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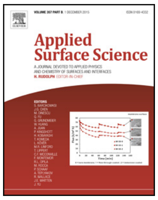

Surface modification of nanoporous alumina layers by deposition of Ag nanoparticles. Effect of alumina pore diameter on the morphology of silver deposit and its influence on SERS activity

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ABSTRACT

Self-organized Al_2O_3 nanoporous/nanotubular (Al_2O_3-NP) oxide layers decorated with silver nanoparticles (Ag-NPs) exhibiting specific properties may serve as attractive SERS substrates for investigating the interactions between an adsorbate and adsorbent, or as stable platforms for detecting various organic compounds. This article presents the influence of the size of the alumina nanopores with a deposit of silver nanoparticles obtained by the magnetron sputtering technique on the morphology of silver film. Moreover, the effect of pore diameter on the intensity of SERS spectra in Ag-NPs/Al_2O_3-NP/Al composites has also been estimated. For such investigations we used pyridine as a probe molecule, since it has a large cross-section for Raman scattering. To characterize the morphology of the composite oxide layer Ag-NPs/Al_2O_3-NP/Al, before and after deposition of Ag-NPs by PVD methods (Physical Vapor Deposition), we used scanning electron microscopy (SEM) and atomic force microscopy (AFM). The surface analytical technique of surface-enhanced Raman spectroscopy (SERS) was used to investigate the surface activity of the composite. The results obtained show that, for a carefully controlled amount of Ag (0.020 mg/cm^2 - deposited on the top of alumina nanopores whose average size varies from ~86 nm up to ~320 nm) in the composites investigated, pore size significantly affects SERS enhancement. We obtained distinctly higher intensities of SERS spectra for substrates with an Ag-NPs deposit having a larger diameter of the alumina nanopores. AFM results suggest that both the lateral and perpendicular distribution of Ag-NPs within and on the top of the largest pores is responsible for the highest SERS activity of the resulting Ag-NPs/Al_2O_3-NP/Al composite layer, since it produces a variety of cavities and slits which function as resonators for the adsorbed molecules. The Ag-NPs/MeO_x-NP/Me composite layers obtained ensure a good reproducibility of the SERS measurements.

1. Introduction

Investigations of Al_2O_3 nanoporous layers have shown that they are promising in a number of important applications. Among these, the most promising are:

(a) a regular array of such nanopores may be used in the construction of different optical plazmonic sensors, in particular, efficient sensors for SERS investigations of adsorbed molecules [1–5],
(b) new perspective substrates for electrocatalysis [6],
(c) a regular array of such nanotubes may be a template for fabrication of nanodots or nanorods [7–9].

Recent investigations of composite materials consisting of nanoporous oxides layers on a parent metal (TiO_2-NT/Ti, Al_2O_3-NP/Al and ZrO_2-NT/Zr where "NT" – stands for nanotubes, "NP" – stands for nanoporous) loaded with nanoparticles of IB metals (Ag, Au, Cu) have shown, moreover, that they do exhibit new and promising functionalities [10–12]. In particular, the new materials Ag-NPs/MeO_x-NP/Me (where "NPs" – stands for nanoparticles) have turned out to be active substrates for surface-enhanced Raman scattering (SERS) measurements in order to study adsorption and to detect minute amounts of certain

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Table 1
Specification of preparation procedures and resulting nanopores.

Sample	Anodization conditions				Pore widening		
	Electrolyte	Temperature [°C]	Potential [V]	Time of 1st → 2nd step [min]	Electrolyte	Temperature [°C]	Time [min]
A	0.3 M $H_2C_2O_4$ aqueous solution	20	40	60 → 9	–	–	–
B			65	60 → 2.5	5% H_3PO_4 aqueous solution	30	30
C	2% H_3PO_4 in CH_3OH/H_2O (1:4 vol.)	0	120	720 → 170	–	–	–

organic compounds. Recently, it has been reported that the presence of an Al substrate at the bottom of a nanoporous aluminium oxide layer covered with Ag can have a considerable impact on SERS activity [13]. This improvement in the SERS activity of the Ag-coated Al_2O_3 NP/Al substrate was attributed to the SPR (Surface Plasmon Resonance) field enhancement in combination with an interference effect. There is a continuous interest in fabrication of new SERS active substrates and in optimization of their activity and reproducibility [14–20].

The Ag–NPs deposit plays an important part due to the specific properties of silver: Ag is known as the most SERS-active metal [21]. It should be pointed out that all the new morphologies thus obtained are characterized by a large specific surface area, which is one of the most important factors affecting the intensity of the SERS spectra [22–24]. Such arrays of Ag particles – coupled electromagnetically to each other – may produce strong resonances; therefore, such substrates may be superior for SERS applications [5,25–27].

When electromagnetic radiation interacts with a nanoparticle formed from a metal with a negative real and small positive imaginary dielectric constant (e.g. silver and gold), it induces a collective oscillation of surface conduction electrons called surface plasmons [28–31]. The oscillations of surface plasmons lead to enhanced electromagnetic fields at some locations in the close proximity of the metal nanoparticle [28–31]. This field enhancement is highly localized, and decays rapidly within a few nm or less from the nanoparticle/dielectric interface [28–31].

In this paper we discuss in more detail the effect of the Ag–NPs deposit, and its distribution on the nanoporous substrate with a controlled diameter of the nanopores, on the SERS activity of the resulting Ag-NPs/MeO_x-NP/Me composite. We also investigate the resulting morphology of the composite when using magnetron sputtering deposition of Ag metal with a strictly controlled – by a quartz microbalance – amount of Ag. The deposition method, in contrast to, e.g., electrochemical deposition, does not introduce uncontrollable solution components which may affect the SERS activity of the substrate. An attempt is also undertaken to investigate in more detail the morphology of the resulting composite, and in particular of the Ag-NPs deposit, by using the AFM technique to study the Ag-NPs lateral and perpendicular distribution to the geometrical surface area of the sample, as well as its effect on SERS activity.

2. Experimental

2.1. Sample preparation

A high-purity (99.999%) aluminum foil supplied by Goodfellow was used as the substrate material. The samples were cleaned in acetone and ethanol, and then electrochemically polished in a 1:4 volume mixture of $HClO_4$ and CH_3CH_2OH by a constant voltage of 20 V for 30 s at 0 °C to achieve a mirror-finished surface. A two-step anodization was performed using a simple electrochemical cell equipped with a powerful circulating cooling system (Thermo Haake, DC10-K15) under a constant cell potential of 40, 65 or 120 V at a temperature of 20 or 0 °C, as indicated in Table 1 [32–34]. The time of the first step was 1 h for anodization in oxalic acid and 12 h for phosphoric acid anodization. After the first anodization, the anodic aluminum oxide (AAO) layer with random and disordered pores was chemically removed by a mixture of 6% of H_3PO_4 and 1.8% H_2CrO_4 for 12 h at 45 °C (Not indicated in Table 1). Subsequently, the samples were re-anodized (under the same conditions) for a short time (2.5 – 11 min for oxalic acid and 170 min for phosphoric acid anodizations) to form a thin nanoporous oxide layer on the Al surface. After anodization, the sample was rinsed with water and dried. Some AAO samples (B) were immersed into a 5% phosphoric acid solution for a defined period of time to widen the nanopores (see Table 1). By combining the two-step anodization performed at various potentials and the pore widening process, three types of nanoporous alumina layers on Al with different pore diameters (samples A–C) were obtained.

2.2. Surface functionalization of the fabricated samples

Alumina nonporous structures were partly covered with an Ag deposit by the sputter deposition technique in a vacuum at a pressure of 3×10^{-3} Pa with DC magnetron sputtering using a LEICA MED020 apparatus; the configuration was perpendicular to the surface of the samples. This configuration was most suitable for penetration of Ag-NP into larger nanopores

Magnetron sputtering: high purity Ar (99.99%) was introduced through a mass flow controller. The glow discharge plasma was obtained at 25 mA and at a pressure of 2.0 Pa. Before deposition, the target was pre-sputtered for about 30 s to remove contaminants from the sample surface. The average amount of metal deposited per cm^2 (0.020 mg/cm^2) was strictly controlled, as was the mass gain (measured with a quartz microbalance) of the samples during the metal deposition process of ~ about 135 s. Of course, both the average and true local amount of the metal deposits may actually vary substantially due to the highly developed specific surface area of the oxide substrates and the resulting non-uniform distribution of the metal deposits.

2.3. Surface investigation methods

SEM. For the morphological characterization of the samples after their anodization and Ag decoration, examinations were carried out with a scanning electron microscope, a FEI NovaNanoSEM 450.

Image processing and analysis. The images obtained were processed using ImageJ software [28]. All images were prepared using its inner thresholding procedure to obtain a binary image. The images were processed further by the “Fill holes” and “Watershed” tools - to correct for weakly labeled pores and to separate non-circular objects, respectively. By using the “Analyze particles” tool of ImageJ, pores were counted, taking account of their size and circularity. Based on the data obtained (pore areas), by expressing the pores as circles of equivalent area, the equivalent pore diameters “$d_{e''}$ were calculated.

AFM. The sample topography was imaged at a higher resolution by means of atomic force microscopy. The AFM system Dimension Icon (Bruker) installed in a glove box (MBrawn) was applied. All images were collected in tapping mode in an argon atmosphere. Standard AFM probes from Bruker were used. For each sample, the