Positron annihilation study of cavities in black Au films

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Abstract. Defects in a black Au film were studied using variable energy positron annihilation spectroscopy. Black Au films exhibit porous morphology similar to cauliflower. This type of structure enhances the optical absorption due to a multiple reflections in the micro-cavities. A nanostructured black Au film was compared with conventional smooth Au films with high reflectivity. The black Au film exhibited a remarkably enhanced $S$-parameter in sub-surface region. This is caused by a narrow para-Positronium contribution to the annihilation peak.

1. Introduction

Light absorbers are needed in optical applications for preventing crosstalk between optical connections and for thermal light-emitting sources. A complete absorption of light from the visible into the infrared spectral region over the whole range of incident angles remains still a challenge [1]. This goal could be achieved in nanostructured metal surfaces containing a broad size distribution of cavities that sustain localized optical excitations [2]. Metals evaporated in the presence of a gas with pressure of about 100 Pa deposit as porous layers called black metals [3]. Their porous structure with percolated micro-cavities leads to high absorbance in the visible to infrared spectral region. Black metals, in particular black Au, are therefore highly suitable as absorbers [4]. The surface morphology and the structure of cavities in sub-surface region are crucial for performance of black metals absorbers. In the present work variable energy positron annihilation spectroscopy (VEPAS) was employed for characterization of cavities in black Au film. Microstructures of black Au and a conventional smooth Au film were compared. Note that a conventional smooth Au films have been already studied by VEPAS in Ref. [5].

2. Experimental details

Black Au films with thickness of $\approx 900$ nm were prepared by thermal deposition on glass substrates in nitrogen atmosphere at the pressure of 200 Pa. Conventional smooth Au films were deposited in vacuum also on the glass substrate. Figure 1 shows Au films after deposition. The smooth Au film deposited in vacuum and shown in Figure 1a exhibits a high reflectivity. On the other hand the nanostructured Au film deposited at 200 Pa appears black, see Figure 1b, because incident light undergoes multiple reflections in cavities and is almost completely absorbed. Note that light absorption occurs on the nanostructured surface only. This is demonstrated in Figure 1c which shows...
the back side of the black Au film, i.e. a view through the glass substrate. Obviously the back side of the black Au film is smooth and exhibit typical metallic appearance with high reflectivity.

Bulk Au (99.9%) annealed at 1000°C for 1h in vacuum (10⁻³ mbar) was used as a reference. The reference sample was characterized by conventional positron lifetime (LT) spectroscopy using a 1 MBq ²²Na source deposited on 2 μm Mylar foil. The LT measurements were performed on a digital spectrometer [6] with time resolution of 145 ps. The source contribution consisting of two components with lifetimes of ≈368 ps, ≈1.5 ns and intensities of ≈10%, ≈1% was always subtracted from spectra.

VEPAS studies were performed on a slow positron beam SPONSOR [7] 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 ± 0.01) keV at 511 keV and evaluated using the S and W parameters that 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 [8] assuming Makhovian positron implantation profile with parameters $m = 1.9, n = 1.6$ and $A = 20.73$ Å keV⁻¹. The F parameter which is proportional to the fraction of positrons forming positronium (Ps), was calculated as $F = (R - R_{\text{min}})/(R_{\text{max}} - R_{\text{min}})$, where $R$ is the ratio of annihilation events recorded below the annihilation peak (energy range 430-500 keV where 3-$\gamma$ annihilation of ortho-Ps contributes) to those in the 511 keV peak. $R_{\text{min}}$ and $R_{\text{max}}$ denote the minimum and the maximum $R$ measured in the experiment. $R_{\text{min}}$ corresponds to situation when no Ps is formed ($E > 15$ keV) while $R_{\text{max}}$ corresponds to maximum Ps yield on the surface ($E = 30$ eV).

Figure 1. Appearance of Au films deposited on glass substrate: (a) smooth Au film; (b) black Au film - front side; (c) black Au film - back side (look through the glass substrate).

3. Results and discussion

3.1 bulk Au samples

LT investigations of annealed bulk Au revealed single component spectrum (except of the source contribution) with lifetime of (118.8 ± 0.2) ps, which agrees with calculated Au bulk lifetime [9]. Hence, the sample exhibits very low defect density and almost all positrons annihilate in the free state.

Figure 2a shows the $S(E)$ curve for the bulk Au annealed at 1000°C. At very low energies positrons are annihilated at the surface and $S$ attains the surface value. At $E \approx 1$ keV the $S(E)$ curve exhibits a local maximum followed by a continuous decrease to the bulk value. The local maximum is likely caused by positrons annihilated in a thin surface oxide layer formed during annealing at 1000°C. Clearly the vacuum in the furnace was not good enough to prevent oxidation completely. This hypothesis was verified by etching the annealed sample in aqua regia (a mixture of HNO₃ and HCl in the molar ratio 1:3) which removed the oxide layer. Figure 2a shows that the $S(E)$ curve for the annealed bulk Au sample after etching does not contain the local maximum at 1 keV anymore and $S$ exhibits a monotonic decrease from the surface value down to the bulk value. The $S-W$ plot for annealed and etched bulk Au presented in Figure 2b is a straight line connecting the point 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 trapped in the surface state and (ii) positrons annihilating in Au bulk. With increasing energy positrons penetrate deeper and deeper into the sample and the fraction of positrons diffusing back to the surface gradually decreases while the fraction of positrons annihilated in bulk grows. The $S-W$ plot for the annealed sample measured prior to etching exhibits first a shift to higher $S$ and lower $W$ due to positrons annihilated in oxide layer. It is followed by a gradual transition to the point for Au bulk. Solid lines in Figure 2a show model curves calculated by VEPFIT assuming a two...
layer model for annealed bulk Au (thin oxide layer and Au bulk) and a single layer model for the annealed and etched sample. One can see in Figure 2a that the model curves describe the experimental points accurately. Fitting yielded a positron diffusion length in Au $L_{+,B} = (134 \pm 1)$ 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 $(40 \pm 1)$ nm was determined by fitting for the annealed bulk Au sample.

![Figure 2. Results of VEPAS studies of bulk Au samples: (a) $S(E)$ curves; (b) $S$-$W$ plot.](image)

### 3.2 Au films

Figure 3a shows $S(E)$ curves for the smooth and the black Au film. For both films $S$ decreases with increasing positron energy from a surface value down to a value when virtually all positrons are annihilated inside the film. This value $S/S_0 \approx 1.08$ is significantly higher than that for annealed bulk Au, cf. Figure 2a. The mean positron diffusion length $L_+ = (24 \pm 1)$ nm obtained for the smooth Au film by VEPFIT is remarkably shorter than $L_{+,B}$ determined for the bulk annealed Au. Higher $S$ parameter and shorter positron diffusion length testify that Au film contains considerable concentration of defects. The $S$-$W$ plot for the smooth Au film shown in Figure 3b is a straight line connecting the surface point with the point corresponding to annihilations inside the Au film. The $S(E)$ curve for the black Au film is at high energies similar to that for the smooth Au film testifying to similar concentration of defects in both films. However, at lower energies ($E < 15$ keV) the black Au sample exhibits higher $S$ parameters than the smooth Au film indicating that its structure differs in the sub-surface region. Proper description of the $S(E)$ curve for the black Au film by VEPFIT requires a two-layer model consisting of (i) sub-surface region where the microstructure differs from that for smooth Au film; (ii) deeper region with microstructure similar to that for smooth Au film. The $S(E)$ curve for black Au film can be well fitted assuming that positron diffusion length in the region (ii) is the same as that in the smooth Au film. One can see in Figure 1c that the black Au film appears metallic when looking at its back side through the transparent substrate. Hence, film layer attached directly to the substrate is
smooth while the region close to the surface is porous. The sub-surface region with an enhanced $S$ in the black Au films obviously corresponds to a nanostructured region containing microscopic cavities (diameter $\approx 200$ nm as determined by AFM [2]) and likely also smaller nano-cavities. The thickness of the sub-surface region obtained from fitting is $(79\pm 3)$ nm and it is characterized by the positron diffusion length $L_+ = (62\pm 4)$ nm. Hence the sub-surface region exhibits a higher $S$ parameter compared to the smooth Au film and the positron diffusion length is higher as well. This can be explained by formation of Ps in micro- and nano-cavities inside the sub-surface layer (i). In metals Ps does not form since any bound state of positron and electron is quickly destroyed by the screening of conduction electrons. However, a thermalized positron escaping from Au through inner surface into a cavity may form Ps by picking an electron on the surface. Narrow para-Ps contribution to the annihilation photo-peak [10] likely caused the observed enhancement of $S$ in the sub-surface region. Enhanced $L_+$ can be explained by Ps diffusion through percolated network of cavities in the sub-surface region. However, cavities in the sub-surface region may not necessarily be interconnected. Isolated cavities with the mean size and/or concentration gradually decreasing with depth from the surface can also explain enhanced $L_+$. Formation of Ps in the sub-surface region (i) was confirmed by behavior of the $F$ parameter plotted in Figure 4. At very low energies ($E< 0.5$ keV) Ps is always formed on metal surfaces. Ps yield on the surface of black Au is lower compared to the smooth Au due to its higher roughness and consequently higher probability of pick-off annihilation. At higher energies $F$ quickly drops to zero in smooth Au while in black Au $F$ is enhanced also in the sub-surface region due to Ps formed in cavities.

![Graph](image.png)

**Figure 4.** Dependence of the $F$ parameter on the positron energy for Au films

4. Conclusions

The microstructure of nanostructured black Au and smooth Au film with high reflectivity was compared. At the depth higher than 80 nm both films contain comparable concentration of defects which is considerable higher than that in well annealed bulk Au reference. Black Au film exhibits enhanced $S$ and $F$ parameters and higher positron diffusion length in sub-surface region. This is likely due to Ps formation in nanostructured sub-surface layer containing micro- and nano-cavities.

Acknowledgements

This work has been supported by the Czech Science Foundation (project P108/12/G043).

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