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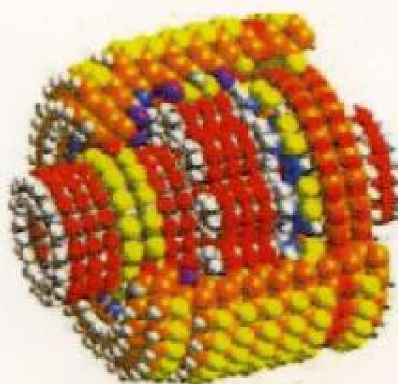

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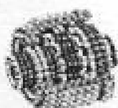

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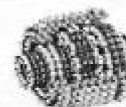

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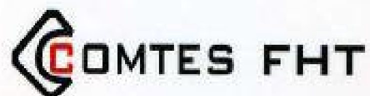

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Hydrogen Trapping at Defects in Nanocrystalline Nb Films

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Abstract. H interaction with defects in thin nanocrystalline Nb films was investigated in this work. Thin Nb films were prepared by the cold cathode beam sputtering. First, microstructure of the as deposited films was characterized. Subsequently, the films were step-by-step electrochemically charged with H. Development of microstructure and evolution of defect structure with increasing H concentration was studied by slow positron implantation spectroscopy combined with X-ray diffraction. It was found that H is trapped at open volume defects at grain interfaces. The nanocrystalline films exhibits significantly extended H solubility in the α-phase. Formation of the β-phase (Nb-H) at higher H concentrations leads to introduction of new defects most probably dislocation loops that are emitted by growing hydride-phase particles.

Introduction

The behaviour of H in a host metal lattice can be significantly influenced by interaction with lattice defects [1]. Defect studies of H-loaded samples are, therefore, highly important for an understanding of H behaviour in metals. Positron annihilation spectroscopy (PAS) is a well-developed non-destructive technique with a high sensitivity to open-volume defects [2] and represents an ideal tool for the investigations of H-defect interactions. The aim of the present work is to investigate micro structural changes in H-loaded thin Nb films. Defect studies of the films were performed by slow positron implantation spectroscopy (SPIS) with measurement of Doppler broadening (DB) of the annihilation line. The H-induced lattice expansion was detected by X-ray diffraction (XRD). The results of these techniques were combined with direct observations of the microstructure by transmission electron microscopy (TEM).

Experimental

Thin Nb films were prepared in an UHV chamber by the cold cathode beam sputtering at room temperature on polished (100) Si substrates. The surface of all samples was covered with a 20 nm thick Pd cap in order to prevent oxidation and to facilitate H absorption. The film thickness of (1120 ± 20) nm was determined by profilometry and by TEM. The samples were step-by-step loaded with H by electrochemical charging, see Ref. [1] for details. Defect studies were performed on a magnetically guided positron beam "SPONSOR" [3] with positron energy adjustable from 0.03 to 36 keV. The energy spectra of the annihilation γ-rays were measured by a Ge detector with an

energy resolution of (1.09 ± 0.01) keV at 511 keV. The DB of the annihilation peak was quantified using the S parameter [2] (i.e. the central area of the peak divided by the net peak area) which is a measure of the fraction of positrons annihilating with low momentum electrons. The H -induced lattice expansion was measured in the out-of -plane direction by XRD at Hasylab (DESY) using synchrotron radiation with the wavelength λ = 1.12 Å. The TEM studies were performed with a Philips CM300SuperTWIN microscope operating at 300 kV. Thin foils for cross sectional TEM were produced by conventional preparation using Gatan precision ion polishing system (PIPS).

Results and Discussion

The TEM observations of the virgin films revealed “column-like” elongated grains (width ≈ 50 nm). In the film’s cross-section the columns are divided horizontally into two “generations” of sub-columns with a height being approximately the half of the film thickness [4]. The “first generation” sub-columns are situated close to the Si substrate, while the “second generation” sub-columns grow on the top of the “first generation”. The nanocrystalline films exhibit a strong (110) texture, i.e. most grains are oriented so that the {110} planes are parallel with the substrate. On the other hand, the lateral orientation of the grains in the substrate plane is completely random. The diffraction profile of the (110) Nb reflection measured on the nanocrystalline virgin film is plotted in Fig. 1a. The asymmetric shape of the profile indicates that it is a superposition of two contributions from the Nb layer with slightly different inter-planar spacing; see Ref. [4] for details. Taking into account the TEM observations, it indicates that the inter-planar spacing, d_{110}, of the {110} planes in the “first generation” and in the “second generation” sub-columns differs. It should be mentioned that the corresponding inter-planar spacing in bulk Nb is d_{110} = 2.3338 Å [5] (the dashed line in Fig. 1a). Thus, it is clear that the d_{110} – lattice spacing in both generations of the sub-columns are significantly larger than in bulk Nb. Moreover, we have found that d_{110} decreases with increasing tilting angle Ψ. Such experimental findings can be explained by compressive stresses in the in-plane direction caused by bonding to the Si substrate. The “first generation” sub-columns are subjected to the highest compressive in-plane stresses because they are attached directly to the Si substrate. The magnitude of the compressive stress decreases with the distance from the interface with substrate. Thus, the “second generation” sub-columns situated on the top of the “first generation” exhibit more relaxed structure because they feel smaller in-plane stresses.

The lattice expansion for the nanocrystalline film is plotted in Fig. 1b as a function of H concentration, x_H. One can see that the lattice constant exhibits approximately linear increase with x_H in the α-phase field. When the hydride-phase (Nb-H) is formed additional peaks corresponding to its orthorhombic structure appear in the XRD spectra. The positions of the phase boundaries are shown by dashed lines. The nanocrystalline film exhibits roughly four times higher H solubility in the α-phase than bulk Nb. The extended H solubility is likely due to the nanocrystalline grain size. It leads to a significant volume fraction of grain boundaries (GBs) which can accumulate more H atoms.

The dependence of the S parameter on the positron energy E for the virgin nanocrystalline film is plotted in Fig. 2a. The S parameter was normalized to that for defect-free bulk Nb. A drop of the S parameter at low energies is due to positron annihilations inside the Pd cap. The increasing fraction of positrons annihilating inside the Nb layer is reflected by an increase of the S parameter starting from E ≈ 1 keV. In the interval from 4 to 22 keV virtually all positrons annihilate inside the Nb layer. Eventually, at high energies E > 22 keV some positrons penetrate into the substrate which leads to a further change of the S parameter. One can see that the S parameter for the Nb layer is significantly larger than 1. This indicates that the Nb layer contains a high density of defects. The

nanocrystalline film exhibits a significant volume fraction of GBs with vacancy-like open-volume defects. As a consequence almost all positrons are trapped in these defects at GBs. The selected S(E) curves for H-loaded films are plotted in Fig. 2a as well. The dependence of the S parameter on x_H in the Nb layer, as it is obtained from fits of the S(E) curves by VEPFIT software package [6] is plotted in Fig. 2b. One can see that the S parameter for the Nb layer is lowered in the films loaded at low H concentrations. The behaviour of the S parameter indicates that similarly to positrons also H is trapped at the open-volume defects. The presence of H bound to such a defect causes an increase of the local electron density, which leads to a decrease of positron localization and, thereby, to a decrease of the S parameter. At higher H concentrations ($x_H > 0.02$), the S parameter reaches a plateau value suggesting that all the available open-volume traps are already filled with H and the local H-concentration in the vicinity of defects reaches a steady state value.

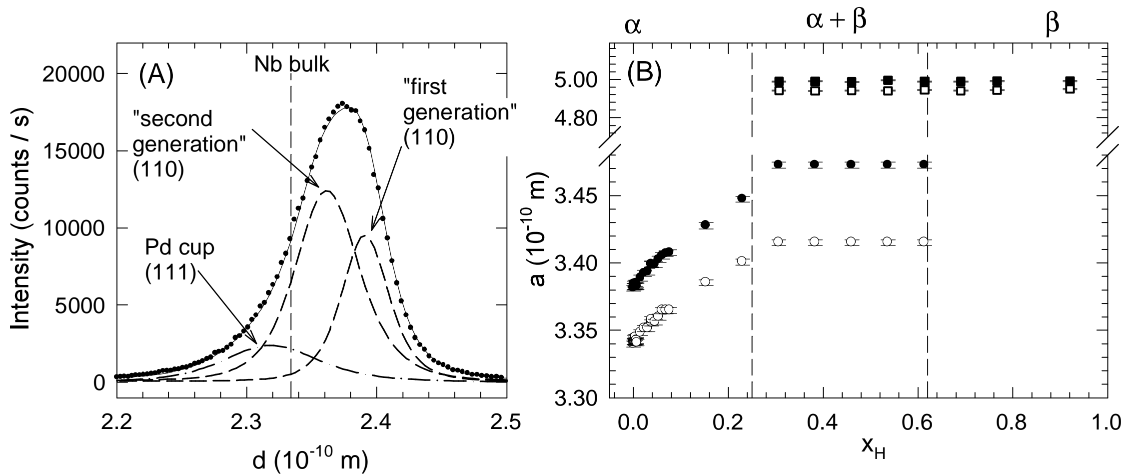

Figure 1 (A) XRD diffraction profile for the virgin film. Fit of the experimental points is plotted by the solid line, while the dashed curves show the individual reflections which contribute to the profile. The distance between the {110} planes in bulk Nb is indicated by the dashed vertical line. (B) The dependence of the lattice constant a on H concentration x_H. The α-phase, "first generation" (full circles), the α-phase, "second generation" (open circles), the β-phase, "first generation" (full squares), β-phase, "second generation" (open squares).

The formation of β-phase particles occurs at x_H larger than 0.25. It is known that dislocation loops may be emitted by growing hydride particles. In addition, positrons can be trapped at misfit defects at the interface between a hydride-phase precipitate and the matrix. Indeed, as one can see in Fig. 2b, the S parameter exhibits an increase when the β-phase precipitates. Thus, we can conclude that the formation of the hydride-phase particles leads to an introduction of new open-volume defects.

Conclusions

In the present work we performed defect studies of H-loaded nanocrystalline Nb films with a thickness of 1.1 μm. The films exhibit a high density of defects already in the virgin state. Most of positrons in the nanocrystalline film annihilates from the trapped state at open-volume defects at GBs. It was found that the H solubility in the α-phase in the nanocrystalline filmsis four times larger than in bulk Nb. The SPIS measurements revealed that H is trapped at open-volume defects at GBs, which is seen by a decrease of the S parameter. Formation of the hydride-phase particles introduces new defects into the films.

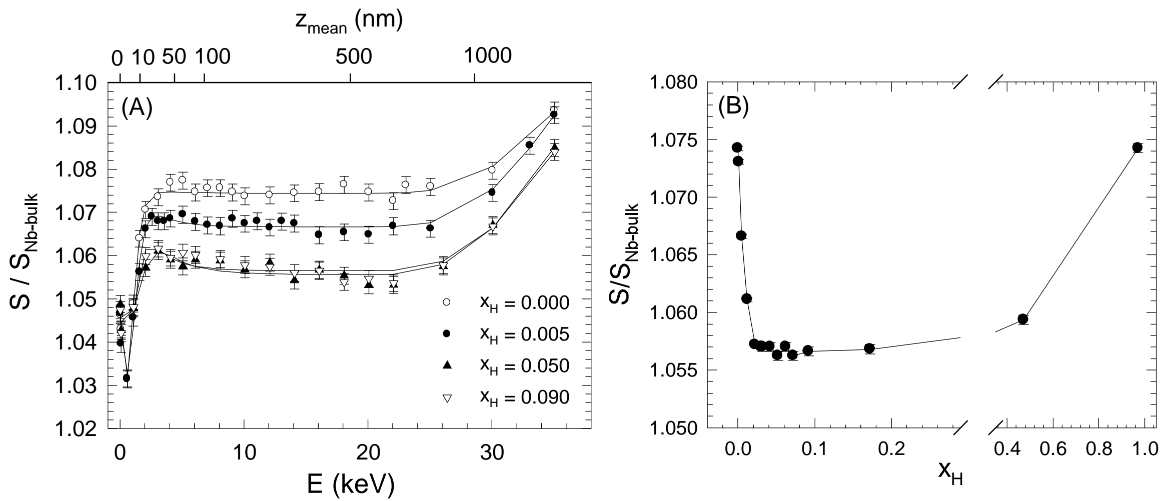

Figure 2 (A) Selected S(E) curves for the virgin film and the film loaded to various H-concentrations. Fits of the experimental points are plotted by the solid lines. The mean positron penetration depth is shown in the upper x-axis. (B) Dependence of the S parameter for the Nb layer obtained from fits of the S(E) curves on H-concentration.

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