Structural studies of thin Pd films loaded with hydrogen

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Introduction. Pd is very important material for hydrogen technologies and is also used as a model system for study of hydrogen behaviour in metal lattice. In a perfect Pd lattice hydrogen occupies octahedral interstitial sites and causes remarkable volume expansion. Hydrogen strongly interacts with defects: it can be trapped at open volumes defects like vacancies, dislocations and grain boundaries and may also introduce new defects. In this work we employed variable energy slow positron spectroscopy (VEPAS) for study of hydrogen interaction with defects in Pd films with various microstructures ranging from epitaxial to nanocrystalline.

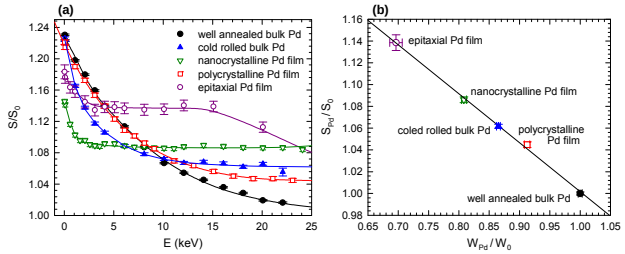
Samples. Three kinds of Pd films were deposited by cold cathode beam sputtering on (11-20) sapphire substrates:

- ***nanocrystalline*** films - deposited at room temperature; thickness (1080 ± 10) nm; nanocrystalline structure consisting of column-like crystallites with the mean width of ~50 nm
- ***polycrystalline*** films - deposited at room temperature and then annealed in vacuum at 800°C for 1h; thickness (1040 ± 10) nm; polycrystalline structure with the grain size of ~2.5 μm
- ***epitaxial*** films - deposited at 800°C; thickness (485 ± 5) nm; single crystals with well defined orientation with respect to the sapphire substrate.

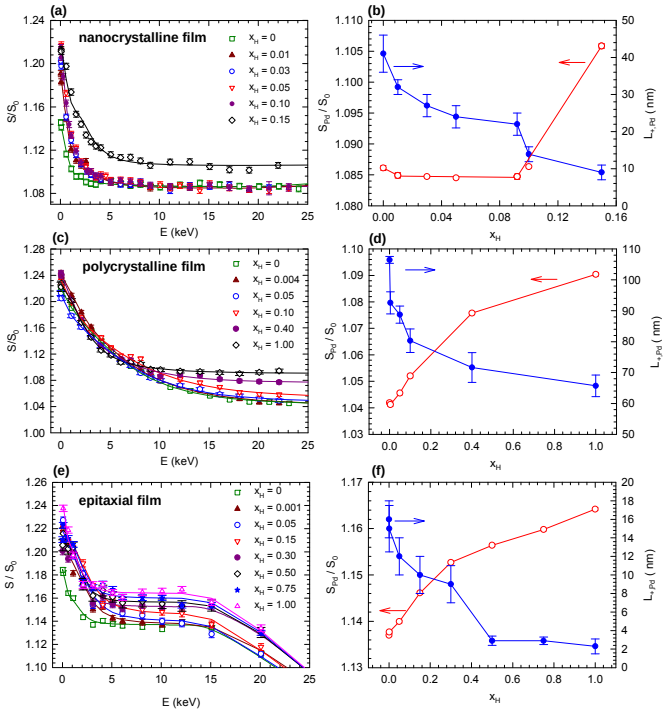
Hydrogen loading was performed electrochemically by constant current pulses in a galvanic cell filled with a mixture of H_3PO_4 and glycerine (1:2).
The hydrogen concentration x_H introduced into the sample was calculated from the transported charge using the Faraday's law.

Methods of characterization.
VEPAS studies were performed on a slow positron beam SPONSOR [1] with positron energy adjustable from 0.03 to 36 keV. Doppler broadening of the annihilation line was measured by a HPGe detector with energy resolution of 1.09 keV at 511 keV and evaluated using the S and W parameters. All S and W parameters were normalized to bulk values S_0, W_0 measured in a well annealed bulk Pd.

Results



(a) S(E) curves for the virgin films and well annealed and cold rolled bulk Pd. Solid lines show model curves calculated by VEPFIT; (b) S-W plot constructed from the bulk values.



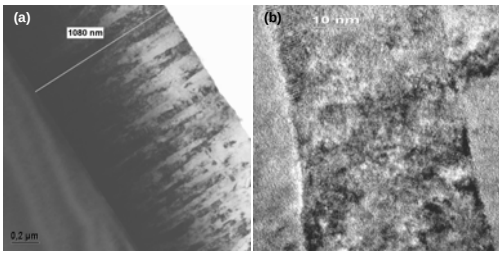
Left panels: dependence of the S parameter on the energy of incident positrons for (a) nanocrystalline, (c) polycrystalline and (e) epitaxial film. Solid lines show model curves calculated by VEPFIT. Right panels: dependence of the bulk S parameter and positron diffusion length on the hydrogen concentration for (b) nanocrystalline, (d) polycrystalline and (f) epitaxial film.

Dislocation densities estimated from VEPAS results by $\rho_D = \frac{1}{\nu_D \tau_B}\left(\frac{L_+^2}{L_{+,B}^2} - 1\right)$,

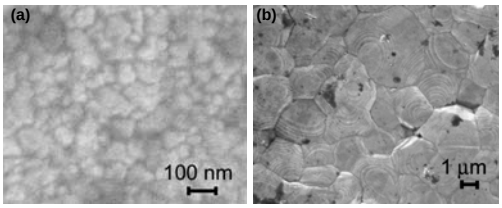
where $\nu_D \approx 10^{-4}$ m^{2}s^{-1} is the specific positron trapping rate for dislocations,
τ_B = (111 ± 1) ps is Pd bulk lifetime,
$L_{+,B}$ = (151 ± 4) nm is the positron diffusion length in defect-free Pd sample

	virgin state		H-loaded up to x_H = 1.0	
sample	L_+ (nm)	ρ_D (m^{-2})	L_+ (nm)	ρ_D (m^{-2})
bulk Pd cold rolled	49 ± 2	(7.6 ± 0.6) × 10^{14}	-	-
polycrystalline Pd film	106 ± 1	(9.2 ± 0.4) × 10^{13}	66 ± 3	(3.8 ± 0.8) × 10^{14}
epitaxial Pd film	16 ± 2	(8 ± 1) × 10^{15}	2.3 ± 0.8	(4 ± 1) × 10^{16}

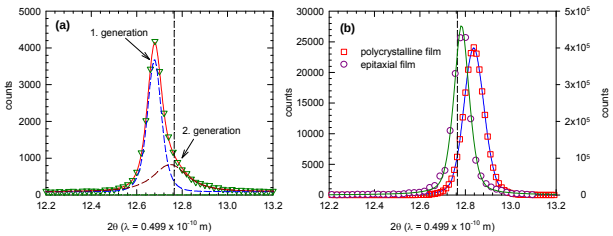
In all Pd samples positrons are confined in similar kind of defects characterized by open volume comparable to monovacancy:
- ***nanocrystalline*** films- grain boundaries
- ***polycrystalline*** films- vacancies associated with dislocations
- ***epitaxial*** films- vacancies associated with misfit dislocations induced by lattice mismatch between the Pd films and the substrate.



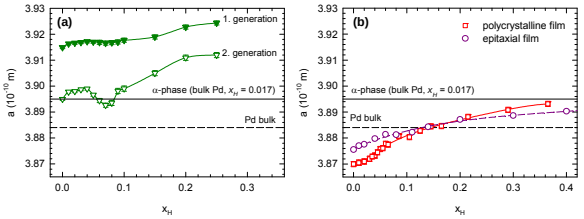
TEM micrographs of nanocrystalline film (in cross-section): (a) TEM bright field image, (b) high resolution TEM image



SEM micrographs of (a) nanocrystalline film (b) polycrystaline film



X-ray diffraction profiles for (111) reflection for the virgin films (a) nanocrystalline film, (b) polycrystalline and epitaxial film. Dashed vertical line shows position of the (111) reflection in bulk Pd



Dependence of lattice parameters of the α-phase on hydrogen concentration introduced into the sample (a) nanocrystalline film, (b) polycrystalline and epitaxial film. Horizontal dashed and solid lines show the lattice constant for the bulk pure Pd and the α-phase with hydrogen concentration of 0.017, respectively

- During **hydrogen loading** of the ***polycrystalline*** and the ***epitaxial*** films stresses induced by absorbed hydrogen lead to plastic deformation which creates dislocations in the films.
- In the ***nanocrystalline*** film hydrogen firstly fills open volume defects at grain boundaries. At hydrogen concentrations $x_H > 0.1$ hydrogen-induced plastic deformation takes place and buckling of the film occurs. At $x_H > 0.15$ the whole film is detached from the substrate

Summary

Hydrogen interaction with defects in Pd films was studied. It was found that hydrogen is trapped at open volume misfit defects at grain boundaries. Moreover, absorbed hydrogen introduces high stresses which inevitably lead to plastic deformation and introduce a high number of dislocations into the film. When the stresses exceed film adhesion to the substrate buckling of the film occurs.

Acknowledgement
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References

[1] Anwand W, Brauer G, Butterling M, Kissenger H-R, Wagner A 2012 Defect and Diffusion Forum 331, p. 25

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