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Defect studies of hydrogen loaded Nb: bulk metals and thin films

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Microstructure investigations of Nb loaded with H are presented in this work. The microstructure was examined by positron annihilation spectroscopy (PAS), combined with X-ray diffraction (XRD) and transmission electron microscopy (TEM). The behaviour of H-loaded bulk samples and thin films was compared. First, the microstructure of the virgin (H-free) specimens was characterized. Subsequently, the development of the microstructure during step-by-step electrochemical H charging was studied. The investigations were performed mainly in the low H concentration region (α-phase), where the Nb-H system represents a single phase interstitial solid solution. In bulk samples it was found that new vacancy-like defects are introduced by H loading. Vacancies surrounded by H were detected also in the electron irradiated bulk samples. Nanocrystalline thin films were produced by sputtering at room temperature. They exhibit a significant volume fraction of grain boundaries with open volume defects which trap H.

1 Introduction It is known that H strongly interacts with open volume defects in a host metal lattice. For example H trapping at Cu vacancies was demonstrated already 28 years ago by PAS [1]. Recently it was shown that H is not only trapped at existing defects, but a high amount of new defects can be created by H loading [2, 3]. However, the nature of the H-induced defects and the mechanism of their creation are still not completely understood. A high sensitivity to open volume defects, sensitivity to the local electronic structure of defects and the local chemical surrounding make PAS an ideal technique for investigations of H interaction with defects. In the present work we employed PAS combined with XRD for the study of H-defect interactions in Nb with various initial defect structures.

2 Experimental Bulk Nb (99.9 %) samples were firstly annealed (1000 °C/ 1 h) to remove all defects. Some samples were subsequently irradiated with 10 MeV electrons up to fluence of 2×10^{21} m^{-2} ($T_{irr} \leq 100$ °C). Nanocrystalline Nb films with a thickness of 1.1 μm were prepared by cathode beam sputtering at room temperature on (100) Si substrates. The surface of all samples was covered with a 30 nm thick Pd cap in order to prevent oxidation and to facilitate H absorption. The samples were step-by-step loaded with H by electrochemical charging [4]. The H concentration x_H in the sample is given as the atomic ratio H/Nb in the whole paper. Defect studies were performed by positron lifetime (PL) spectroscopy using a fast-fast PL spectrometer with timing resolution of 160 ps [5], coincidence Doppler broad-

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ening (CDB), and slow positron implantation spectroscopy (SPIS) at a magnetically guided positron beam "SPONSOR" [6] with positron energy adjustable from 0.03 to 36 keV. Calculations of positron lifetimes and high momentum profiles (HMP's) were performed by the atomic superposition method (ATSUP) using 128 Nb, see [7] for details. The lattice expansion was measured by XRD on Philips Expert diffractometer using Cu-K_α radiation.

3 Results and discussion

3.1 Annealed Nb The annealed Nb can be considered as a "defect-free" material because it exhibits a single component PL spectrum with a lifetime τ_B = 128 ps, which agrees well with the calculated bulk Nb lifetime [7]. We have shown that new defects with a lifetime ≈150 ps are created by H loading in the α-phase range ($x_H < 0.06$). It was found that a H atom trapped at a vacancy is not situated directly in the vacancy, but is located on the line between the vacancy and the nearest neighbor octahedral interstitial position at the distance of about 1.2 Å away from the vacancy. There are 6 such positions (crystalographically equivalent) around a vacancy. If they are filled gradually with H, the lifetime of trapped positrons monotonically decreases from τ_v = 222 ps for H-free vacancy to 127 ps for vacancy surrounded by 6 H atoms (v-6H). The lifetime of about 150 ps observed in the experiment corresponds to a vacancy surrounded by 4 H atoms (v-4H). In the present work we performed a "loading-unloading" experiment in order to test the stability of the H-induced vacancies. The annealed sample was step-by-step H loaded, i.e. the H-induced vacancies were created. The dependence of the intensity I_2 of positrons trapped at v-4H complexes is plotted in Fig. 1 (left panel). The concentration of v-4H defects was calculated from the 2-state trapping model using the trapping coefficient $\nu = 1 \times 10^{14}$ at.s^{-1} and is plotted in Fig. 1 as well. One can see from the Figure that the concentration of v-4H defects is three orders of magnitude lower than x_H. Thus, most of H occupies the regular tetrahedral interstitial positions (T_H) in the regular lattice, while only a small fraction of H formed vacancies and is trapped in vicinity of them. The H loading leads to a lattice expansion which is seen as an increase of the lattice constant a (Fig. 1, left panel). At x_H = 0.015 the loading was stopped and the sample was subsequently electrochemically unloaded using constant voltage U = 0.8 V of opposite polarity. The lattice constant returned to that for the H-free Nb. This suggests that H in the T_H interstitial lattice positions was removed by unloading. On the other hand, I_2 and also the lifetime τ_2 = 150 ps remain unchanged during unloading. It testifies that the trapped H is not removed and the v-4H complexes are present also in the unloaded specimen.

3.2 Electron irradiated Nb Three samples are compared: irradiated bare Nb, the former sample with a Pd cap sputtered after irradiation, and Nb irradiated with Pd cap. A two component fit resulted in a defect component with a lifetime in the range of 191–184 ps, i.e. remarkably shorter than τ_v. This indicates that vacancies created by irradiation are associated with H. Namely, the irradiated samples contain a mixture of v-H and v-2H complexes. The PL results of the 3-component decomposition are shown in Table 1. Clearly the dominant defects are v-2H. Sputtering the Pd cap after sample irradiation does not change the defect structure. On the other hand, the sample irradiated with Pd cap exhibits a higher ratio of v-2H to v-H complexes, i.e. it contains more H. This is most probably due to the catalytic effect of Pd which facilitates dissociation of H_2 molecule on the surface [4]. The presence of H attached to vacancies can be at least qualitatively proved by CDB. Figure 2 (left panel) shows calculated HMP ratio curves for Nb vacancy surrounded by H atoms. Before the discussion about these profiles, it should be mentioned that the calculated HMP profiles do not contain the contribution from the valence electrons and a comparison with the experiment is meaningful only for momenta higher than about of 8×10^{-3} m_0c, i.e. the region shown by a hatched mark in Fig. 2. One can see in the Figure that the presence of H attached to a vacancy leads to the appearance of a peak like feature centered at 15×10^{-3} m_0c in the ratio curve. This contribution increases with an increase of the number of H atoms surrounding the vacancy. Indeed, the experimental HMP ratio curves measured by CDB on the irradiated samples exhibit a peak at 15×10^{-3} m_0c, which is higher for the sample irradiated with Pd cap, i.e. containing more H (see Fig. 2 right panel).

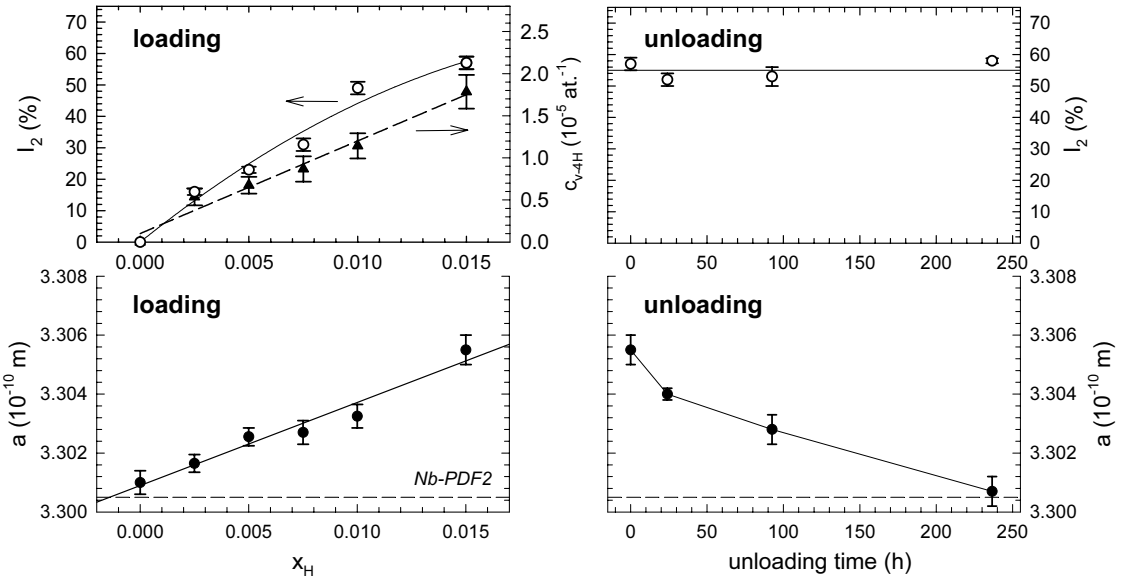

Fig. 1 The H "loading-unloading" experiment. Left panels: loading – the intensity I_2 of trapped positrons (open circles), the concentration $c_{v\text{-}4H}$ of H-induced v-4H complexes (full triangles), and the lattice constant a (full circles) as a function of H concentration x_H. Right panels: unloading – intensity I_2 of trapped positrons (open circles), the lattice constant a (full circles) as a function of the unloading time.

Table 1 Positron lifetimes τ_i and relative intensities I_i resolved in PL spectra of irradiated Nb samples. The lifetime τ_2 and τ_3 were fixed at 182 ps (v-2H) and 204 ps (v-H), respectively. The concentration of v-2H and v-H complexes calculated from the 3-state trapping model are shown in the last two columns. The errors given in parentheses correspond to the last digit.

Sample	τ_1 (ps)	I_1 (%)	τ_2 (ps)	I_2 (%)	τ_3 (ps)	I_3 (%)	$c_{v\text{-}2H}$ (10^{-5} at.$^{-1}$)	$c_{v\text{-}H}$ (10^{-5} at.$^{-1}$)
Nb bare irrad.	43(8)	14(2)	182 Fix	61(2)	204 Fix	25(3)	10.7(5)	4.9(5)
Nb bare irrad. + Pd cap after irrad.	44(9)	14(2)	182 Fix	57(2)	204 Fix	29(4)	10.2(5)	5.3(5)
Nb irrad. with Pd cap	48(5)	15(2)	182 Fix	74(1)	204 Fix	11(3)	12.0(7)	1.8(5)

3.3 Nanocrystalline Nb films The $S(E)$ curves for the H loaded Nb film are plotted in Fig. 3 (left panel). The local minimum at ≈1 keV is due to positron annihilations inside the Pd cap. In the interval 4-22 keV virtually all positrons annihilate inside the Nb layer and S remains approximately constant. Eventually, at high energies $E > 22$ keV some positrons penetrate into the Si substrate which leads to a further increase of S. The TEM investigations show that the film exhibits elongated column-like grains, typically around 50 nm in width. Nanocrystalline grain size leads to a high volume fraction of grain boundaries (GB's). Thus, virtually all positrons diffuse to GB's and are trapped at open volume defects there. It is demonstrated by a high value of S for the H-free sample. The open volume defects at GB's represent trapping sites also for H atoms. Trapping of H in the open volume defects at GB's causes a strong decrease of the S parameter for the Nb layer, S_{Nb}, in the H-loaded films (see Fig. 3, right panel). Above $x_H = 0.02$, S_{Nb} reaches a plateau value suggesting that all the available open-volume traps at GB's are already filled and the local concentration of H in the vicinity of the defects reaches a steady state value.

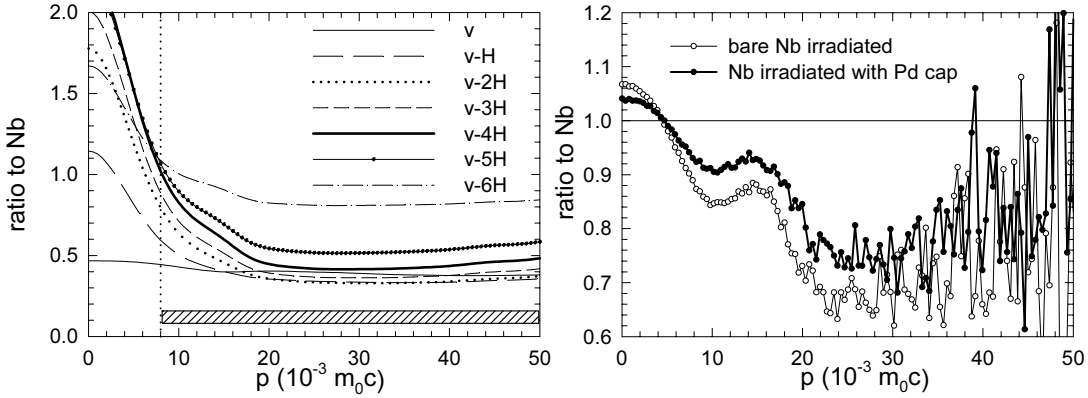

Fig. 2 Left panel: the calculated HMP ratio curves for bare Nb vacancy (v) and Nb vacancy surrounded by *n* H atoms (v-*n*H); Right panel: the experimental HMP ratio curves for the electron irradiated Nb.

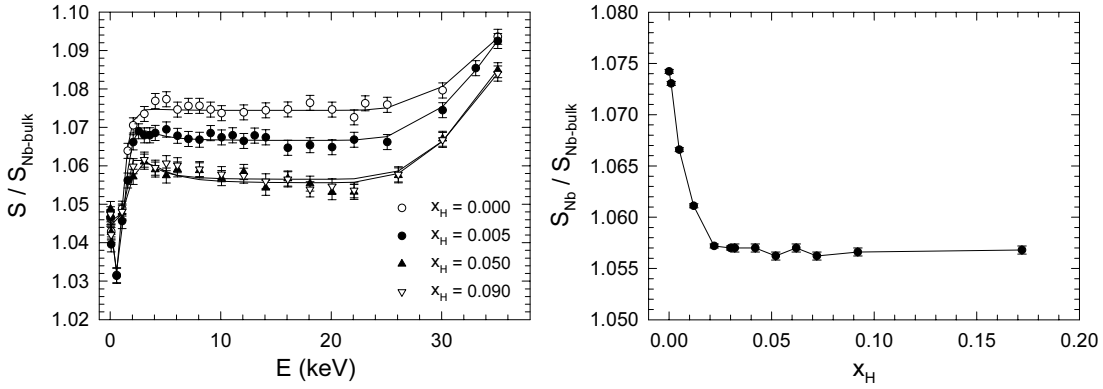

Fig. 3 Left panel: selected *S(E)* curves for the virgin film and the film loaded to various concentrations of H; Right panel: dependence of the *S* parameter for Nb layer obtained from fit of the *S(E)* curves, on x_H.

4 Conclusions We showed that H-induced v-4H complexes are stable and cannot be removed by electrochemical unloading, while the H which occupies the regular tetrahedral interstitial sites was removed. The v-2H and v-H complexes are created in electron irradiated Nb. We demonstrated that H attached to vacancy can be detected by CDB. The SPIS studies of nanocrystalline thin Nb films revealed that H is trapped at open-volume defects at GB's which is seen by a strong decrease of the *S* parameter.

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