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Hydrogen-induced defects in Pd films

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Hydrogen absorbed in crystalline solids causes a lattice expansion and the formation of hydride phases. Contrary to free standing bulk samples, thin films are fixed at substrates, which prevent their in-plane expansion. This makes hydrogen-induced expansion of thin films highly anisotropic and leads to the formation of high stresses in hydrogen loaded thin films. As a consequence, lattice defects may be created in thin films loaded with hydrogen. This work reports about defects created by hydrogen loading in epitaxial Pd films deposited on Al_2O_3 substrates by cold cathode beam sputtering. Hydrogen-induced defects are characterized by positron annihilation spectroscopy performed with variable energy slow positron beams. Extended studies of defect depth profile and its development with increasing concentration of hydrogen are performed by measurement of Doppler broadening of annihilation profile using a continuous positron beam. Selected states are investigated also by positron lifetime spectroscopy on an intense pulsed positron beam. Firstly, the microstructure of virgin films is characterized. Subsequently, the hydrogen concentration in the films is increased step-by-step by electrochemical charging. The development of the film microstructure and the evolution of defects are investigated.

1 Introduction Hydrogen dissolved in a host metal causes a lattice expansion, which is isotropic in free standing bulk samples. However, in thin films the in-plane expansion is hindered by clamping of the film to the substrate. Hence, the hydrogen-induced expansion of thin films is highly anisotropic. As a consequence, high stresses (up to several GPa) may occur due to hydrogen loading [1]. Hydrogen-induced stresses grow with increasing hydrogen content, and if exceeding the yield stress may cause plastic deformation of the film. Thus, dislocations may be formed in these films. Moreover, hydride phases are formed from a certain hydrogen concentration. Since the structure of hydrides differs from that of the virgin host metal, misfit defects are created at the interfaces between a hydride phase and the matrix, and dislocation loops may be emitted by growing hydride particles [2]. Knowledge about defects created by hydrogen loading of thin films is important not only for potential applications, but also for an understanding of the specific behaviour of hydrogen in thin films [3]. An investigation of hydrogen-induced defects in epitaxial Pd films was performed in this work. Positron annihilation spectroscopy (PAS) with a variable energy slow positron beam was used as a principal technique for the determination of the defect depth profile in the films studied. Two complementary PAS techniques were used: (i) Doppler broadening (DB) spectroscopy at a continuous positron beam and (ii) positron lifetime (LT) studies with an intense pulsed positron beam.

2 Experimental Pd films with a thickness of 490 ± 5 nm determined by stylus profilometry were epinastically deposited on a $(11\bar{2}0)$ single crystal Al_2O_3 substrate. The deposition was performed in an UHV chamber by cold cathode beam sputtering at substrate temperature of 800 °C.

DB studies were performed using a magnetically guided continuous positron beam "SPONSOR" [4] with a positron energy adjustable from 0.03 to 36 keV. The broadening of the annihilation line was measured by a Ge detector with an energy resolution of 1.09 ± 0.01 keV at 511 keV and evaluated using the lineshape parameter S.

LT measurements were performed using a pulsed low energy positron system (PLEPS) [5] available at the high-intensity positron source NEPOMUC [6] at the Munich research reactor FRM II. The energy of incident positrons in PLEPS can be adjusted in the range from 0.5 to 18 keV. The time resolution of PLEPS was ~ 400 ps (FWHM of the resolution function) at all positron energies.

Hydrogen loading was performed electrochemically [7] in a galvanic cell filled with an electrolyte consisting of a 1:2 mixture of H_3PO_4 and glycerine. Hydrogen concentration in the film can be calculated from Faraday's law and is expressed as the atomic ratio H/Pd in this paper.

3 Results and discussion Figure 1 shows a dependence of the S parameter on positron energy E for the virgin film and the S(E) curves for selected hydrogen-loaded films. Moreover, S(E) curve for a well annealed (1000°C/1h in vacuum) reference bulk Pd specimen is plotted in Fig. 1. The reference bulk Pd specimen exhibits a single component LT spectrum with lifetime of 112.0 ± 0.5 ps, which agrees well with the calculated Pd bulk positron lifetime [8]. Hence, defect density in the reference bulk specimen is very low, and it can be considered as a defect-free material. Positron diffusion length of 151 ± 4 nm was obtained from fitting of the S(E) curve of the reference bulk Pd specimen by VEPFIT software package [9]. All S parameters are normalized to the bulk $S_0 = 0.4968(7)$ value measured on the reference bulk Pd sample.

The S(E) curves measured on Pd films exhibit the following features: (i) a decrease of S at low energies up to 4 keV due to decreasing fraction of positrons diffusing back to the surface followed by (ii) a plateau-like behaviour in the energy range from 4 to 15 keV, where positrons annihilate mostly inside the Pd film, and (iii) a further decrease of S at energies E > 18 keV, where positrons already penetrate into the Al_2O_3 substrate. The S(E) curves measured on thin films can be well fitted by VEPFIT assuming a two-layer model (see upper panel in Fig. 1) consisting of a Pd layer with a thickness known from profilometry and the Al_2O_3 substrate. The fitted parameters for the Pd layer, i.e. S parameter and positron diffusion length, are plotted in Fig. 2.

It is obvious that in comparison with the reference bulk Pd specimen, virgin film exhibits significantly higher S parameter and shorter positron diffusion length. It clearly indicates that the virgin film is not a perfect crystal, but contains open volume defects which trap positrons. It is known that epitaxial films contain an array of misfit dislocations, which accommodate the lattice mismatch between the film and the substrate [10]. It is expected that density of misfit dislocations increases from the surface towards the film-substrate interface due to increasing distortion of the film lattice. However, the S(E) curve is found to be rather flat throughout the whole Pd layer, which indicates the presence of additional defects distributed uniformly in side the Pd layer.

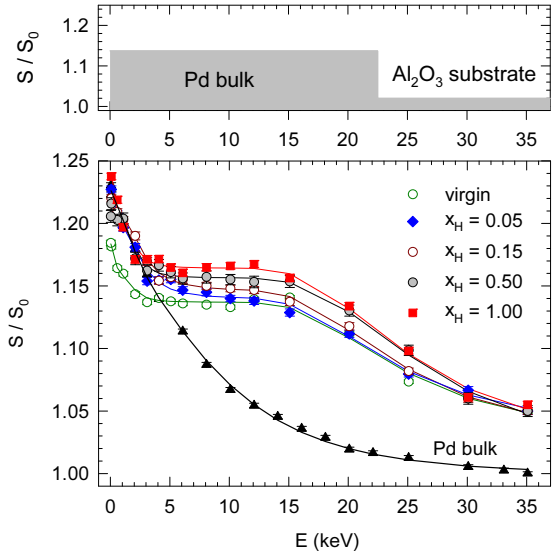

Figure 1 (Color online) Dependence of normalized S parameter on positron energy E for the reference bulk Pd specimen (Pd bulk) and epitaxial Pd films in various states: as-deposited film (virgin) and selected curves of films loaded with hydrogen up to hydrogen concentration x_H. The upper panel of the figure shows the box model used in fitting of the S(E) curves measured on Pd films by VEPFIT. The fitted curves are plotted by solid lines.

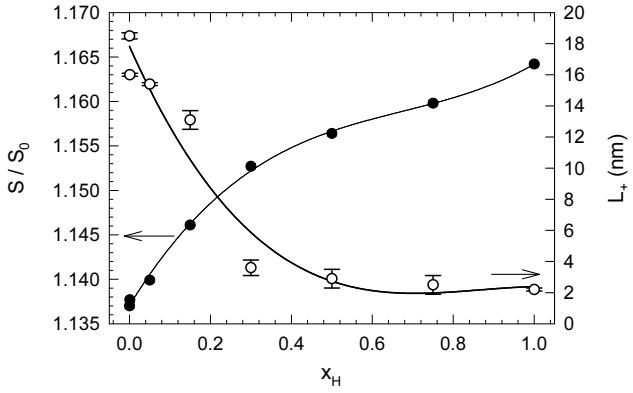

Figure 2 Normalized S parameter and positron diffusion length L_+ for a Pd layer obtained from fitting of the experimental S(E) curves plotted as a function of hydrogen concentration x_H. Solid lines are polynomial fits to guide the eye only.

The defect depth profile in the virgin film was measured also by LT spectroscopy. The LT spectrum for a positron energy E = 18 keV, i.e. the energy where positrons annihilate mainly at the interface between the film and the substrate, exhibits only a single component with a lifetime of 160 ± 1 ps. Since this lifetime is slightly shorter than the calculated lifetime of positrons trapped in a Pd monova-

cancy [8], it is concluded that positrons are trapped at misfit dislocations. This is in agreement with a high density of misfit dislocations expected to be present at the interface of the film and the substrate. The LT spectrum measured with an energy of the incident positrons of E = 0.5 keV exhibits a single component spectrum with a lifetime of 350 ± 1 ps coming from positrons annihilating on the film surface. LT spectra measured at other energies can be decomposed into two components. Lifetimes τ_1 and τ_2 of these components and relative intensity I_1 of the shorter component are plotted in Fig. 3 as a function of positron energy. Positron lifetimes $\tau_1 \sim 170$ ps and $\tau_2 \sim 370$ ps remain approximately constant, while I_1 strongly increases with positron energy. One can see in Fig. 3B that I_1 exhibits (i) a steep increase at very low energies (E < 5 keV) due to rapidly decreasing fraction of positrons diffusing back to the surface followed by (ii) a slower increase at higher energies. The latter effect reflects increasing density of misfit dislocations in the vicinity of the interface with substrate. The lifetime τ_2 remains in the range 350-400 ps even at E > 5 keV, where the fraction of positrons diffusing back to the surface becomes negligible. This indicates that virgin films contain besides misfit dislocations also larger vacancy clusters or voids. The behaviour of I_1 reflects the changed fractions of positrons trapped at these two competing positron traps: close to the interface with substrate almost all positrons are trapped at dense network of misfit dislocations, while going towards the surface more positrons become trapped at vacancy clusters.

One can see in Figs. 1 and 2 that hydrogen loading leads to an increase of S parameter in the Pd layer accompanied by a shortening of positron diffusion length. This is a clear indication that new defects were introduced by hydrogen loading. Hydrogen-induced defects are formed already at low hydrogen concentrations. The identification of defects created by hydrogen loading was performed by LT studies of selected Pd films loaded with hydrogen. As one can see in Fig. 3B, the intensity of positrons trapped at misfit dislocations becomes enhanced in hydrogen loaded films. This gives evidence that dislocations were created by hydrogen loading either due to plastic deformation initiated by hydrogen-induced stresses or by precipitation of hydride particles. In addition, a weak, well separated long ortho-positronium (o-Ps) component was observed at low positron energies in LT spectra of hydrogen loaded films. Appearance of o-Ps component indicates surface roughening of hydrogen-loaded films and formation of large cavities in the subsurface layer.

4 Conclusions Defect studies of virgin and hydrogen loaded epitaxial Pd films on Al_2O_3 substrate were performed in the present work. Virgin films contain already a high density of defects: positrons are trapped at misfit dislocations located mainly close to the interface with the substrate and at larger vacancy clusters. Hydrogen loading introduces new defects identified as dislocations created by plastic deformation initiated by hydrogen-induced stresses or by growing hydride particles.

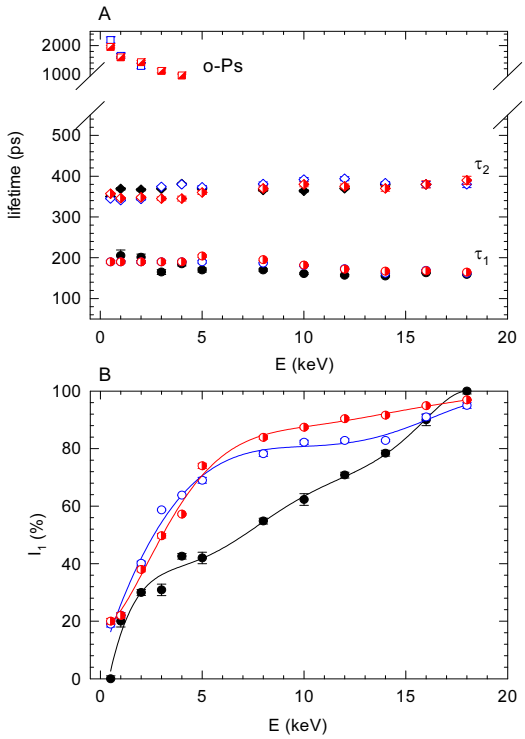

Figure 3 (Color online) Results of LT investigations of Pd films: (A) positron lifetimes resolved in LT spectra, (B) intensity I_1 of the shorter component attributed to misfit dislocations as a function of positron energy. The following states were measured: virgin film (full symbols) and films loaded with hydrogen up to concentration $x_H = 0.05$ (open symbols) and $x_H = 0.50$ (half filled symbols). Solid lines are polynomial fits to guide the eye only.

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