 60 L of oxygen exposure; the as-deposited cerium is trivalent. The Ce after oxygen exposure shows both the trivalent and the tetravalent species.

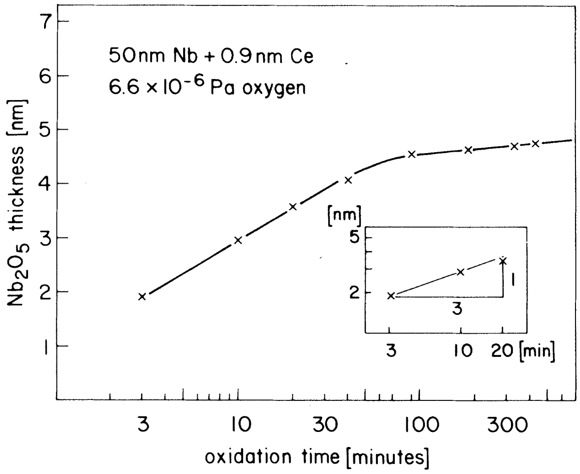

FIG. 4. The thickness of the Nb_2O_5 layer as a function of the logarithm of the oxidation time at 300 K. The diagram shows fast growth until around 4-nm thickness characterized by a $\frac{1}{3}$ slope in log-log presentation (inset) which changes to slow growth characterized by a logarithmic time dependence.

Because the Mott potential,[16] which develops upon oxidation, is larger in cerium than in niobium, cerium oxidizes more easily than niobium.[17] The oxidized cerium on the surface contains a large fraction of CeO_2 which can be reduced to Ce_2O_3 by niobium, since the heat of decomposition of Nb_2O_5 (referring to the formation of 1 mole of oxygen) is 146.8 kcal, while that of CeO_2 is only 125 kcal.[18] (Because the heat of decomposition of Ce_2O_3 is 305 kcal,[18] niobium cannot reduce Ce_2O_3.) With continuing oxygen exposure, the CeO_2 which lost oxygen to Nb will reoxidize at the surface, thereby providing oxygen ions for the further catalytic oxidation of niobium.

In a second experiment, we studied the kinetics of the catalytic oxidation of niobium at 6.6×10^{-6} Pa oxygen pressure, using a freshly deposited film of 50 nm of Nb covered by 0.9 nm of Ce. XPS spectra were taken at exposure times between 1 min and 7 h. After 1 min of exposure (3 L) the spectrum did not show Nb_2O_5 since the cerium on the surface oxidizes first. The next spectrum was taken after 3 min, representing 9 L of oxygen exposure. Here already 1.9 nm of Nb_2O_5 is formed. Figure 4 shows the thickness of the Nb_2O_5 layer [calculated by Eq. (1)] as a function of the logarithm of the oxidation time. The diagram shows two stages: an initial fast growth until around 4-nm thickness, which changes to slow growth characterized by a logarithmic time dependence. The first stage can be fitted with a cubic rate law (Fig. 4 inset).

The observed kinetics of the Nb-oxide growth can be described in general by the model of Fromhold and Cook[19] which is based on the two theories of Mott[20,21] and the theory of Cabrera and Mott.[22] According to this model, in the early phase oxide growth rate is limited by ion diffusion, in the later phase by electron tunneling through the oxide. A cubic growth law was not considered by Fromhold and Cook for ion diffusion but is included in the Cabrera-Mott theory and derived for the case when the rate of growth is determined by the concentration gradient of the diffusing ions and their number at the surface is proportional to the field created by the Mott potential.[17,22] The final logarithmic time dependence corresponds to film growth limited by electron tunneling. The transition film thickness is about 4 nm which is in agreement with the prediction of Fromhold and Cook[19] if we take the niobium-oxide barrier height to be 0.85 eV.[23] So both stages of oxide growth predicted by theory[19,20] seem to be demonstrated experimentally.

As described above, the catalytic activity of the cerium enables us to grow significant amounts of Nb_2O_5 under well-controlled UHV conditions. The thicknesses are much larger than obtained with pure niobium at atmospheric pressure after comparable exposure times. We found that one important characteristic of the cerium catalyst is its trivalent-to-tetravalent valence change during surface oxidation. We also observed catalytic activity in other rare earths exhibiting trivalent-to-tetravalent valence change, such as praseodymium and terbium, and studied the pressure dependence of the oxidation kinetics for all three (Ce, Pr, Tb). The results of this investigation will be presented elsewhere.

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