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Thickness dependence of the hydrogen solubility in epitaxial Nb(110) films grown on Al_2O_3(11.0) substrates

A. Abromeit[a,*], R. Siebrecht[a], G. Song[a], H. Zabel[a], F. Klose[b], D. Nagengast[b], A. Weidinger[b]

[a]*Fakultät für Physik und Astronomie, Institut für Festkörperphysik Ruhr-Universität Bochum, D-44780 Bochum FRG*
[b]*Hahn–Meitner-Institut, Glienicker Strasse 100, D-14109 Berlin FRG*

Abstract

Hydrogen solubility isotherms of thin epitaxial Nb(110) films were measured via in-situ X-ray Bragg scattering. The lattice parameters were converted to H-concentrations through additional neutron reflectivity measurements on the same samples at specific points on the isotherms. The isotherms depend strongly on the film thickness, as regards the slope in the plateau region and the saturation concentration.

Keywords: Epitaxy; Thin films; X-ray scattering isotherms; Nb films

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1. Introduction

Reliable solubility isotherms for hydrogen in thin metal films are currently much needed [1,2]. On one hand the isotherms provide important information on the hydrogen–hydrogen (H–H) and hydrogen–metal (H–M) interaction parameters and the phase transitions as a function of the dimensionality of the system. In particular, we expect that the structural, elastic, and electronic boundary conditions may have an important impact on the solubility isotherms in thin films, and those need to be well defined [3,4]. On the other hand, it is not easy to obtain reliable solubility data. First, the total amount of dissolved hydrogen is rather small and difficult to determine, and second, the aforementioned boundary conditions are in some cases hard to control.

2. Experimental details

We have grown Nb films by molecular beam epitaxial methods on Al_2O_3(11.0) substrates with thicknesses ranging from $D=320$ to 5270 Å. All samples were capped with a thin Pd overlayer to enhance the catalytic dissociation of the hydrogen molecules and to protect the Nb film against oxidation. Details of the sample preparation are described elsewhere [5]. We have determined the layer thicknesses by X-ray reflectivity measurements and by Rutherford backscattering. Solubility isotherms were measured for temperatures from 423 K to 573 K and for H_2 pressures up to 1000 mbar by in-situ X-ray monitoring of the lattice expansion in the direction normal to the film plane. The conversion from lattice expansion to H-concentrations was achieved by unpolarized neutron reflectivity measurements using the V6 reflectometer at the Berlin Neutron Scattering Center.

3. Results

Fig. 1 shows two typical solubility isotherms for Nb film thicknesses $D=320$ and 780 Å and at a temperature of 473 K. The external hydrogen pressure is plotted as a function of relative lattice parameter changes, $\Delta a/a$, in the direction normal to the (110) plane. These measurements show that the solubility at small concentrations is independent of D while the lattice expansion in saturation clearly depends on D. Furthermore, the slope in the plateau region also depends on D. From fits to the isotherms, as shown by the solid lines in Fig. 1, we can conclude that in thin Nb films the H–Nb interaction is the same as in bulk, in agreement with earlier results by Steiger et al. [1], and that the H–H interaction as well as the saturation concentration strongly depend on the film thickness [5]. For instance, at $D=320$ Å the critical temperature for the α–α' phase transition is only about 275 K, far below the bulk value of 444 K [6].

In order to extract interaction energies from X-ray measurements, the relative lattice parameter changes $\Delta a/a$ need to be converted to H-concentrations $c_H=N_H/N_{Nb}$,

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[*] Corresponding author.

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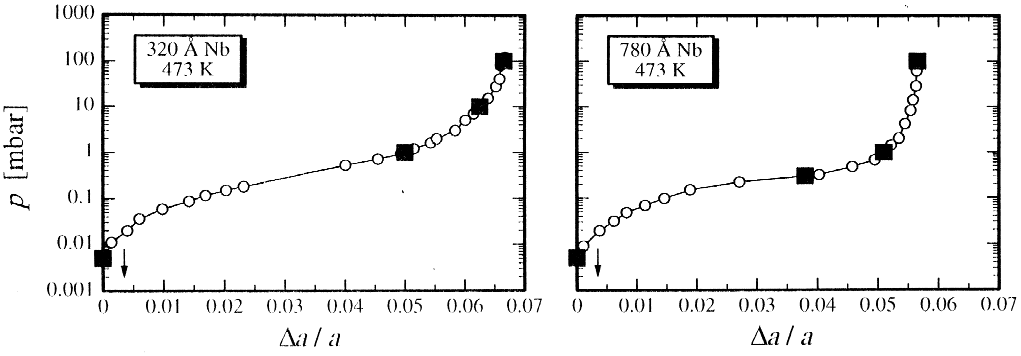

Fig. 1. X-ray in-situ measurements of solubility isotherms of a 320 Å and 780 Å thick epitaxial Nb(110) film on sapphire substrates. Solid lines show fits to the curves using a standard model for the hydrogen solubility. Solid squares mark points where also neutron reflectivity data have been taken on the same samples. The arrows in the logarithmic plot point to essential zero hydrogen concentration for the first reflectivity scan.

where N_H and N_{Nb} are the atomic number densities of hydrogen and niobium, respectively. For the bulk, the proportionality factor $f=(\Delta a/a)/c_H$ is well known (0.058) and it is a constant up to high c_H [7]. However, for thin films the case is not so clear. For small c_H often a tetragonal distortion of the lattice is observed due to the epitaxial bonding of the film to the substrate [8], which may, in addition, result in an anomalously large lattice expansion [9]. Beyond a critical concentration, $c_{c,H}$, the lattice expansion is expected to be more isotropic due to the creation of domain boundaries and dislocations.

We have now determined the hydrogen concentration by additional neutron reflectivity measurements on two of the same samples used previously for the X-ray results. Reflectivity data were taken under the same in-situ conditions as for the X-ray measurements and at several specific points along the isotherms, as indicated by solid squares in Fig. 1. For unpolarized thermal neutrons the refractive index is given by:

$$n = 1 - \frac{2\pi}{k_0^2}(N_{Nb}b_{Nb} + N_H b_H) = 1 - \frac{2\pi}{k_0^2}N_{Nb}(b_{Nb} + c_H b_h)$$

Here b_{Nb} and b_H are the coherent scattering lengths for Nb and H, respectively, and the product $N\times b$ is usually referred to as the scattering length density. k_0 is the wave number of the neutrons.Thus the refractive index depends linearly on c_H. Adding hydrogen to Nb will expand the Nb film and change the optical contrast between the film and the sapphire substrate. The latter effect is due to the rather large and negative coherent scattering length of H ($b_H=-3.739$ fm) as compared to the positive scattering length of Nb ($b_{Nb}=7.054$ fm). For instance, for hydrogen free Nb the difference of the scattering length densities between film and substrate is $\Delta(N\times b)=1.78\times10^6$ m^2 which increases to 3.85×10^6 m^2 at a hydrogen concentration of $c_H=1$. Both effects, the film expansion and the change of the optical contrast can be observed by measuring thin film oscillations as a function of the scattering vector $Q=2k_0 \sin\theta$ (θ is the angle of the incident and reflected neutron beam to the sample surface) at very small Q values close to the condition for total external reflection. The film expansion causes a shift of the thin film fringes to smaller scattering vectors while the change of the optical contrast changes the overall intensity of the specularly reflected beam.

Fig. 2 shows neutron reflectivity measurements of the 320 and 780 Å thick Nb films at different hydrogen pressures. The finite thickness oscillations at small Q are clearly visible. Their overall shape changes with increasing hydrogen concentration. However, quantitative values can only be obtained through fits to the data points. Therefore, all reflectivity curves were fitted using a modified Parratt formalism [10], taking into account thicknesses, scattering length densities, and roughnesses of the three layers in the system.

From the fits we derived the concentrations c_H as a function of $p(H_2)$. X-rays provided $\Delta a/a$ as a function of $p(H_2)$. Combining both, we obtain $\Delta a/a=f\times c_H$. The results for both films are plotted in Fig. 3. For the 320 Å thick film the expansion at small H-concentration is larger than in bulk, in agreement with earlier N^{15} measurements of the hydrogen density profile in Nb films [9], while at higher concentrations the expansion coefficient approaches the bulk value. The 780 Å thick film exhibits an expansion coefficient which is close to the bulk value. It should be mentioned that both films were already exposed to high hydrogen concentrations during the X-ray experiments, while anomalous elastic behavior is only expected for virgin samples in the small hydrogen concentration regime.

4. Discussion

There is a clear dependence of the solubility isotherms on the film thickness. The most striking feature is the much larger lattice expansion observed in saturation as compared to the bulk behavior. The neutron results confirm that the larger lattice expansion corresponds to an enhanced hydro-

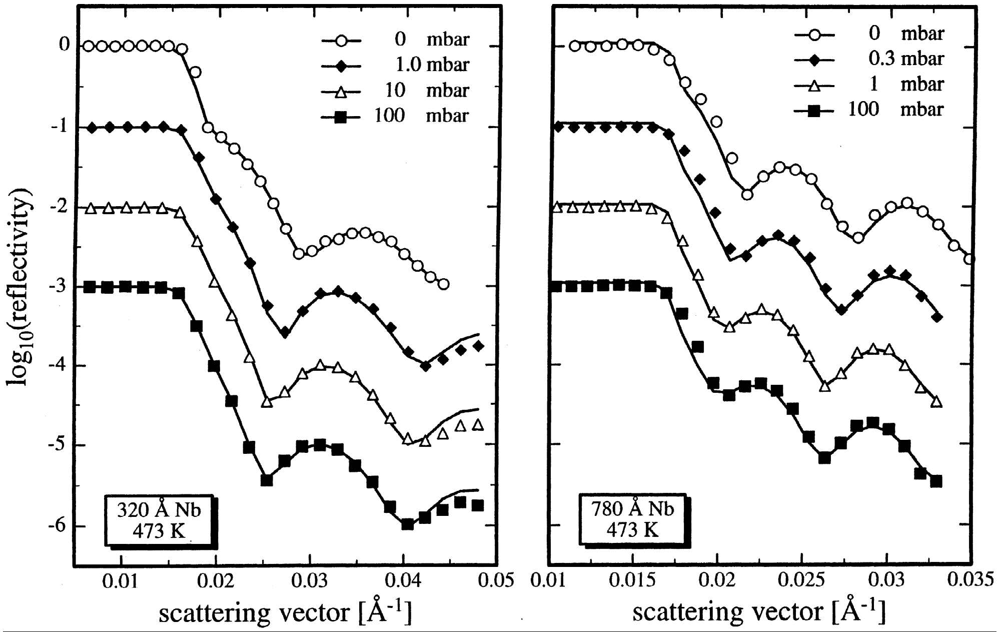

Fig. 2. Neutron reflectivities of two Nb samples with 320 Å and 780 Å thickness at fixed temperature of 437 K and different hydrogen pressures. Symbols show the data points, straight lines the fits (curves for hydrogen loaded samples are shifted for illustration).

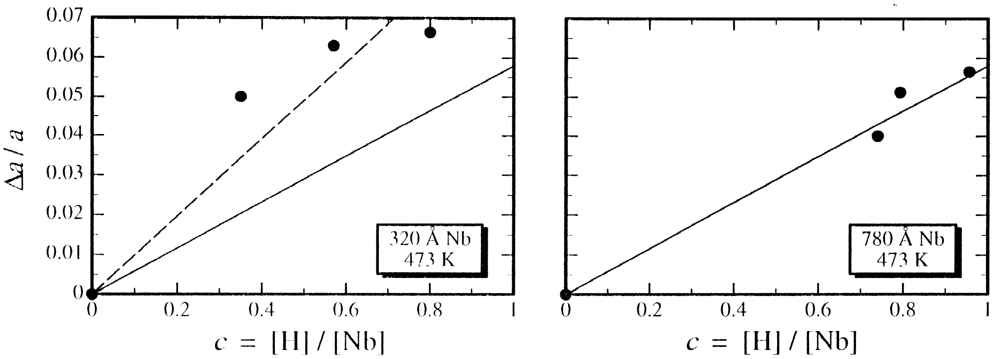

Fig. 3. Lattice expansion as a function of hydrogen concentration for the 320 Å and 780 Å thick Nb film. Solid lines show the slope of 0.058 in agreement with bulk behavior, the dashed line is a guide to the eye with a slope of 0.1.

gen concentration. Thus, thin Nb films exposed to a hydrogen gas pressure of about 1 bar can take up roughly 50% or more hydrogen than bulk samples. The enhanced saturation concentration implies a decreased mutual H–H blocking, which may be due to the elastic or electronic boundary conditions in thin films. This effect certainly requires further investigations. In spite of the large hydrogen concentration and the concomitant large lattice expansion in saturation, no loss of adhesion of the film to the substrate has been noticed. This property together with the depression of the critical temperature make Nb films on sapphire substrates attractive for thin film hydrogen getters: at high hydrogen concentrations no peeling off effects or embrittlements due to phase transitions have to be suspected.

Acknowledgments

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