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Surface modification of Nb-films during hydrogen loading

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Abstract

In this paper we present STM images of thin epitaxial Nb-films taken in situ during H_2 gas-exposure. We find that the in-plane stresses relax by forming misfit dislocations near the substrate–film interface visible as glide steps at the film surface. The orientation of different glide steps at the surface shows that (011) and $(1\bar{2}1)$ glide planes are involved. Also, we show that the arrangement of the hydride is irregular in lateral direction and grows vertically through the complete film.

Keywords: Thin films; Scanning tunneling microscopy

1. Introduction

When niobium is loaded with hydrogen the lattice expands. In thin films this results in high stresses, since in-plane expansion is hindered by clamping of the film to the substrate [1–3]. For Nb–H compressive stresses up to -3.4 GPa are measured with an initial stress increase of about -9.7(GPa)/(H/Nb) [2,4]. Above a certain H-concentration the stress starts to relax, resulting in a reduced stress increase during further hydrogen uptake. In Ref. [3], where Gd–H was measured, various possibilities for stress relaxation were suggested based on dislocations formation. These dislocations can be in the form of loops which are emitted from hydride precipitates. At the film surface these loops are visible as small islands. Another possibility is the formation of misfit dislocations near the substrate–film interface. This mechanism leads to a glide step at the film surface. To figure out which relaxation mechanism is present in Nb–H films scanning tunneling microscope measurements are performed in situ during hydrogen loading.

When the hydride is formed the lattice expands dramatically in vertical direction. The film thickness change (Δd) can be calculated by [2]

$$\Delta d = \Delta c_{\mathrm{H}} \times 0.136 \times d_{\mathrm{film}} \quad (1)$$

whereby no in-plane expansion is allowed. In Eq. (1) d_{film} is the film thickness, Δc_{H} the hydrogen atomic fraction and 0.136 is the Nb-film expansion coefficient [5,6]. Therefore it is possible with STM to localize regions where the hydride is formed and where the film is still in the α-phase. Furthermore, the thickness increase shows if the hydride occupies the film from top to bottom. Due to this difference the topographical arrangement of the hydride in the two-phase region can be measured, which will also be illustrated in this paper.

2. Experimental

A $(11\bar{2}0)$ sapphire substrate with a miscut of less than 0.1° is used, on which Nb-films grow (110)-textured [7–9]. The films are prepared by Ar-sputtering (sputter rate: 0.6 nm/min) in an UHV-system with a base pressure better than 2×10^{-8} Pa. To see changes on an atomic scale it is necessary to work with smooth surfaces and therefore epitaxial films are prepared, by heating the substrate up to 800 °C. During heating the base pressure is increasing to about 1×10^{-5} Pa. For the sputtering process an argon pressure of 8×10^{-3} Pa is used. Partial pressures of other gases during deposition are: H_2O, 6×10^{-6} Pa; H_2, $2–7\times10^{-6}$ Pa; N_2 and CO, $2–20\times10^{-7}$ Pa; O_2, $1–30\times10^{-8}$ Pa. Films with thicknesses between 50 and 100 nm are prepared.

After preparation the film is transferred to a UHV-STM without breaking the UHV conditions. Therefore, no cap layer is necessary to protect the Nb-film, which is benefi-

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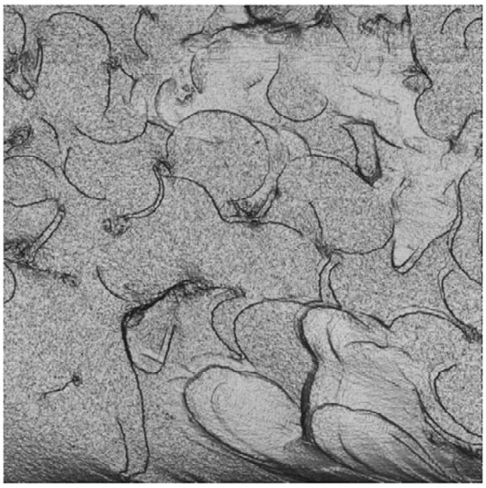

Fig. 1. The 400×400-nm^2 surface morphology of the Nb-film: monoatomic steps and terraces are visible. Shown is the derivate of the height, stressing height differences.

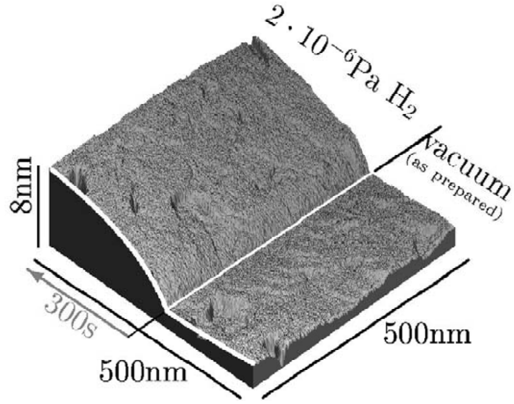

Fig. 2. Surface topography of a 100-nm Nb-film exposed to 2×10^{-6} Pa after reaching the sample middle (500×500 nm^2); when the film is exposed to hydrogen the height increases with an exponential time dependency ($1-e^{-t}$).

cial for STM-measurements since changes in the film would be hard to detect with a capping layer. For gas-phase loading a catalyst is needed. In this work small Pd islands are chosen. The amount of deposited Pd is equivalent to one monolayer.

All the STM pictures of the films shown in this paper are taken in constant current mode at room temperature. Mechanically thinned Pt/Ir tips are used, with $I_{\text{gap}}=1$ nA, $U_{\text{gap}}=0.2$ V. The scanning speed varies from 0.5 to 4.5 μm/s. Due to this relatively slow scanning speed *x*- and *y*-coordinates are also time coordinates. The time scale in the *x*-direction is about 1 s, but the time scale of the full *y*-range is between 10 and 45 min.

The surface morphology of the as-prepared film is shown in Fig. 1. The visible surface steps have a height of 0.2 nm, which is about one atomic step in ⟨110⟩ direction. The maximum height difference in Fig. 1 of the 400×400-nm^2 sized area is 2 nm, the terrace diameter is about 100 nm and the roughness on each terrace is about 0.05 nm. After this characterization Pd islands are grown on the Nb-film at room temperature. This increases the films roughness by a factor of 1.5. Hydrogen exposure is performed during STM-measurements to look at hydride formation and relaxation mechanisms.

3. Results and discussion

3.1. Height change in the α-phase

When the film is exposed to hydrogen, the height of the film increases with an exponential time dependency ($1-e^{-t}$), as shown in Fig. 2. The figure shows two interesting features: the time dependence and the magnitude of the height increase marked by the white line. The time dependence cannot be explained simply in terms of hydrogen diffusion because the diffusion time in a 100-nm thick film is less than 1 ms (diffusion in a plate [10]), assuming the hydrogen diffusion coefficient in bulk niobium [11]. An explanation can be found in the low rate of hydrogen diffusing into the film, because of the low pressure and the fact that hydrogen only dissociates at the palladium islands.

The height increase by about 6 nm is too large to be explained by mere lattice expansion, since the maximum lattice expansion expected in the α-phase, is with Eq. (1) and $c_{\alpha,\max}=6\%$, less than 1 nm. However, bending of the sample can explain the height change. When the film is loaded with H_2 high in-plane stress occurs that bends the sample [2]. By taking an in-plane stress of $\langle\sigma\rangle/c_{\mathrm{H}}=-9.7$ GPa [4], and Stoney's equation [12] a 9 nm height increase occurs in the center of the sample assuming that both ends are fixed to the holding plate. Due to this bending of samples it becomes difficult to measure by STM the height change resulting from the plain out-of-plane lattice expansion in the α-phase. Thick substrates have to be used.

3.2. Hydride formation and plastic deformation

At a pressure of 2×10^{-4} Pa a morphology change in the form of a sharp step of 6 nm occurs, as can be seen in Fig. 3. The transition occurs within 1 s. The roughness increases by a factor of 20. Also, glide steps as traces of dislocation lines are visible. Two directions of lines are favored, indicated by solid lines in Fig. 3. These two directions span an angle of 98° and result from glide planes of bcc niobium cutting the (110) surface. Possible slip planes for a bcc metal are: {110}, {112} and {123} [13]. Calculations show that slip on a (011)- and a $(1\bar{2}1)$-plane gives 100°, in good agreement with the measured angle. Then, the proper directions of the dislocation lines are $\langle1\bar{1}1\rangle$ and $\langle\bar{1}13\rangle$. Assuming a miscibility gap of $\Delta c=0.5$

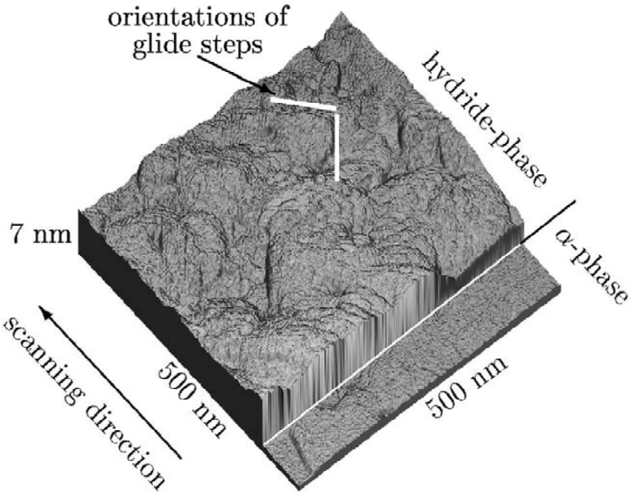

Fig. 3. Hydride formation in a 100-nm Nb-film. After 14-min exposure to 2×10^{-4} Pa sudden height increase occurs. In the hydrided region glide steps are visible, two of them are marked by white lines.

H/Nb [4] gives, with Eq. (1), a height difference of 6 nm between the α-phase film thickness and the hydride film thickness. This is in good accordance with the measured step height. Additionally, this proves that the hydride is formed through the complete film.

Fig. 4 shows a 10×10-μm^2 image of the sample after loading at 2×10^{-4} Pa H_2 for 66 min. After this exposure the Nb–H film is in the two-phase field. The local difference in height can be used to distinguish between the α-phase and the hydride. The darker regions in the figure are still in the α-phase. The hydride is located below the bright regions with a high roughness and visible glide steps. The local spreading of the hydride is irregular. Ridges as found by Nagengast et al. [14] in the case of Y–H, are not found here.

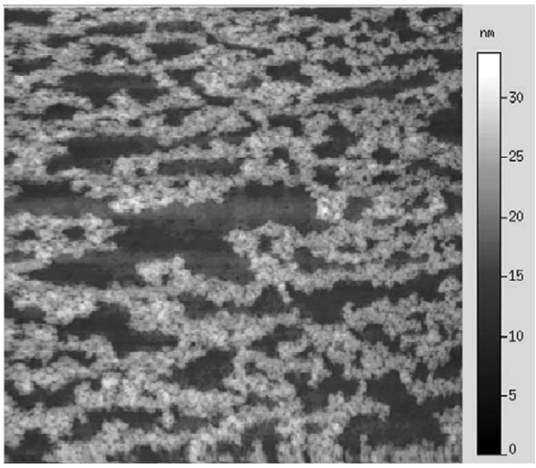

Fig. 4. A 10×10-μm^2 overview of the Nb sample after 66 min at 10^{-4} Pa hydrogen gas exposure. Hydride and α-phase co-exist: bright regions marks the hydride, dark regions the α-phase.

4. Conclusions

STM is a powerful tool to study hydrogenation of thin epitaxial niobium films at relatively low hydrogen pressures.

Hydrogen dissolution in the matrix causes high in-plane stresses and a large height increase by bending of the substrate. This increase is not only much larger than the increase due to out-of-plane lattice expansion but also depends on the measuring position. Therefore, it is difficult to study the out-of-plane expansion in the α-phase by STM, when the substrate is thin.

The transition from the α- to the hydride-phase occurs at 2×10^{-4} Pa and can be seen by a step of about 6 nm$\approx 0.5\times0.136\times d_{\mathrm{film}}$ (with a miscibility gap of $\Delta c=0.5$ H/Nb [4]), proving that the hydride forms through the complete underlying film. On the hydride surface the roughness is increased by a factor of 20 as compared to the α-phase and glide steps are visible. This transition is faster than 1 s. Analysis of glide steps found on the hydride surface shows that the system has two possible glide planes: (011) and $(1\bar{2}1)$. Apparently, stresses are only relaxed by the formation of misfit dislocations at the substrate–film interface leading to the observed glide steps. Islands that form by punching out dislocation loops as reported in [3] are not found for Nb–H. As shown in Fig. 4 the hydride-phase shows an irregular pattern with no preferred lateral direction.

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