Contribution ID: **25** Type: **poster**

Study of nanoscopic porosity in black metals by positron annihilation spectroscopy

Tuesday, 25 June 2019 13:30 (1h 30m)

Thermal evaporation or magnetron sputtering of metals in carefully adjusted low pressure (~100 Pa) of nitrogen gas enables deposition of peculiar porous structures known as black metals. Because of their unique morphology black metals highly absorb light in the visible to infrared spectral region. The surface of black metals 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. Black metals are used in electronic devices for optical sensing and imaging, solar cells, camouflage and gas sensors. The physical mechanism leading to formation of peculiar porous structure of black metals is not completely understood yet and parameters for their preparation were found empirically. The development of black metals with morphology of nanoscopic porosity tailored for specific application requires understanding of the mechanism of growth of these materials.
Positronium (Ps), i.e. hydrogen-like bound state of electron and positron, is excellent non-destructive probe of nanoscopic pores in solids. 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 containing micro-cavities a thermalized positron may pick an electron on inner surface and escape into a cavity 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 cavity. Hence, measurement of o-Ps lifetime enables determination of size distribution of microcavities.
In the present work black Al, Au and Pd films prepared by magnetron sputtering and thermal evaporation were characterized by positron annihilation spectroscopy. Porous black films were compared with conventional smooth films. It was found that Ps is formed in smooth films on the surface only while in black metals it is formed in the whole film. The size distribution of micro-cavities in black metal films prepared by thermal deposition and magnetron sputtering was determined. Moreover, the development of the size and morphology of nanoscopic porosity with increasing film thickness was examined. It was found that the film first grows on a substrate as a smooth layer. Above certain critical thickness of a few nm the film starts to grow as a porous layer and its roughness gradually increases with increasing thickness.

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Session Classification: Poster session