Defect studies of nanostructured black Au films

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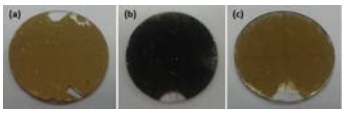
Introduction. Light absorbers are needed in optical applications for preventing crosstalk between optical connections and for thermal light-emitting sources [1]. However, the ability to absorb light completely for any incident direction remains still a challenge. Full omnidirectional absorption of light could be achieved in nanostructured metal surfaces that sustain localized optical excitations. Light is absorbed over the whole range of incident angles and wavelength range of absorption can be adjusted by scaling the dimensions of micro-cavities [2].
Metals evaporated in the presence of a gas with pressure of about 100 Pa deposit as porous layers called black metals [3]. Due to their porous structure with percolated micro-cavities they possess high absorbance in the visible to infrared spectral region [3]. Black metals, in particular black Au, are therefore highly suitable as absorbers in the infrared range [2]. The surface morphology and the structure of nano-sized pores and cavities in sub-surface region of black metals are crucial for their performance, i.e. absorption ability and the range of wavelength absorbed. Characterization of the microscopic porosity represents therefore an important task. In the present work variable energy positron annihilation spectroscopy (VEPAS) was employed for characterization of open volume defects in black Au films. Defect structure of black Au films was compared with that for a conventional smooth Au film with high reflectivity.

Samples.

- ***Nanostructured black Au films*** with thickness of ≈900 nm were prepared by thermal deposition on glass substrates in nitrogen atmosphere at the pressure of 300 Pa. They appear black on the nanostructured surface, because incident light undergoes multiple reflections in micro-cavities and is almost completely absorbed.
- ***Conventional smooth Au films*** were deposited in vacuum on the glass substrate. They exhibit a high reflectivity.
- ***Bulk Au*** (99.9%) annealed at 1000°C for 1h in vacuum (10^{-3} mbar) was used as a reference sample.



Appearance of Au films deposited on glass substrate: (a) smooth Au film; (b) black Au film - front side; (c) black Au film - back side

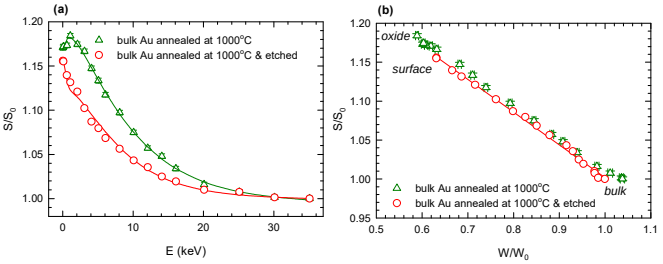
Methods of characterization.

- ***Conventional positron lifetime (LT) spectroscopy***: The bulk reference sample was characterized by LT spectroscopy using a 1 MBq ^{22}Na source deposited on 2 μm Mylar foil. The LT measurements were performed using a digital spectrometer [4] with time resolution of 145 ps (FWHM of resolution function for ^{22}Na). The source contribution consisting of two components with lifetimes of ≈ 368 ps, ≈1.5 ns and corresponding intensities of ≈10%, ≈1% was always subtracted from LT spectra.
- ***Variable Energy Positron Annihilation Spectroscopy (VEPAS)*** were performed on a slow positron beam SPONSOR [5] 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 (1.06 ± 0.01) 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 the annealed bulk Au reference for the energy of incident positrons E = 35 keV. The dependence of the S parameter on the positron energy was analyzed using the VEPFIT code [6].

Results

Bulk Au samples

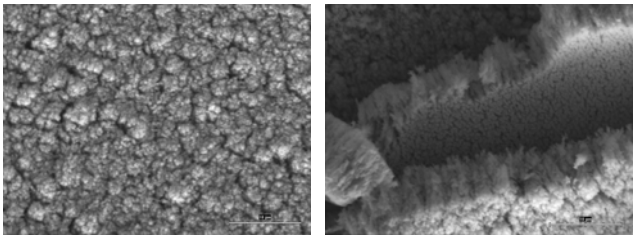
- LT investigations: **a single component spectrum with lifetime of (118.8 ± 0.2) ps** (calculated bulk lifetime calculated for Au (119 ps) [7])⇒In the bulk Au sample **positrons are annihilated in the free state.**
- VEPAS: At very low energies almost all positrons are annihilated at the surface and S attains the surface value. The local maximum at E ≈ 1 keV is caused by positrons annihilated in a thin surface layer of oxide formed during annealing at elevated temperature. The S(E) curve for the annealed bulk Au sample after etching in aqua regia (a mixture of HNO_3 and HCl acids in the molar ratio 1:3) does not contain the local maximum at 1 keV anymore and the S parameter exhibits a monotonic decrease from the surface value down to the bulk value. The S-W plot for annealed and etched bulk Au is a straight line connecting the point in the S-W space corresponding to positron annihilation on the surface with the point corresponding to annihilation in Au bulk. This testifies that there are only **two positron states** in the annealed and subsequently etched sample: (i) **positrons annihilating in the surface state** and (ii) **positrons annihilating in the Au bulk**. Fitting yielded the **mean positron diffusion length** in Au $L_{+,B}$ **= (134 ± 1) nm** for both samples. This value falls into the range 100 – 200 nm expected for positron diffusion length in defect-free metals. The **thickness of the oxide layer** of **(40 ± 1) nm** was determined by fitting for the annealed bulk Au sample.



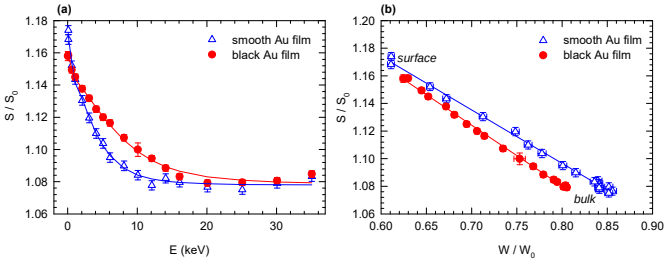
Results of VEPAS studies of bulk Au samples: (a) S(E) curves; (b) S-W plot. Solid lines show model curves calculated by VEPFIT assuming two layer model for annealed bulk Au (thin oxide layer and Au bulk) and single layer model for annealed and etched sample

Au films

- VEPAS: For both films the S parameter gradually decreases with increasing positron energy from a surface value down to a value representing the case when virtually all positrons are annihilated inside the film. This value S/S_0 ≈1.08 is remarkably higher than the bulk value for annealed bulk Au sample. It indicates that Au films contain open volume defects (vacancies, misfit dislocations, vacancy-like misfit defects at crystallite interfaces) trapping positrons.
- **Smooth Au film**: The S(E) curve was fitted by VEPFIT using a single layer model. The **mean positron diffusion length L_+ = (24 ± 1) nm** obtained from fitting is remarkable shorter than $L_{+,B}$ = (134 ± 1) nm determined in the bulk annealed Au. Higher S parameter and shorter positron diffusion length compared to the annealed bulk Au testify that Au films contain considerable concentration of open volume defects. The S-W plot for the smooth Au film is a straight line connecting the surface point with the point corresponding to positrons annihilated inside the Au film.
- **Black Au film:** The S(E) curve exhibits at high energies similar S parameter as that for smooth Au film. This testifies that the concentration of open volume is similar in both kinds of films. However, at lower energies (E < 15 keV) the black Au film exhibits higher S parameters compared to those for smooth Au film. This testifies that structure of black Au film in sub-surface region differs from that of smooth Au film. Proper description of S(E) curve for black Au film by VEPFIT requires **two-layer** model consisting of (i) **sub-surface region which microstructure differs from that for smooth Au film**; (ii) **bulk region of the film with microstructure similar to that in the smooth Au film**. Similarity of the **bulk region** in black and smooth Au films is confirmed also by the **positron diffusion length L_+ = (21 ± 3) nm** obtained from fitting for the black Au film. This value is practically the same as that obtained for the smooth Au film. The sub-surface region with enhanced S parameter in the black Au films obviously corresponds to nanostructured region containing microscopic cavities and nano-sized pores. The **thickness of the sub-surface region** obtained from fitting is **(79±3) nm**. The **positron diffusion length for the sub-surface region** obtained from fitting is **L_+ = (62±4) nm**. Hence the sub-surface region exhibits higher S parameter compared to the smooth Au film but the positron diffusion length is higher as well. This can be explained by **formation of positronium (Ps) in micro-cavities inside the sub-surface region**. In metals Ps is not formed since any bound sate of positron and electron is quickly destroyed by screening effect of conduction electrons. However a thermalized positron escaping from Au through inner surface into a micro-cavity may form Ps by picking an electron on the surface. Narrow para-Ps contribution to the annihilation photo-peak likely caused the observed enhancement of the S parameter in the sub-surface region. Ps localized in micro-cavities can diffuse through the percolated network of cavities in the sub-surface region and the diffusion length determined by VEPAS might be, therefore, longer than that measured deep inside the film.



SEM images of Au black film



Results of VEPAS studies of Au films: (a) S(E) curves; (b) S-W plot. Solid lines show model curves calculated by VEPFIT assuming two layer model for black Au film ((i) sub-surface region which microstructure differs from that for smooth Au film; (ii) bulk region of the film with microstructure similar to that in the smooth Au film) and single layer model for the smooth Au film.

Summary

- In the bulk region both films contain comparable concentration of defects which is considerable higher than that in well annealed bulk Au.
- Black Au exhibits enhanced S parameter and positron diffusion length in sub-surface region. This is most probably due to Ps forming in nanostructured black Au in micro-cavities and diffusing through percolated network of these micro-cavities.

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References

[1] Teperik T V, García de Abajo F J, Borisov A G, Abdelsalam M, Bartlett P N, Sugawara Y & Baumberg J J 2008 Nature Photonics 2 299
[2] Novotný M, Fitl P, Krasilnikova Sytchkova A, Bulíř J, Lančok J, Pokorný P 2009 Cent. Eur. J. Phys. 7 327
[3] Pfund A H 1930 Rev. Sci. Instrum. 1 397
[4] Bečvář F, Čížek J, Procházka I, Janotová J 2005 Nucl. Instrum. Methods A 539 372
[5] Anwand W, Brauer G, Butterling M, Kissenger H R and Wagner A. 2012 Def. Diff. Forum 331 25
[6] van Veen A, Schut H, Clement M, de Nijs J M M, Kruseman A, Ijpma M R 1995 Appl. Surf. Sci. 85 216
[7] Campillo Robles M, Ogando E , Plazaola F 2007 J. Phys.: Condens. Matter 19 176222

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