

# STUDY OF NANOSCOPIC POROSITY IN BLACK METALS BY POSITRON ANNIHILATION SPECTROSCOPY\*

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Black and smooth Al films were characterized by the variable energy positron annihilation spectroscopy (VEPAS). It was found that in smooth films positronium (Ps) is formed on the surface only while in black metal films, it is formed also in nanoscopic pores inside the film. The mean pore size increases from the substrate to the surface due to increasing film roughness.

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## 1. Introduction

Thermal evaporation or magnetron sputtering of metals in carefully adjusted low pressure ( $\sim 100$  Pa) of  $N_2$  gas enables deposition of peculiar porous structures known as black metals (BMs) [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 can be used in electronic devices for optical sensing, camouflage and gas sensors [2, 3]. The physical mechanism leading to formation of peculiar porous structure of BMs is not completely understood yet

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and parameters for their preparation were found empirically [4]. The development of BMs with morphology tailored for specific applications requires better understanding of the mechanism of growth of these materials.

Positronium (Ps), *i.e.* a hydrogen-like bound state of electron and positron [5], is an excellent non-destructive probe of nanoscopic pores in solids [6]. In conventional metals, Ps does not form because any bound state of positron and electron is quickly destroyed by the screening of conduction electrons. However, in porous metals, a thermalized positron may pick an electron on inner surface and escape into a pore forming Ps. Ortho-positronium (o-Ps) formed by this process decays predominantly by pick-off annihilation and its lifetime is determined by the scattering rate on the walls of the pore [5, 7]. In the present work, Ps is employed for characterization of nanoscopic porosity in black and smooth Al films prepared by magnetron sputtering.

## 2. Experimental details

Al films with thicknesses of 140 and 325 nm were deposited at room temperature by DC pulsed (10 Hz) magnetron sputtering on fused silica (FS) substrates. Smooth films were prepared using pure Ar atmosphere, while black Al films were deposited in Ar atmosphere (total pressure of 0.5 Pa) with around 5% of nitrogen. Morphology of Al films was characterized by scanning electron microscopy (SEM) using an FEI Quanta 200F microscope. VEPAS studies were carried out on a pulsed variable energy slow positron beam MePS [8]. The energy of incident positrons was varied in the range from 1 to 16 keV. It corresponds to the mean positron penetration depth into Al from 15 to 1250 nm calculated using the Makhovian positron implantation profile [9]. Positron lifetime spectra were measured using a digital spectrometer with time resolution of  $\sim 250$  ps. A total statistics of  $10^7$  annihilation events was collected in each spectrum.

## 3. Results and discussion

The microstructure of smooth and black Al film differs significantly as documented by SEM micrographs shown in Fig. 1. The smooth film consists of nanocrystalline column-like grains and exhibits a low surface roughness, see Fig. 1(a). In contrast, black Al film is characterized by porous structure with pores and cavities of various sizes and a high surface roughness, see Fig. 1(b).

Results of VEPAS investigations of smooth and black Al films are shown in Fig. 2. Positron lifetime spectra were decomposed into two components: (i) a contribution of positrons annihilated as particles (*i.e.* without forming Ps) with lifetime  $\tau_1$  which is plotted in Figs. 2(a), (d); (ii) a long-lived

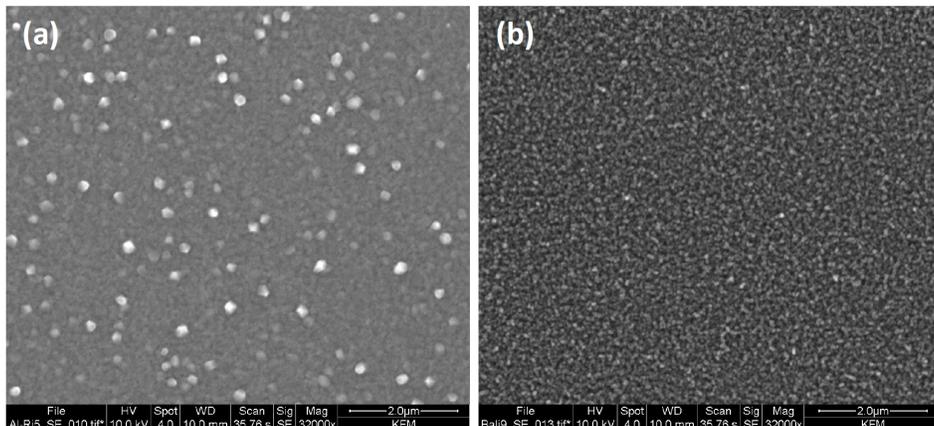


Fig. 1. Secondary electron SEM images of surface of (a) smooth Al film; (b) black Al film with thickness of 325 nm.

component  $\tau_{o-Ps}$  plotted in Figs. 2(b), (e) is a contribution of o-Ps pick-off annihilation. Relative intensity of Ps contribution (*i.e.* sum of ortho- and para-Ps contributions) is plotted in Figs. 2(c), (f). Vertical dashed line in Fig. 2 indicates the energy for which the mean positron penetration depth correspond to the thickness of Al film, *i.e.* the interface between the Al layer and FS substrate.

The smooth and black films do not differ in the energy range where positrons are annihilating in FS substrate, *i.e.*  $E > 4$  keV and  $E > 7$  keV for 140 and 325 nm film, respectively. Lifetime of positrons annihilated in FS is significantly higher than that for Al layer which is reflected by a pronounced increase of positron lifetime at high energies in Figs. 2(a), (d). Moreover, Ps is formed in FS substrate. This leads to a pronounced increase of the Ps intensity in Figs. 2(c), (f). The lifetime of o-Ps in FS is around 1.6 ns, see Figs. 2(b), (e).

The smooth and black films, however, differ significantly in the energy range corresponding to the Al layer, *i.e.*  $E < 4$  and  $E < 7$  keV for 140 and 325 nm film, respectively. This testifies to different microstructure of smooth and black Al film. At low energies ( $E \approx 1$  keV), a majority of positrons is annihilated on the surface and positron lifetime in Figs. 2(a), (d) corresponds to the surface state. With increasing energy, positrons penetrate deeper into the sample and the fraction of positrons diffusing back to the surface gradually decreases. This is reflected by a decrease of the positron lifetime in Figs. 2(a), (d) which reaches local minimum at  $E \approx 2$  and 4 keV (corresponding to the mean positron penetration depth of 45 and 135 nm) for the 140 and 325 nm film, respectively. At higher energies, positrons start

to penetrate into the FS substrate which is reflected by a gradual increase of positron lifetime in Figs. 2(a), (d). Black films exhibit higher positron lifetime. It gives clear evidence that the black films contain larger open volume defects than the smooth films.

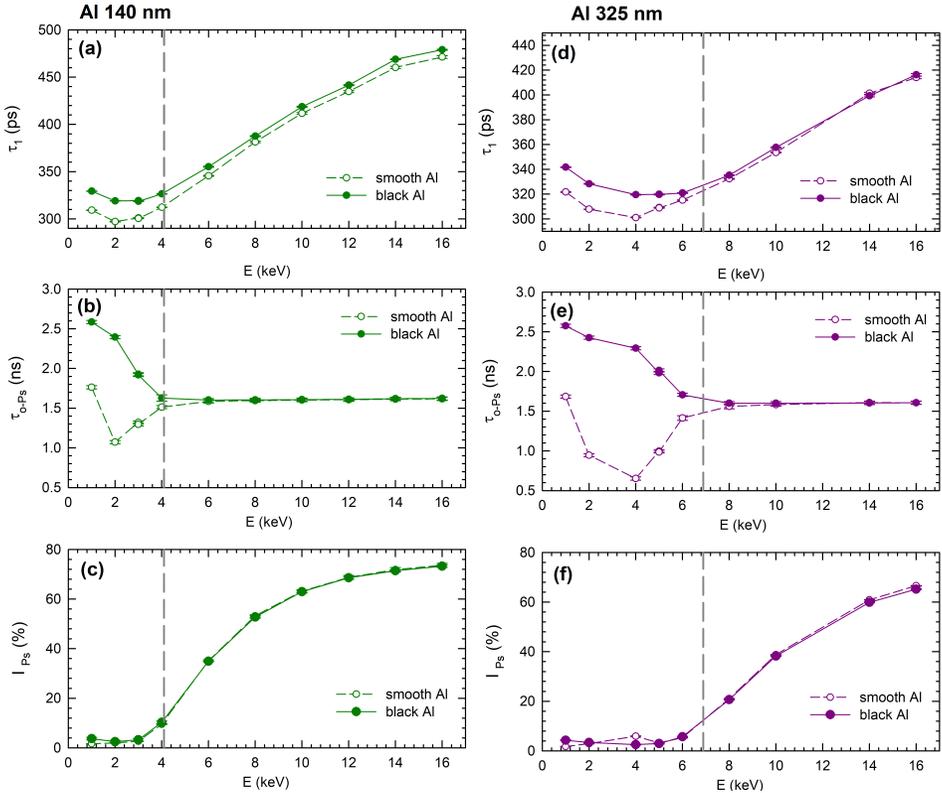


Fig. 2. Results of VEPAS investigations of black and smooth Al films with thickness of 140 nm (a), (b), (c) and 325 nm (d), (e), (f).

The Ps contribution is always present in Al films at low positron energies, see Figs. 2(b), (e), due to Ps formation in natural  $\text{Al}_2\text{O}_3$  oxide layer on the Al surface. As a fraction of positrons diffusing back to the surface decreases, the Ps contribution in the smooth films decreases as well. However, when positrons start to penetrate into FS substrate, the Ps contribution rises again due to Ps formed inside FS. In black films, Ps is formed not only on the surface but also inside the Al layer, and the o-Ps lifetime is significantly longer than in the smooth film, see Figs. 2(b), (e). It testifies that the black Al films contain a considerable density of open volume pores. The o-Ps lifetime measured in the black metal Al films increases with decreasing positron energy indicating increasing pore size when going from substrate to

the surface. This is in accordance with growing roughness with increasing film thickness. Using the Tao–Eldrup model [5, 7], one can estimate that the mean size of microscopic pores in the black metal Al film falls into the range from 4.4 to 5.8 Å.

#### 4. Conclusions

Microstructure and open volume defects in black and smooth Al films were characterized. Black Al films contain larger open volume defects than smooth films. Moreover, black Al films contain nanoscopic pores with the mean size of 4.4–5.8 Å.

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