

# Microstructure and Nanoscopic Porosity in Black Pd Films

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In the present work the microstructure of a black Pd film prepared by thermal evaporation and a glossy Pd film deposited by magnetron sputtering was compared. While the glossy Pd film exhibits typical polycrystalline structure with column-like grains, the black Pd film has fractal-like porous structure. Positron annihilation spectroscopy revealed that positronium is formed in nanoscopic cavities of the black Pd film. In conventional metals positronium does not form due to screening by conduction electrons. However, in porous metals containing nanoscopic porosity a thermalized positron may pick an electron on inner surface of a pore and escape into a cavity forming positronium. The average size of nanoscopic pores in the black Pd film was determined from the lifetime of long-lived ortho-positronium component.

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## 1. Introduction

Metals of highly porous structure are called black metals (BM) or metal blacks [1]. Surface of BMs appears dark since light incident on the surface is completely absorbed in multiple reflections in fractal-like structure of percolated micro-cavities with a broad size distribution. BMs have found applications in the electronics devices for optical sensing and imaging, energy harvesting, gas sensors, camouflage, etc. [2–6]. Use of BMs in gas sensor applications profits from their extraordinary large surface area, e.g., 60 m<sup>2</sup>/g for black Pd [5]. BM films of various elements are deposited usually by thermal evaporation in carefully adjusted low pressure ( $\sim 100$  Pa) of N<sub>2</sub> gas [7, 8]. It has been reported that BMs can be prepared also by magnetron sputtering in Ar with small amount of N<sub>2</sub> [6–10]. In the growth of metallic films in PVD systems contamination from residual atmosphere should be considered [11]. Deposition parameters leading to formation of BMs were found empirically but it is still not understood why these parameters result in deposition of BM films. In particular the mode of growth of BMs is still unclear.

The aim of the present work is characterization of microstructure of glossy and black Pd film using variable

energy positron annihilation spectroscopy (VEPAS) [12] combined with electron microscopy. Positronium (Ps) is hydrogen-like bound state of electron and positron [13]. In conventional metals Ps is not formed since any bound state between positron and electron is almost immediately destroyed by screening of surrounding conductive electrons [14]. However, in porous structures a positron can pick an electron on the inner surface of a pore forming Ps which becomes localized inside the pore [15]. The lifetime of pick-off annihilation of ortho-Ps (o-Ps) is determined by open volume of cavity where o-Ps is localized [13, 16]. This makes Ps an excellent non-destructive probe of nanoscopic pores in solids.

## 2. Experimental details

Glossy Pd films with thicknesses of 1.35  $\mu\text{m}$  were deposited on fused silica substrates at room temperature by RF (13.56 MHz) magnetron sputtering using Ar atmosphere. Black Pd films with thickness of 3.7  $\mu\text{m}$  were prepared by thermal evaporation from tungsten boat on Si (100) substrate. The substrates were situated 52 mm above evaporation source. The evaporation was proceed in nitrogen ambient (purity 5N) at pressure of 200 Pa. Morphology of glossy and black Pd films was examined by scanning electron microscopy (SEM) using a FEI Quanta 200F microscope. VEPAS was employed for investigation of lattice defects and nanoscopic porosity in both kinds of Pd films. VEPAS studies were carried out on a pulsed variable energy slow positron beam MePS [17]. The energy of incident positrons was varied in the range

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from 1 to 16 keV. It corresponds to the mean positron penetration depth into Pd from 3 to 280 nm calculated using the Makhovian positron implantation profile [12]. Positron lifetime spectra were measured using a digital spectrometer with time resolution of  $\approx 250$  ps (FWHM of the resolution function).

### 3. Results and discussion

Figure 1 shows SEM micrographs of glossy Pd film. It consists of column-like grains with a width around 200 nm. Microstructure of a black Pd shown in Fig. 2 is completely different. In contrast to the glossy film black Pd exhibits porous fractal-like structure consisting of radial units with large surface area.

Positron lifetime spectra measured using positrons with incident energy of 8 keV (corresponding to the mean positron penetration depth into Pd of 93 nm) are compared in Fig. 3. Obviously, the spectrum for black Pd film contains a well resolved long-lived component which comes from pick-off annihilation of o-Ps while for the glossy Pd film such long-lived component is absent. This gives clear evidence that Ps is not formed inside the glossy Pd film but it is formed inside the black Pd film due to its porous structure containing nanoscopic cavities.

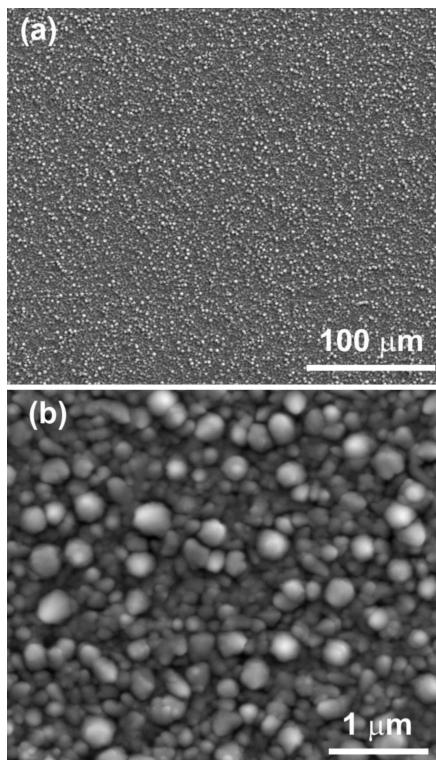


Fig. 1. SEM micrographs (secondary electrons) of surface of a glossy Pd film prepared by magnetron sputtering on fused silica substrate (a) overview of the film (b) detail in higher magnification.

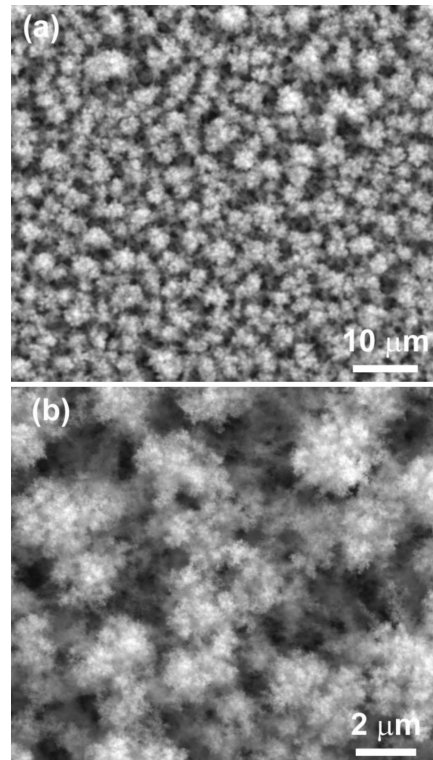


Fig. 2. SEM micrographs (secondary electrons) of surface of a black Pd film deposited on Si substrate by thermal evaporation on Si substrate (a) overview of the film (b) detail in higher magnification.

Figure 4 shows the development of the mean positron lifetime as a function of the energy  $E$  of incident positrons for both films. The mean positron penetration depth is indicated at the upper horizontal axis. The energy of incident positrons was varied in the range from 1 to 16 keV, which corresponds to the mean positron stopping depth from 33 to 280 nm. Hence, considering the thickness of Pd films (1350 and 3700 nm for the glossy and the black Pd film) it is clear that all positrons are stopped inside the Pd layer. The mean positron lifetime is a robust parameter which is not affected by mutual correlations among fitting parameters. The development of the mean lifetime gives, therefore, a useful hint at differences between both films. From inspection of Fig. 4 one can conclude that black Pd film exhibits a significantly higher mean lifetime than the glossy film in the whole energy range. This is clearly due to long-lived o-Ps contribution which is present in the spectra of black Pd film but is absent in the glossy film. The mean lifetime for the glossy Pd film slightly decreases with depth. On the other hand, the mean lifetime of the black Pd film increases with depth and exhibits a local maximum at the positron energy of 8 keV.

More information about the microstructure of Pd films can be obtained from decomposition of positron lifetime spectra into individual components. The lifetimes of exponential components resolved in positron lifetime

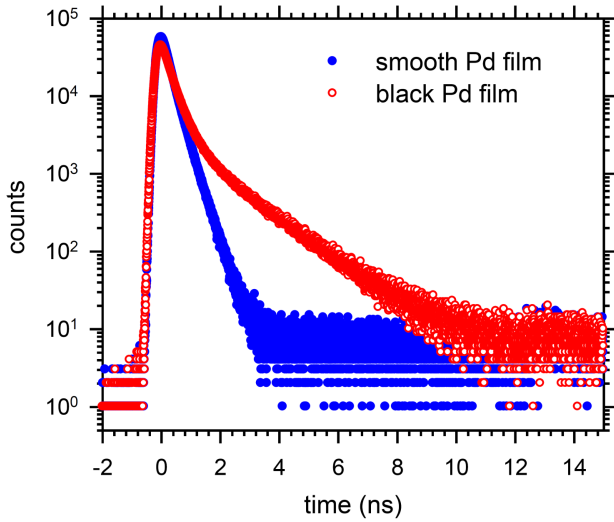


Fig. 3. Comparison of positron lifetime spectra of glossy and black Pd film measured using positrons with incident energy of 8 keV which corresponds to the mean positron penetration depth into Pd of 93 nm.

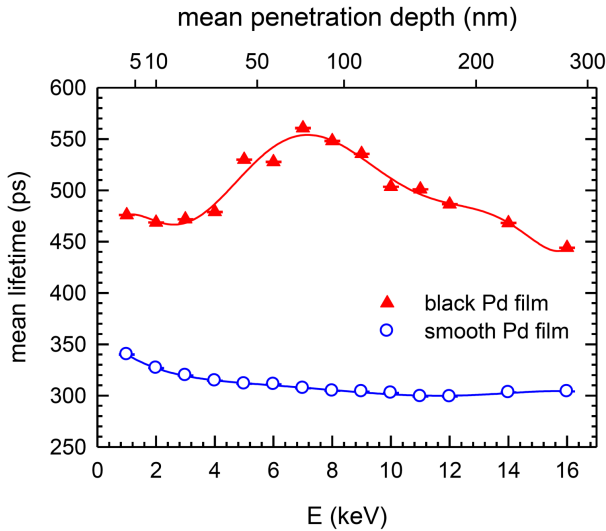


Fig. 4. The development of the mean positron lifetime as a function of the energy of incident positrons for the glossy and black Pd film. The mean positron penetration depth is indicated in the upper horizontal axis.

spectra of the glossy Pd film (except the Ps contribution) are shown in Fig. 5a. The shorter component with lifetime  $\tau_1 \approx 220$  ps is close to the calculated lifetime for monovacancy in Pd [18]. Hence, this component represents a contribution of positrons trapped in vacancy-like defects (misfit defects at grain boundaries, misfit dislocations, and monovacancies). Lifetime of this component remains approximately constant with depth. The longer component with lifetime  $\tau_2 \approx 380$  ps represents mainly a contribution of positrons annihilated in the surface state, i.e., trapped at potential well on the surface of

the Pd film [12]. Lifetime of this component slightly increases with depth. The development of relative intensities  $I_1$  and  $I_2$  of the corresponding components is plotted in Fig. 5b. At low energies the majority of positrons is annihilated on the surface. With increasing energy positrons penetrate deeper into the Pd film and the fraction of positrons diffusing back to the surface decreases. This is reflected by a decrease of the intensity  $I_2$  and a complementary increase of the intensity  $I_1$ . No contribution of free positrons was resolved in the spectra. It indicates that glossy Pd film exhibits a high density of vacancy-like defects and virtually all positrons are annihilated in trapped state at these defects.

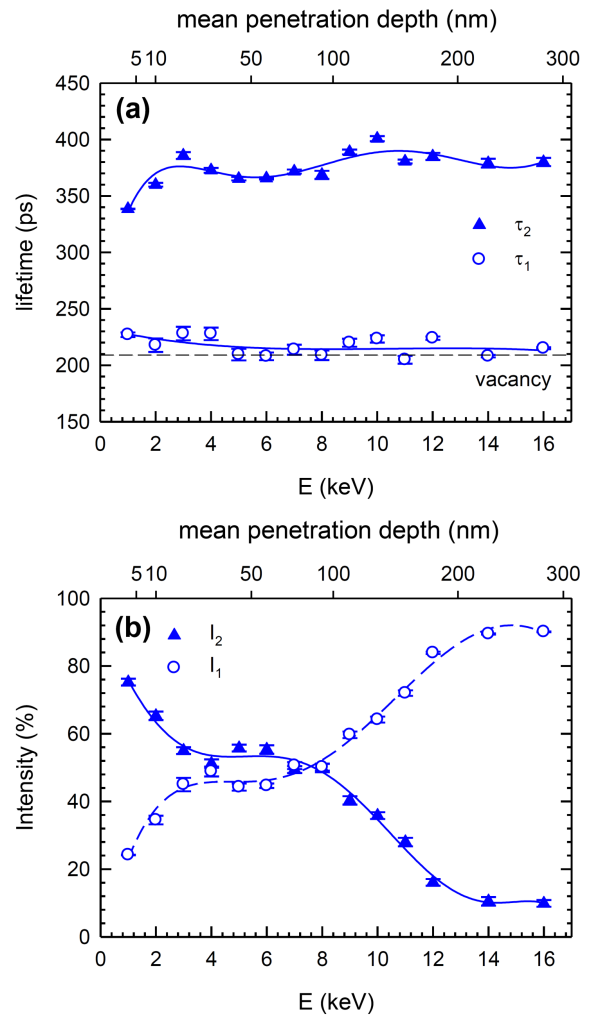


Fig. 5. Results of positron lifetime spectroscopy for the glossy Pd film: (a) lifetimes of exponential components (except of the Ps contribution); (b) corresponding relative intensities. Vertical dashed line in the left panel indicates calculated lifetime for positrons trapped in monovacancy in Pd. The mean positron penetration depth is indicated in the upper horizontal axis.

The results of decomposition of positron lifetime spectra of black Pd film are plotted in Fig. 6. The spectra can be well described by two exponential components corresponding to positrons annihilated as particles and a long-live Ps contribution which is plotted separately in Fig. 7. The component with lifetime  $\tau_1 \approx 270$  ps represents a contribution of positrons trapped in Pd film at defects with open volumes larger than monovacancies (small vacancy clusters). The longer component with lifetime  $\tau_2 \approx 415$  ps comes from positrons annihilated in the surface state. One can see in Fig. 6b that intensity  $I_2$  of the surface contribution gradually decreases with depth due to decreasing fraction of positrons diffusing back to the surface. Similarly to the glossy Pd film no contribution of free positrons was observed in the black Pd film. Hence, the black Pd film contains high density of defects with open volume higher than that of monovacancy.

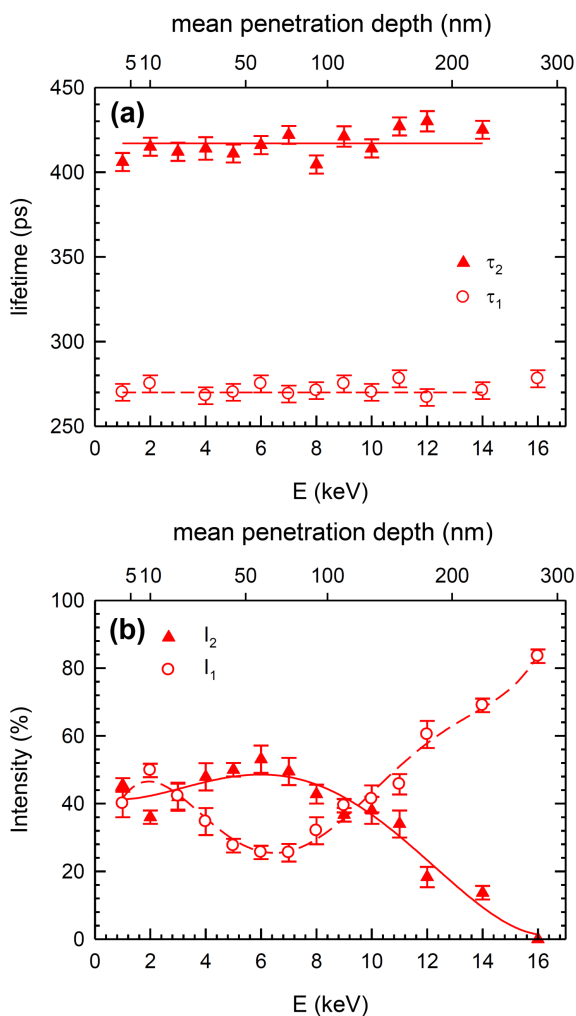


Fig. 6. Results of positron lifetime spectroscopy for the black Pd film: (a) lifetimes of exponential components except of the Ps contribution; (b) corresponding relative intensities. The mean positron penetration depth is indicated in the upper horizontal axis.

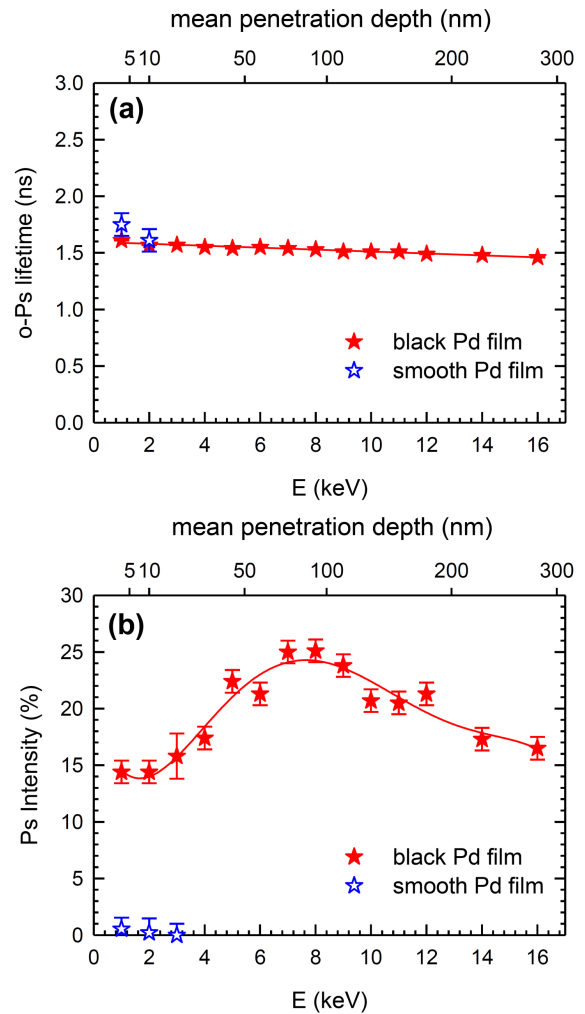


Fig. 7. (a) Lifetime of the o-Ps component; (b) intensity of the Ps contribution.

The lifetime and intensity of Ps contribution for both films are plotted in Fig. 7a and b, respectively. In almost every material Ps is formed on the surface by thermalized positrons diffusing back to the surface and forming Ps with an electron on the surface. The Ps binding energy is 6.8 eV [13]. This energy is transferred into the kinetic energy of Ps atom which is emitted from the surface to vacuum [19]. One can see that in the case of the glossy Pd film Ps is formed on the surface only. The long-lived Ps contribution was present in positron lifetime spectra of the glossy film at low energies only, its intensity is very low ( $I_{Ps} < 1\%$ ) and diminishes for  $E > 2$  keV. In contrast to this in the case of the black Pd film the intensity of the long-lived Ps contribution is significantly higher ( $I_{Ps} \geq 15\%$ ) and it even increases with depth, see Fig. 7b. Hence, in the black Pd film Ps is formed in the whole volume due to porous structure of black Pd. The formation of Ps occurs by coupling of thermalized positron with an electron on the inner surface of a pore. Ps atom created by this mechanism is localized in the pore and is

eventually annihilated there. Since o-Ps decays predominantly by the pick-off annihilation process the lifetime of the o-Ps component is determined by the open volume of the pore. Using the Tao-Eldrup model [10, 13] one obtains that the average size of nanoscopic pores in the black Pd film is  $(0.48 \pm 0.03)$  nm. Almost constant value of the o-Ps lifetime, presented in Fig. 7a, indicates that the size distribution of nanoscopic pores does not change significantly with depth. However, the intensity of the Ps contribution increases with depth and reaches a local maximum at the depth range 50–100 nm. It indicates that the Ps yield is enhanced in the sub-surface region of the black Pd film. In depths exceeding 100 nm the Ps intensity slightly decreases again but remains around 15% even for the highest positron energy used ( $E = 16$  keV) corresponding to the stopping depth of 280 nm.

#### 4. Conclusions

The microstructure of a black Pd film prepared by thermal evaporation was examined and compared with a glossy Pd film deposited by magnetron sputtering. Glossy Pd film exhibits a typical polycrystalline structure consisting of column-like grains. Black Pd film consists of fractal-like radial units and contains nanoscopic porosity. Positron annihilation studies revealed that glossy Pd film contains vacancy-like defects. Black Pd film contains larger defects and in addition nanoscopic pores where Ps is formed. The average size of these pores is  $(0.48 \pm 0.03)$  nm.

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