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The role of niobium oxide as a surface catalyst for hydrogen absorption

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Abstract

The catalytic activity of niobium oxide for hydrogen absorption is determined using an optical indicator technique to measure hydrogen sorption kinetics. The catalytic activity of NbO_x is studied as a function of the oxygen concentration determined from electron spectroscopy. STM measurements display a clustered NbO_x surface, disproving a diffusion-controlled kinetics. The catalytic effect results from dissociation of hydrogen by niobium oxide. The measured activation energy depends strongly on the oxygen concentration and reaches a minimum of 0.6 eV at the highest oxygen content ($x = 2.5$, i.e., Nb_2O_5). Pure Nb does not display a catalytic effect. Oxide surfaces with a high concentration of artificial oxygen vacancies are less catalytically active.

Keywords: Niobium oxide; Hydrogen absorption; Catalysis; Hydrogenography; Surface structure

1. Introduction

Limited energy resources and increasing pollution associated with classical energy production have stimulated the search for cleaner, cheaper, and more efficient energy technologies. One promising technology involves hydrogen that can be used in fuel cells stored in metal hydrides and switchable mirrors for smart window coatings [1,2]. An important feature of these systems is the hydrogen uptake kinetics. According to diffusion data, hydrogen transport inside metals or metal hydrides is sufficiently fast to provide high hydrogen absorption and desorption rates at room temperature. However, in most systems, only slow rates are observed, providing one indication (among others) that the surface properties of the metal grains determine their H sorption kinetics [3,5].

Several empirical studies demonstrate the possibility of enhancing kinetics by introducing special additives (catalysts) to the metal hydride system. Still, the exact phase of the additive, its role, and the corresponding mechanisms have remained unclear, sparking controversy about the origin of the effect. In particular, Huot et al. reported a catalytic effect of transition elements like Nb and Ta in bulk (nanocrystalline) Mg hydrides and attributed their catalytic effect to the formation of a metastable niobium (tantalum) hydride phase that acts as a gateway through which hydrogen released from MgH_2 flows [6]. Recent studies have called into question whether pure transition metals have any significant catalytic activity, however [7]. Based on studies of empirical hydrogen uptake kinetics, the catalytic effect of transition elements has been attributed to the presence of oxygen, which forms oxides with the transition metals [7]. It has also been demonstrated that among several transition metal oxides, the catalytic effect of Nb_2O_5 is superior for both hydrogen absorption and desorption [7]. Although these empirical studies demonstrate the catalytic effect of oxides, the exact role of the additive and the corresponding mechanisms remain unclear. The kind and number of active sites have to be known to improve already established additives and to also develop new catalysts at lower temperatures and for other light metal hydrides (e.g., alanates).

The present study aimed to gain a better understanding of the function of niobium oxide as a catalyst for hydrogen absorption, and to identify (and thereby exclude) possibly active species. Thus we carried out systematic absorption experiments

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for various levels of oxidation of the oxide. For this, we followed a novel indicator method [9,10]. Our thin-film approach used an yttrium indicator layer, the hydrogen uptake of which can be monitored optically. The metallic indicator layer has a high affinity for hydrogen but cannot absorb it directly, because of its nonactive oxide top layer. This thin oxide layer transports hydrogen to the optically active indicator layer once the molecular hydrogen is dissociated [3] by a catalyst (e.g., Pd clusters [11]). On this layer we deposited catalysts (NbO_x) and studied their catalytic effect as a function of composition, thickness, temperature, and hydrogen pressure. Using thin films has the advantage of allowing us to probe and modify the surface using well-established surface science techniques, such as X-ray photoelectron spectroscopy (XPS) and Ar ion bombardment. Thus we corroborated the results of Barkhordarian et al. that niobium oxide is indeed the catalytically active species [7]. In addition, we measured the activation energy and absorption rate as a function of the surface composition of NbO_x. We found that the catalytic effect correlated with the degree of surface oxidation.

2. Experiment

For these experiments, polycrystalline Y, Nb, and NbO_x were grown on glass substrates using a DC sputtering system. The argon pressure was 10^{-2} mbar, and the background pressure was $<10^{-7}$ mbar. Niobium oxide films were prepared by reactive sputtering in an Ar/O atmosphere. The partial pressure of oxygen was adjusted to obtain various oxidation states [15]. The metallic Nb films were covered with a thin oxide skin due to exposure to 10^{-2} mbar oxygen and subsequent transport through air. The yttrium films were surface-oxidized by exposing them to air for 2 min. The surface composition of the films was evaluated by XPS. The experiments were performed in a VG ESCALAB 5 photoelectron spectrometer at a base pressure $>10^{-9}$ mbar. The photoelectrons were excited by Mg-K_α radiation (1253.6 eV). The energy scale of the spectrometer was calibrated by setting the Au $4f_{7/2}$ level to 84.0 eV and the Au Fermi level to 0 eV. The experimental energy resolution was around 1 eV. To vary the amount of oxygen and to produce oxygen vacancies, the samples were bombarded with Ar ions with energy up to 3 keV using the Specs ion source IQE 11/35. Then the surface composition was checked in situ by Auger electron spectroscopy (AES). STM images were obtained with an Omicron UHV scanning probe microscope in constant current mode for the topography images and constant height mode for current imaging. The STM data were collected using an electrochemically etched tungsten tip.

The optical setup for measuring catalytic activity is described elsewhere [12]. Surface-oxidized, 130-nm-thick yttrium films were used as indicators for the H concentration, because yttrium displays large optical changes on hydrogen incorporation [2,10]. Pure yttrium and yttrium with a hydrogen concentration $x_H \leqslant 0.21$ (α-phase) are shiny metals. The dihydride YH_2 (β-phase) is also metallic, but has a weak transparency at a photon energy around 1.9 eV. YH_3 (γ-phase) is an insulator with a band gap of 2.68 eV [13]. The metal–insulator transition due to the hydrogen uptake by yttrium is optically monitored and thus indicates the catalytic activity of the corresponding cap layer. The time between the opening of the H_2 valve and the first maximum (corresponding to the infrared transparency window of the β-phase) is defined as the switching time τ of the film. The reciprocal value of τ is proportional to the hydrogen uptake rate of the yttrium film. Alternatively, recording the logarithmic change of transmission directly yields a measure of the hydrogen uptake rate. As shown previously [9], the two methods give the same results.

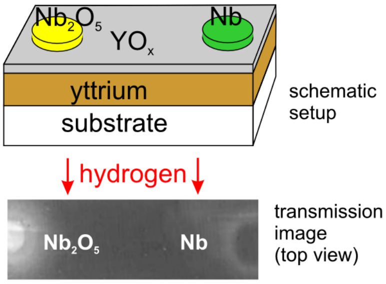

Fig. 1. The top image sketches the sample setup to evidence the catalytic effect of Nb_2O_5. The sample is exposed to 2 bar hydrogen at 250 °C for 1 h. The transmission image (bottom) of the hydrogenated sample shows transparency (bright intensity), i.e., hydrogen uptake, only under the oxide layer.

3. Results and discussion

Using the indicator technique, we probed the catalytic activity for hydrogen absorption of both NbO_x and surface-oxidized Nb in a single experiment.

Fig. 1 shows the transmission image of a surface-oxidized yttrium film capped with a spot of 5 nm Nb_2O_5 and 5 nm surface-oxidized Nb after hydrogen exposure at 2 bar and 523 K for 1 h. The indicator film under the Nb_2O_5 film contained absorbed hydrogen, evidence of a catalytic effect. The film under the thin Nb layer remained metallic; here the hydrogen uptake was strongly reduced [35]. However, the spot displayed a small halo, probably due to catalytically active Nb_2O_5 formed by a full oxidation of the metallic Nb film at the thin borders of the Nb. The observation fits perfectly well with that of Barkhordarian et al. [7], who observed enhanced hydrogen sorption kinetics of V-doped Mg after subsequent contamination with oxygen [14]. The yttrium indicator layer has a high affinity for hydrogen but is not able to absorb it directly, because of its nonactive oxide top layer (see Fig. 1; the uncovered part of the film remains black). The nonactive oxide layer transports hydrogen to the optically active indicator layer once the molecular hydrogen is dissociated [3,11]. We thus conclude that the catalytic effect resulted from dissociation of hydrogen by niobium oxide. Apart from these qualitative considerations, the method indicates the quantitative catalytic activity of the capping layer. The amount of hydrogen absorbed in the yttrium layer is 2 per yttrium atom, because we defined the switching time by the appearance of the dihydride peak [9]. Switching times of around 7500 s correspond to an averaged uptake rate of about $R = 1 \times 10^{14}\ H_2\ s^{-1}\ cm^{-2}$. At 2 bar and 525 K, the impingement rate of hydrogen is $N_{H_2} = 3.2 \times 10^{24}\ H_2\ s^{-1}\ cm^{-2}$, from which a dissociation rate of $R_D = R/N_{H_2} = 3 \times 10^{-11}$ is obtained. This small value provides another indication that the hydrogen uptake rate is dissociation-limited.

To shed light on the role of oxygen in catalytic properties, we grew NbO_x layers on yttrium films under various oxygen background pressures, resulting in various oxygen compositions of the NbO_x layer [15]. We measured the hydrogen uptake of each layer using the aforementioned indicator method and found increasing catalytic activity with increasing oxygen pressure, supporting the hypothesis that the oxide is the catalytically active species. However, making a quantitative statement is difficult because of uncertainties in the growth procedure.

To circumvent these technical problems, we grew NbO_x layers with locally varying oxygen content among the samples (i.e., gradient samples). The oxide gradient was evaluated by introducing 10^{-4} mbar oxygen through a tube toward one side of the 70-mm-long sample during Nb sputtering at an argon pressure of 10^{-2} mbar. This led to a locally higher partial oxygen pressure, resulting in an oxygen gradient of the NbO_x over the entire sample. The niobium oxide gradient layer was deposited on top of the indicator film.

The whole sample was exposed to 2 bar hydrogen, while the transmission was recorded as a function of time and position. In Fig. 2, a vertical line scan through the gray-scale image at a fixed position represents the optical transmission as a function of time at a given oxygen concentration, enabling us to study the catalytic activity of the NbO_x-layer as a function of its oxygen content by measuring the evolution of the transmission of the indicator film. The absolute uptake rate (averaged over the whole absorption process) was obtained by measuring the switching time up to the so-called dihydride peak [9], that is, the time needed to fill the whole film with two hydrogen atoms per atom of yttrium (see above). However, in first order, the logarithmic transmission $\ln T_{opt}$ of the underlying yttrium layer was proportional to hydrogen content (within the α and β phases). Thus the change in $\ln T_{opt}$ with time t was a measure of the instantaneous hydrogen uptake rate $R(t) \propto (\mathrm{d} \ln T_{opt}(t))/\mathrm{d}t$. In this paper we neglect the proportionality constant and define $R \equiv (\mathrm{d} \ln T_{opt})/\mathrm{d}t$. As shown in Fig. 2, catalytic activity immediately increased with increasing oxygen content, as measured by XPS. The temperature during hydrogen exposure increased from $T_1 = 498$ K, $T_2 = 523$ K, $T_3 = 548$ K to $T_4 = 573$ K. The corresponding values were calculated from the slopes. The response of the gradient layer $R(T)$ depended strongly on the location, as shown in Fig. 2b. The corresponding averaged rates $R(T)$ were calculated from the fitted slopes of the nearly linear uptake rates $R = \mathrm{d} \ln T_{opt}/\mathrm{d}t$ (see Figs. 2b and c) and plotted as a function of temperature in an Arrhenius plot, from which the activation energies as a function of the location were calculated. The location with the lowest activation energy was that with the highest oxygen content.

Obviously, the activation energy varied with oxygen content (location) and reached a maximum value of 1.4 eV and a minimum value of 0.6 eV (≈62 kJ/mol). The value of 62 kJ/mol is in good agreement with the results for bulk desorption measurements of Nb_2O_5 doped Mg [8], for which identical activation energy was found. This may be taken as an indication that identical phases, and thus identical mechanisms, are present despite the different experimental conditions. The uptake rates cross each other at $T = 1000/1.82\ \mathrm{K}^{-1} = 550$ K, which may be interpreted as an isokinetical point due to a compensation effect in Arrhenius parameters [18]. This could point to a change in the rate-limiting step, in agreement with the results of Barkhordarian et al. [8], who found a change of kinetics at the same temperature. But in contrast, the physical significance of a compensation effect, which is deduced from the simultaneous determination of the apparent prefactor and apparent activation energy from an Arrhenius analysis, is under discussion [19]. The reason for this is that an Arrhenius analysis is based on the assumption that only one barrier determines the kinetics, which is true only under very special conditions. As a matter of fact, this assumption is no longer valid if the rate-limiting step changes and an Arrhenius analysis becomes problematic.

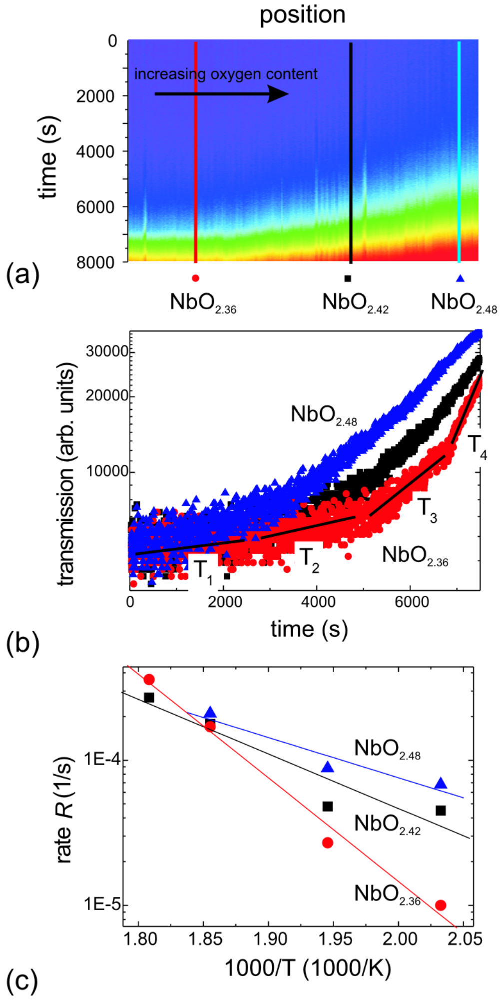

Fig. 2. (a) Transmission of a surface-oxidized yttrium sample capped with 5 nm thick niobium oxide gradient during hydrogen exposure at 2 bar, as a function of location and time. The temperature is changed during hydrogenation from $T_1 = 498$ K, $T_2 = 523$ K, $T_3 = 548$ K to $T_4 = 573$ K. Bright intensities display high transmission. Three representative linescans at fixed positions are plotted for further analysis in (b). The slopes $R(T)$ are plotted as a function of temperature in an Arrhenius plot, from which the corresponding activation energies are calculated (c).

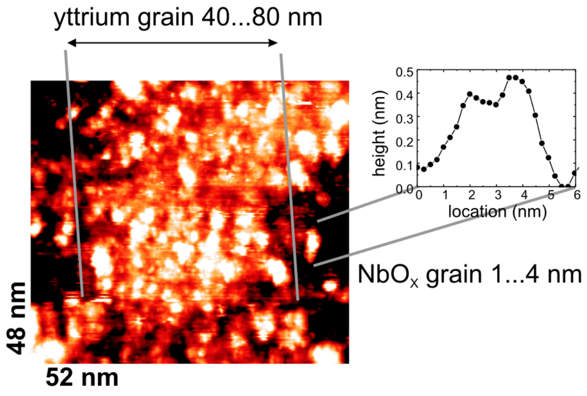

Fig. 3. Morphology of a 4 nm $NbO_{2.48}$-layer on a 130 nm thick polycrystalline yttrium film as measured by UHV-STM. Maximum height difference is 0.60 nm, bias voltage 3 V, current 0.1 nA. Small grains associated with the $NbO_{2.48}$-layer are typically 1–4 nm in diameter. The inset shows a linescan through such a grain.

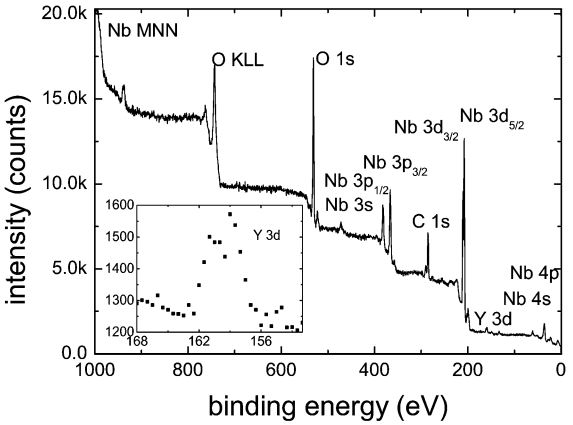

Fig. 4. XPS-measurement of 4 nm $NbO_{2.48}$-layer on a 130 nm thick polycrystalline yttrium film. The inset shows an enlargement of the Y3d peaks. The intensity ratio is $I(\mathrm{Y}3d)/I(\mathrm{Nb}3d) = 3.3 \times 10^{-2}$.

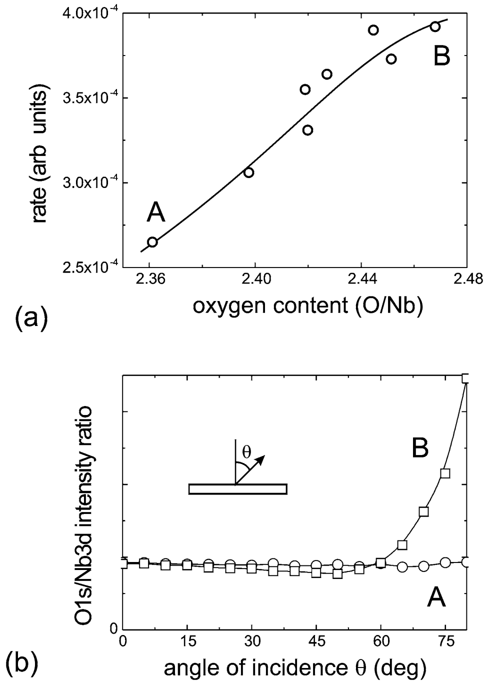

Fig. 5. (a) Hydrogen absorption rates as a function of the surface composition, measured by the O1s/Nb3d ratio of the corresponding XPS lines. (b) Normalized XPS O1s/Nb3d intensity ratio as a function of the angle of incidence for positions with lowest (A) and highest (B) oxygen concentration, also indicated in (a).

Changes in film structure can have a significant influence on hydrogen uptake rate. Because a closed oxide layer represents a relatively high diffusion barrier for H, the exact morphology of the NbO_x can influence the hydrogenation process. Therefore, we used STM to determine the morphology of the NbO_x-covered yttrium films. Fig. 3 shows a typical UHV-STM image of a 130-nm-thick Y layer covered by a 2-nm-thick $NbO_{2.48}$ layer. We found relatively large clusters covered by little islands, the latter being approximately 1.4 nm in diameter. The larger clusters were associated with yttrium grains [16]. The smaller clusters were observed only whenever NbO_x was deposited on the Y film. However, we did not observe any striking morphological changes when the oxygen content varied from $NbO_{2.36}$ to $NbO_{2.48}$. We conclude that the change in hydrogen uptake was not due to a change in morphology of the NbO_x layer. Note, however, that although the morphology as shown in Fig. 3 is not as well defined as has been reported in single-crystal model studies, it represents the typical microstructure of a realistic metal hydride storage material [17]. The presence of a clustered NbO_x-surface with a high number of grain boundaries guarantees rapid transport of hydrogen toward the yttrium via surface diffusion on clusters [3,20]. Indeed, thin NbO_x layers block interdiffusion between a Pd layer and the active metal hydride without strong reduction of the hydrogen kinetics even at room temperature [21].

This interpretation of the morphology was confirmed by XPS measurements shown in Fig. 4. All peaks were assigned to excitations of Nb and O atoms. Only a very weak Y3d peak (intensity ratio $I(\mathrm{Y}3d)/I(\mathrm{Nb}3d) = 3.3 \times 10^{-2}$) was visible, from which we conclude that we are dealing with a fully covered but polycrystalline NbO_x surface (excitation length of 1000 eV electrons $\lambda \approx 1.5$ nm [22], film thickness 2 nm). Variation of the $I(\mathrm{Y}3d)/I(\mathrm{Nb}3d)$ ratio was not observed as a function of oxygen content, only as a function of thickness. However, the experiments were performed at constant thickness, and indeed no variation of the intensity ratio was found.

For quantitative analysis of the oxygen content, we used the simplified assumption that the number of photoelectrons in a specific spectral peak n_i is proportional to the concentration C_i of the element i [22]

$$n_i = S_i \cdot C_i \quad \Rightarrow \quad C_i = \frac{n_i/S_i}{\sum_i n_i/S_i},$$

where S_i are the sensitivity factors of the element. We used the empirically derived sensitivity factors $S_{\mathrm{Nb}}^{3d_{5/2}} = 1.57$ for Nb and $S_{\mathrm{O}}^{1s} = 0.66$ for O [22]. The graph in Fig. 5a clearly shows a correlation between the hydrogen uptake rate (i.e., catalytic activity of the NbO_x-layer) and the exact stoichiometry x, and therefore quantifies the aforementioned qualitative observations. However, the deviation from stoichiometric Nb_2O_5 was rather small, whereas the uptake rate doubled within this deviation. This suggests that the catalytic activity of NbO_x was related to a peculiarity of the Nb_2O_5 surface. To prove this assumption, we performed angular resolved photoemission on the gradient sample for positions with the lowest and highest oxygen concentrations (see Fig. 5b). For high oxygen concentration, the XPS $O1s/Nb3d$ intensity ratio increased significantly with the angle of incidence, as would be expected for an oxygen terminated surface. For low oxygen concentrations, the ratio remained nearly constant. Thus, the change in total composition was due mainly to changes in the *surface termination*, whereas the underlying bulk composition remained nearly constant. From these findings, we can conclude that the catalytic activity is correlated with the amount of *surface oxygen*.

However, all of the surface oxygen atoms on Nb_2O_5 nanoparticles are not supposed to be the catalytic sites for hydrogen dissociation. Catalytic activity has been reported to originate from oxygen vacancies on transition metal oxide surfaces, that is, on oxygen-deficient surfaces. For example, it has been proven that oxygen vacancies act as active sites for water dissociation on rutile $TiO_2(110)$ [23,24]. Furthermore, hydrogen was suggested to preferably occupy surface oxygen vacancies [25]. Nonetheless, there is hard evidence that hydrogen also interacts with surface oxygen sites [26].

Because understanding the role of catalytically active oxygen vacancies is important to interpreting the hydrogen absorption process, we investigated the catalytic activity of a Nb_2O_5 layer in which various defect concentrations were implemented by Ar ion bombardment. For this, a 150-nm surface-oxidized yttrium film was covered with 5 nm Nb_2O_5 by reactive sputtering. The film was then locally bombarded with 3 keV Ar ions. Because of the similar weight, Ar ions preferably remove oxygen from the Nb_2O_5, resulting in oxygen vacancies in the film. The number and distribution of vacancies were simulated using SRIM [28]. We calculated a mean penetration depth of about 5 nm with a maximum vacancy concentration directly at the surface. To measure the defect concentration experimentally, the surface oxygen/niobium ratio was estimated by AES. Then the whole film was exposed to hydrogen and simultaneously its transmission was monitored. The Nb_2O_5 capping layer was bombarded with 3 keV Ar ions with a dose of $I_{\mathrm{Ar}} \times t = 1.2$ mC and 2.4 mC at positions A and B, respectively. A representative transmission image, shown in Fig. 6, indicates two black craters at the Ar-bombarded positions, under which the yttrium layer has not absorbed any hydrogen. These two craters correspond to Nb_2O_5 with a high defect concentration, evidenced by the lower oxygen content at these positions (see Fig. 6). Evidently, the decrease in catalytic activity does not depend on the dose (i.e., oxygen vacancy concentration). The borders have a slightly higher oxygen concentration (compare the AES measurements), probably due to scattering of oxygen atoms during Ar ion bombardment, and thus this effect scales with the Ar ion dose. Further sputtering leads to a complete removal of the NbO_x layer. This transition is relatively abrupt, indicating a sharp interface between NbO_x and Y_2O_3.

The reduction of the catalytic effect by Ar bombardment clearly demonstrates that artificially induced oxygen vacancies are not the origin of the catalytic activity of Nb_2O_5 [30].

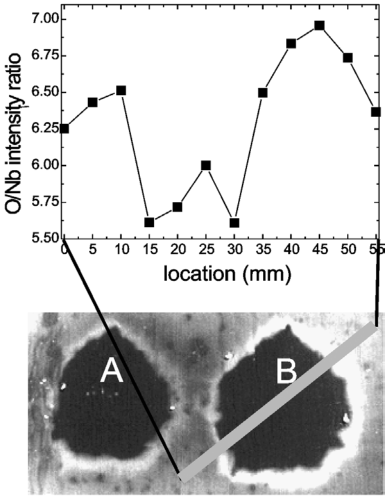

Fig. 6. Transmission image (bottom) of an yttrium film capped with 5 nm Nb_2O_5 during hydrogen exposure at 2 bar, 523 K. Bright intensities display high transmission. The top image shows the O/Nb Auger intensity ratio of the Ar-ion bombarded surface along the indicated line in region B in the transmission image.

The details of the process are beyond the scope of this paper; however, we propose that hydrogen adsorption originates from thermodynamically induced surface vacancies. At higher temperatures, the surface might be in quasi-equilibrium with the hydrogen gas creating such vacancies. The density of catalytically active sites will then be nearly independent of its as-prepared state. Accordingly, the hydrogen uptake rates do not differ at higher, which is indeed found (see Fig. 2). In such an interpretation temperatures, the state of the subsurface layers of the catalyst cannot be neglected. A relation between surface and bulk defects of sputtered NbO_x was indeed found by Ullman et al. [31], who showed that the defect structure of the outermost surface depends in a subtle way on the number of point defects in the underlying layers. Therefore, an oxide layer on top of metallic Nb is expected to behave differently than a similar oxide layer on top of Nb_2O_5. Indeed, we found that an oxygen-covered Nb film is less catalytically active than Nb_2O_5 (see Fig. 1). Another piece of evidence supporting this explanation is the thickness dependence of the catalytic effect; only Nb_2O_5 thin films of around 3 nm thickness are catalytically active. This agrees with previous observations that hydrogen is not activated on bulk Nb_2O_5 [27,33], but rather is enhanced due to interaction with the underlying oxide support.

Similar effects were found for the O_2- and H_2-adsorption on ZnO [32], which is also catalytically active for hydrogen absorption [34]. In particular, the energy for adsorption was found to depend on the kind and density of vacancies on the ZnO surface.

4. Conclusions

In this study we have investigated the mechanism of a hydrogen absorption process catalyzed by a thin niobium oxide layer. For this, we correlated the chemical and electronic structure of the catalyst with its catalytic activity. By electron spectroscopy, we found that we can produce a thin NbO_x film with lateral gradient in the surface oxygen content. Monitoring the optical properties of the underlying indicator layer on hydrogen uptake, we directly established a relation between catalytic properties of NbO_x and its oxygen content. The catalytic effect results from dissociation of hydrogen by niobium oxide. We found that the activation energies for catalytic absorption were large (≈1.4 eV) for an oxygen-deficient surface and decreased with increasing oxygen content, reaching a minimum of 0.6 eV at the highest oxygen content ($x = 2.5$; i.e., Nb_2O_5). Pure Nb did not display a catalytic effect, confirming the results of Barkhordarian [8], showing that indeed Nb_2O_5 is catalytically active in the hydrogen absorption process. STM measurements displayed a clustered but smooth NbO_x surface. The artificial creation of oxygen vacancies by Ar bombardment reduced the catalytic activity, indicating that these vacancies likely do not play a crucial role. We propose a mechanism of hydrogen adsorption via thermodynamically induced surface vacancies. At the same time, the level of subsurface layer oxidation seems to play a role. This corresponds to earlier findings that found a rather subtle relation between surface and bulk properties and their effect on the hydrogen uptake rate [29]. This study may stimulate further elucidation of the complicated hydrogen sorption mechanisms by more sophisticated surface science and bulk methods.

Acknowledgments

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