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

J. Čížek*,1, I. Procházka1, S. Daniš1, O. Melikhova1, M. Vlach1, N. Žaludová1, G. Brauer2, W. Anwand2, A. Mücklich2, R. Gemma3, E. Nikitin3, R. Kirchheim3, and A. Pundt3

1 Faculty of Mathematics and Physics, Charles University in Prague, V. Holešovičkách 2, 180 00 Praha 8, Czech Republic
2 Institut für Ionenstrahlphysik und Materialforschung, Forschungszentrum Rossendorf, Postfach 510119, 01314 Dresden, Germany
3 Institut für Materialphysik, Universität Göttingen, Friedrich-Hund-Platz 1, 37077 Göttingen, Germany

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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.

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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 ≤ 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-
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$_\alpha$ 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 $\tau_B = 128$ ps, which agrees well with the calculated bulk Nb lifetime [7]. We have shown that new defects with a lifetime $\approx 150$ ps are created by H loading in the $\alpha$-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 (crystallographically equivalent) around a vacancy. If they are filled gradually with H, the lifetime of trapped positrons monotonically decreases from $\tau_v = 222$ 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 $\tau_2 = 150$ 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 $\tau_v$. 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 $8 \times 10^{-3}$ m$\cdot$c, 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 $15 \times 10^{-3}$ m$\cdot$c 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 $15 \times 10^{-3}$ m$\cdot$c, 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 \( c_{v-4H} \) 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 \( \tau \) and relative intensities \( I \) resolved in PL spectra of irradiated Nb samples. The lifetime \( \tau_2 \) and \( \tau_3 \) 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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \tau_1 ) (ps)</th>
<th>( I_1 ) (%)</th>
<th>( \tau_2 ) (ps)</th>
<th>( I_2 ) (%)</th>
<th>( \tau_3 ) (ps)</th>
<th>( I_3 ) (%)</th>
<th>( c_{v-2H} ) ( \times 10^{-5} ) at.(^{-1} )</th>
<th>( c_{v-H} ) ( \times 10^{-5} ) at.(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb bare irrad.</td>
<td>43(8)</td>
<td>14(2)</td>
<td>182 Fix</td>
<td>61(2)</td>
<td>204 Fix</td>
<td>25(3)</td>
<td>10.7(5)</td>
<td>4.9(5)</td>
</tr>
<tr>
<td>Nb bare irrad. + Pd cap after irrad.</td>
<td>44(9)</td>
<td>14(2)</td>
<td>182 Fix</td>
<td>57(2)</td>
<td>204 Fix</td>
<td>29(4)</td>
<td>10.2(5)</td>
<td>5.3(5)</td>
</tr>
<tr>
<td>Nb irrad. with Pd cap</td>
<td>48(5)</td>
<td>15(2)</td>
<td>182 Fix</td>
<td>74(1)</td>
<td>204 Fix</td>
<td>11(3)</td>
<td>12.0(7)</td>
<td>1.8(5)</td>
</tr>
</tbody>
</table>

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 \( \approx 1 \) 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, \( S_{\text{HB}} \), in the H-loaded films (see Fig. 3, right panel). Above \( x_H = 0.02 \), \( S_{\text{HB}} \) 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.
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 SPIIS 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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