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Thin Hf layers in Nb studied by the perturbed angular correlation method. II. The effect of hydrogen on the Nb-Hf-Nb samples

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Nb-Hf-Nb sandwich samples were charged electrolytically with hydrogen and investigated by the perturbed angular correlation method and the ^{15}N-profiling method. The accumulation of hydrogen in the Hf layer and hydrogen diffusion were studied.

I. INTRODUCTION

In this paper we report the results on the behavior of hydrogen in the Nb-Hf-Nb sandwich samples described in paper I.[1] Again, the measuring method is the perturbed angular correlation (PAC) technique. In addition, the ^{15}N-nuclear-reaction method was applied to obtain hydrogen-depth profiles.

The behavior of hydrogen in bulk Nb and bulk Hf is well known.[2,3] In Nb, hydrogen is highly mobile at room temperature and soluble in the α phase (statistical distribution) up to several percents. For higher concentrations, hydrogen precipitates in Nb and forms a β-phase hydride (phase separation). In Hf, hydrogen is practically insoluble in the α phase at room temperature, but it forms a very stable hafnium dihydride. Hydrogen is immobile in Hf at room temperature.

Nb-H and Hf-H were also investigated with the perturbed angular correlation method.[4,5] Thus, all parameters of the bulk systems are well known and it will be interesting to see which changes occur if the two systems are in contact. A drastic effect is expected due to the different affinities of hydrogen in Hf and Nb, which should result in an accumulation of hydrogen in Hf. However, kinematic effects at the Nb/Hf interface and the fact that the Hf layer is embedded between Nb sheets, thus preventing an unrestricted lattice expansion, should modify simple extrapolations from the bulk properties.

II. EXPERIMENTAL DETAILS

The Nb-Hf-Nb sample preparation was the same as described in paper I.[1] The hydrogen charging was done electrolytically at 80 °C with a current of 50 mA in dilute H_2SO_4 solution for 5 to 60 min. The resulting overall hydrogen concentration was determined after the measurements by vacuum extraction. Since the hydrogen uptake is strongly dependent on the surface conditions there was no clear correlation between the charging time and the final hydrogen concentration in the sample.

The treatment of the PAC spectra is described in some detail in Paper I.[1] In the hydrogen-charged samples that we describe here, we found almost no orientation dependence of the PAC spectra (see further) and therefore the standard analysis could be used. From the experimental coincidence spectra $N_{ij}(\theta,t)$ [for definitions and reference to the literature see Paper I (Ref. 1)] we formed the ratio

$$R(t)=\frac{2}{3}\left[\left(\frac{N_{13}(180°,t)N_{24}(180°,t)}{N_{14}(90°,t)N_{23}(90°,t)}\right)^{1/2}-1\right] \tag{1}$$

and the equivalent one with other detector combinations and fitted it with the theoretical function $A_{\text{eff}}G_{\text{eff}}(t)$ with

$$G_{\text{eff}}(t)=e^{-\lambda t}\left[s_0+\sum_{n=1}^{3}s_n e^{-\delta\omega_n t}\cos(\omega_n t)\right]. \tag{2}$$

In contrast to the formulas in Paper I,[1] we here included a dynamical relaxation with rate λ in the fitting function in order to account for the relaxation induced by the diffusing hydrogen.

The hydrogen depth profile was measured by the ^{15}N-nuclear-reaction method.[6] In this experiment, the γ yield of the $^{1}\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ reaction is recorded as a function of the incident ^{15}N energy. Because of the stopping power of the sample, the ^{15}N ions are slowed down while passing the sample until they reach 6.4 MeV, where the cross section of the reaction has a sharp resonance. Below and above this energy, the reaction cross section is several orders of magnitude smaller. Therefore, each incident energy corresponds to a certain depth in the sample and the γ yield is directly proportional to the hydrogen concentration at this depth.

III. EFFECTS OF HYDROGEN

A. Accumulation of hydrogen in the Hf layer

Figure 1 shows two typical PAC spectra and their Fourier transform of a Nb-Hf-Nb sandwich sample be-

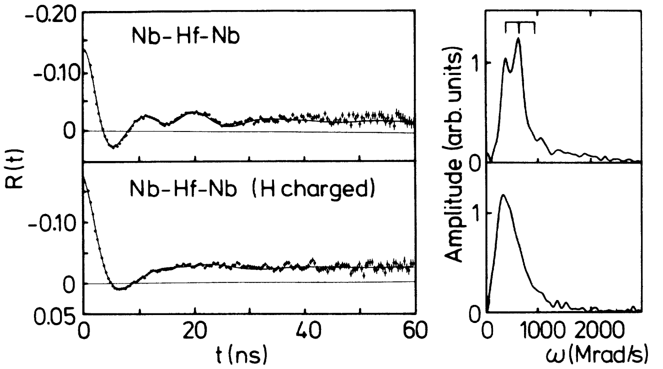

FIG. 1. PAC spectra and their Fourier transforms for a Nb-Hf-Nb sandwich sample with a Hf thickness $d = 44$ nm before and after hydrogen charging (for H concentration see Fig. 2).

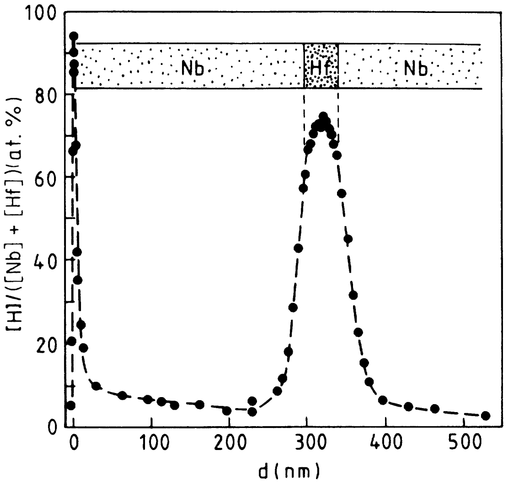

FIG. 2. Hydrogen depth profile of a Nb-Hf-Nb-layered structure as measured by the ^{15}N-nuclear-reaction method. The layer thickness measured by a quartz monitor during evaporation was 250 nm for Nb and 44 nm for Hf.

fore and after hydrogen charging. In the uncharged sample (upper spectrum) clear oscillations of the anisotropy with time are observed. These oscillations disappear if the sample is charged with hydrogen (lower spectrum). The PAC spectrum of the H-charged sample in Fig. 1 has the form observed in Ref. 5 for $HfH_{1.64}$ (mainly δ phase) indicating a high hydrogen concentration in the Hf layer. However, because of the similarity of the PAC spectra in the α and δ phases of the Hf-H system, no quantitative statement on the H concentration can be made.

The δ phase of Hf-H has a cubic structure and therefore in principle no electric-field gradient (EFG) should be seen at the probe site. However, the random distribution of hydrogen vacancies in the substoichiometric (referred to HfH_2) δ phase induces an EFG that shows up in the PAC spectra. Because of the randomness of the vacancy distribution, no strong orientation dependence is expected in accordance with the experiment.

Figure 2 shows the hydrogen profile of the same sample measured with the ^{15}N-nuclear-reaction method[6] at the Hahn-Meitner-Institute in Berlin. Besides the surface peak that is due to hydrogen containing adsorbates, a clear enhancement of hydrogen in the Hf layer can be seen. This is expected since the formation enthalpy is higher for hafnium-hydride than for niobium-hydride.[2,3]

It is noteworthy that the H concentration in the layer ([H]/[Hf] = 0.75) is far below the δ-phase concentration ([H]/[Hf] = 1.64), which would be expected to form, if the chemical potential of the Hf-H and Nb-H systems are compared. Thus, the lower concentration in the present data suggests that the strain in the embedded Hf layer prevents the unrestricted accumulation of H in Hf. More experiments on this subject are in progress.

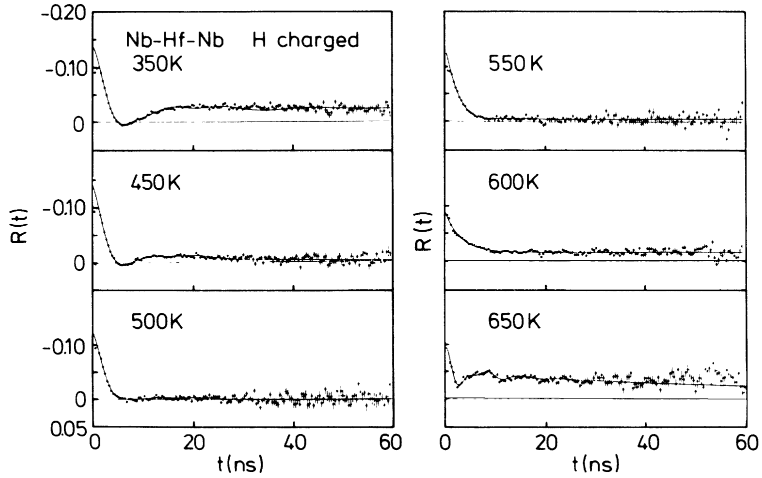

FIG. 3. PAC spectra of a hydrogen-charged Nb-Hf-Nb sandwich sample [d(Hf) = 50 nm] at different measuring temperatures ($\vartheta = 0°$, $\varphi = 45°$).

B. Hydrogen diffusion

So far only room-temperature data were presented. At higher temperatures, significant changes in the PAC spectra were observed as can be seen in Fig. 3. These changes are due to hydrogen diffusion and to oxidation of the Hf layer as will be discussed now.

The spectrum at 350 K in Fig. 3 is typical for a static interaction. The significant feature is the constant nonzero anisotropy $R(t)$ at long times, the so-called hard-core value. This part goes to zero, if dynamical effects occur. The spectrum at 450 K shows already a relaxation of the hard-core contribution and at 500 K this component has completely disappeared. Above 500 K, the decay of $R(t)$ becomes slower (see spectra at 550 and 600 K) indicating the onset of motional narrowing.

These features are attributed to the hydrogen sublattice in the Hf-H system. Below 350 K, hydrogen is immobile in Hf and the observed static quadrupole interaction is attributed to holes in the hydride structure or more generally to the neither full nor empty hydrogen shell around the probe atom. With increasing temperature, the hydrogen atoms start to diffuse, thereby producing a fluctuating electric-field gradient, which leads to a relaxation of the spin alignment of the probe atoms.

The relaxation rate λ extracted from the PAC spectra is displayed in Fig. 4 as a function of the inverse temperature $1/T$. For comparison, the data for hydrogen[4] and tritium[7] in bulk Hf are shown as dashed and dashed-dotted lines, respectively.

In the low-temperature regime ($T < 450$ K), the present data on Hf films agree well with the bulk data of Ref. 4 for the Hf-H system. The tritium results are shifted in this regime to slightly higher temperatures indicating that tritium becomes mobile at somewhat higher temperatures. The activation energy for hydrogen diffusion extracted from the present data is $E_a = 0.45 \pm 0.05$ eV, in good agreement with the values of Refs. 4 and 7.

The decrease of λ in Fig. 4 on the high-temperature side is due to motional narrowing. The present data show a behavior, which is intermediate between that seen in bulk Hf for hydrogen and tritium. However, this does not necessarily mean that the hydrogen diffusion in the Hf layer is intermediate between these two cases, since the maximum value of λ and the turnover temperature depend strongly on the interaction that has to be averaged and thus different hydrogen concentrations or other sources of the interaction may be the cause of the differences. Therefore, on the high-temperature side only the slope of λ versus $1/T$ is significant. In the present case, this slope is approximately the same as on the low-temperature side giving again an activation energy in the order of 0.45 eV.

Thus, the present data suggest that hydrogen diffusion in a 50-nm Hf layer embedded in Nb is approximately the same as in bulk Hf. However, for thinner layers deviations may occur.

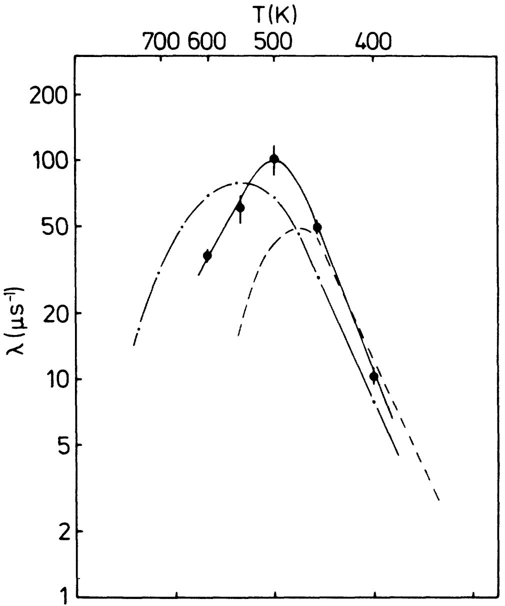

FIG. 4. The dynamic relaxation constant λ of a hydrogen-charged Nb-Hf-Nb sandwich sample [d(Hf) = 50 nm] in dependence of the inverse measuring temperature. The points with error bars are the present data; the dashed line corresponds to the data for hydrogen in bulk Hf, extracted from the publication by Damasceno *et al.* (Ref. 5) and the dashed-dotted line to the data for tritium in bulk Hf extracted from the work of Forker *et al.* (Ref. 7).

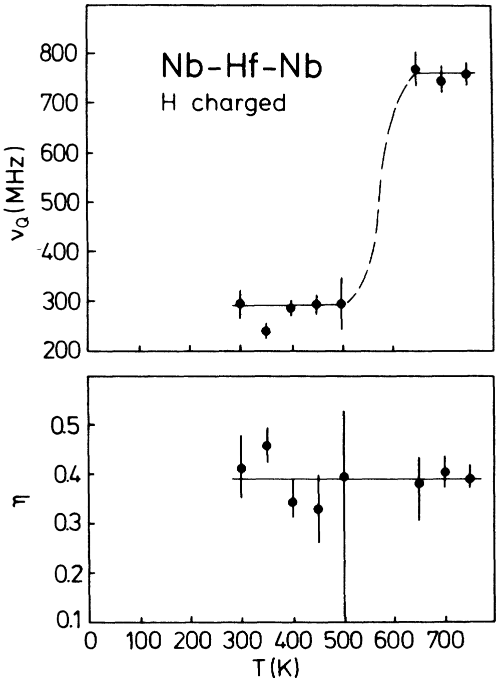

FIG. 5. The quadrupole-interaction constant ν_Q and the asymmetry parameter η of a hydrogen-charged Nb-Hf-Nb sandwich sample in dependence of the measuring temperature [d(Hf) = 50 nm]. The increase of ν_Q from 300 to 750 MHz around 600 K is due to the oxidation of the Hf layer.

Beyond 600 K, the diffusion behavior could not be studied since the Hf layer became oxidized. This can be seen on the spectrum at 650 K in Fig. 3. There, an interaction as known[8,9] for HfO_2 is observed. The damping of the oscillation indicates that the oxide is strongly disturbed. We assume that around 650 K the diffusion front of oxygen from the surface has reached the Hf layer and has formed a stable Hf oxide. The oxidation is irreversible.

Figure 5 gives the quadrupole interaction constant ν_Q and the asymmetry parameter η of a hydrogen-charged Nb-Hf-Nb sandwich sample as a function of the measuring temperature. The increase of ν_Q from 300 to 750 MHz around 600 K is due to the oxidation of the Hf layer.

IV. CONCLUSION

The expected accumulation of hydrogen in the Hf layer of a Nb-Hf-Nb sandwich sample was observed. The PAC method gives qualitative information on the hydrogen concentration in a Hf layer, but no quantitative values can be extracted since the PAC spectra of somewhat distorted Hf and hafnium hydride (δ phase) are similar. The absolute H concentration can be measured with the ^{15}N-nuclear-reaction method.

With the PAC method, dynamical effects in a buried layer can be studied. This is a unique feature of the method. In the present case the hydrogen diffusion in a Hf layer embedded in Nb was studied. We find for a 50-nm-thick layer that the diffusion is the same as in bulk Hf.

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