



Influence of the silver deposition method on the activity of platforms for chemometric surface-enhanced Raman scattering measurements: Silver films on ZrO₂ nanopore arrays



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ABSTRACT

Deposition of plasmonic metal nanoparticles on nanostructured oxide templates is an important part in preparation and design of suitable substrates for surface-enhanced Raman scattering (SERS) measurements. In this contribution we analyze the influence of the Ag deposition methods (magnetron sputtering and evaporation in vacuum, which are often used interchangeably) on SERS activity of the resultant Ag-n/ZrO₂/Zr composite samples fabricated. We found that deposition of the same amount of Ag (0.020 mg/cm²) on the ZrO₂ nanoporous layers using magnetron sputtering and evaporation in vacuum leads to formation of two different surface morphologies, which can be distinguished on the basis of high-resolution scanning electron microscopy (HR-SEM) measurements. Those differences distinctly affect SERS intensity measured for probe molecules: pyridine and sodium 2-mercaptoethanesulfonate. SERS substrates obtained using evaporation technique are ca. 1.5 times more efficient than substrates prepared using magnetron sputtering.

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1. Introduction

For many years Raman spectroscopy has not been treated as a useful analytical tool because “standard” Raman scattering has very low efficiency. For example, typical value of the total Raman scattering cross-section is ca. 10⁻²⁹ cm² per molecule, whereas cross-sections for ultraviolet absorption are equal to ca. 10⁻¹⁸ cm² [1]. Even cross-sections for adsorption in infrared are ca. 8 orders of magnitude larger than those of “standard” Raman scattering [1]. By utilizing electromagnetic nanoresonators constructed from certain metal nano-clusters the Raman scattering cross-sections can be, however, increased by many orders of magnitude, thus making Raman measurements utilizing nanoresonators one of the most sensitive and nowadays widely applied analytical techniques. This technique is called from the historical reasons surface enhanced Raman scattering – SERS. It is worth mentioning, that in some cases the efficiency of generation of the SERS signals is so large, that monitoring of the reliable spectra of a single molecule is even possible [2–4].

One of the most important problems in carrying out practical SERS measurements is preparation of reproducible and highly-active SERS substrates. There is a large number of various techniques used for preparation of SERS substrates, for example, assembling of plasmonic metal nanoparticles on various substrates, deposition of plasmonic films on various nanostructured substrates, nanolithography methods, including electron-beam lithography and focused ion beam milling, and various template-based methodologies used to generate metallic nanopatterns [5]. In many of these techniques the very important step of the preparation of SERS substrate is deposition of the plasmonic metal. For example, previous investigations have shown that Ag evaporation on nanotubular zirconia, titania and alumina substrates results in fabrication of reproducible SERS active platforms suitable for fundamental research [6–9]. Such platforms exhibit a homogeneous and well-ordered structure reflecting the ZrO₂ nanopore arrays. The regularity of the structure and a very large specific surface area of the silver film provided a good reproducibility and a high intensity of SERS spectra for different adsorbates. So far the research of many groups focused on improving reproducibility of the nanostructured substrate and finding more suitable patterns fabricated on the surface. To the best of our knowledge the influence of plasmonic metal deposition at ZrO₂ layers by different physical vapour deposition (PVD) methods on the SERS activity, has not been analyzed, yet. In this contribution for the first time we compare two

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standard methods used (often interchangeably) for the deposition of nanometric silver films: magnetron sputtering and evaporation deposition in vacuum.

2. Experimental

2.1. Nanostructured ZrO₂

A zirconium foil (99.2% purity, Goodfellow) with 0.25 mm thickness was cut into 1 cm × 1 cm specimens. Before anodization, the Zr samples were cleaned in acetone and ethanol. To achieve a mirror finished surface, the samples were chemically polished in an HF/HNO₃/H₂O (1:4:2) mixture, rinsed twice with deionized water, then rinsed with ethanol and dried. Two-step anodizations were carried out using an electrochemical system equipped with a potential supply and a Teflon O-ring cell with a Pt grid as a cathode. The first anodization was performed at 12 V for 30 min in a stirred electrolyte consisting of 1 M (NH₄)₂SO₄ and 0.08 M NH₄F. Afterwards, the porous oxide film thus formed was mechanically removed using an adhesive tape. The second anodization step was performed for 2 min under the same conditions as the first one.

2.2. Silver Deposition

The zirconia nanoporous structures were partly covered with an Ag deposit for SERS investigations by PVD methods. Deposition of Ag nanoparticles (0.02 mg/cm²) was performed using an evaporation method in a vacuum ($p = 3 \cdot 10^{-3}$ Pa), for this purpose we applied a JEE-4X JEOL device and DC magnetron sputtering technique using a Leica EM MED020 apparatus. The average amount of metal deposited per cm² was strictly controlled by quartz microbalance *in situ* measurements. Certainly, both the true average amount and local amount of the metal deposits may vary substantially due to the highly-developed specific surface area of the nanoporous arrays and the resulting non-uniform distribution of the metal deposits. The configuration of the setup was perpendicular to the surface of the sample. For the 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 cm² (0.020 mg/cm²) was strictly controlled during the metal deposition process of ~135 s.

2.3. HR-SEM/AFM

For the morphological characterization of the samples after their anodization and Ag enhancement, examinations were carried out with a scanning electron microscope by using backscattered electron detector (BSE), an FEI NovaNanoSEM 450. The topography of the samples was imaged at a high resolution by means of atomic force microscopy (AFM). An AFM system Dimension Icon (Bruker) installed in a glove box (MBraun) was used. All images were collected in tapping mode in an argon atmosphere. Standard AFM probes from Bruker were used. For each sample, the microscopic investigations were repeated several times across different surface areas to gather statistical information by means of the AFM technique.

2.4. XPS

The chemical composition of the oxide layers before and after silver deposition process by PVD methods was examined using photoelectron spectroscopy (Microlab 350 - Thermo Electron). The chemical state of surface species was identified using the high energy resolution spherical sector analyzer of the spectrometer (SSA). XPS spectra were excited using AlK_α ($h\nu = 1486.6$ eV) radiation as a source. The high-resolution spectra were recorded using 40 eV pass energy with the step 0.1 eV. A

Shirley background subtraction was made to obtain the XPS signal intensity. The peaks were fitted using an asymmetric Gaussian/Lorentzian mixed function. The measured binding energies were corrected in reference to the energy of C 1s peak at 285 eV. Advantage-based data system software (Version 4.88) was used for data processing.

2.5. SERS Measurements

For the SERS investigations, the following probe compounds were used: sodium 2-mercaptoethanesulfonate (Merck) and pyridine (Ubichem Limited). All compounds were of high purity and were used as received without further purification or treatment. Raman spectra were collected with a Horiba Jobin-Yvon Labram HR800 spectrometer equipped with an Olympus BX40 microscope with a 50× long-distance objective, a 600 groove/mm holographic grating, and a Peltier-cooled (1024 × 256 pixel) CCD detector. An He-Ne laser (632.8 nm) provided the excitation radiation. The excited surface area was about 1.5–2 μm². SERS spectra of 2-mercaptoethanesulfonate adsorbed from a 0.005 M aqueous solution and pyridine adsorbed from 0.05 M pyridine + 0.1 M KCl solution were measured at different spots randomly chosen at the macroscopic surface area of the sample under investigation. At least a dozen points were investigated for each sample.

3. Results and Discussion

3.1. Morphological Characterization of Nanoporous Zirconia Layers

The anodization process of Zr samples leads to the formation of nanoporous zirconia layers as shown in Fig. 1a. The 12 V anodized sample is characterized by regular hexagonal structure, where degree of surface coverage by nanopores is about 65%. It is surprising that such a freestanding membranes growth is always perpendicular to the parent Zr metal surface [7,10] and usually has an amorphous internal structure [10,11].

A careful analysis of the SEM images using the ImageJ software [12] of nanoporous layer revealed that the average diameter of the pores is multimodal: 18 ± 6 nm and 26 ± 9 nm (Fig. 1b). AFM investigations of the as-received samples correlate well with the statistical analysis of SEM data, and our observations show, that the maximum size of the pores with walls is 25–35 nm, which gives a pore hole diameter of 15–20 nm. The specific surface area calculated from the AFM image for 1 μm² projected area was 1.14 μm². Our previous experience with oxidation of Al, which is characterized by bimodal distribution of nanopores, suggested that a strictly controlled enhancement with Ag deposit (magnetron sputtering) may lead to a functionalization of the nanotubular zirconia layer to a SERS active platform for fundamental SERS investigations of adsorbates [13]. Nanoporous zirconium oxide layers thus obtained with regular morphologies coated with Ag nanoparticles should act as nanoresonators with defined geometry and surface development.

3.2. Effect of Ag-n deposition

More detailed information about the morphology of the Ag deposit comes from the HR-SEM investigations. Fig. 2 shows typical SEM images of zirconia nanopores layers with an Ag deposits (0.02 mg/cm²) obtained by magnetron sputtering (a) and evaporation methods (b). One can see a regular network of usually hexagonal nanopores, whose size, however, becomes reduced due to Ag deposition as a results of magnetron sputtering, see Fig. 2a. Evidently, the Ag nano-particles are located mostly at the top of the nanopore network. Some pores are even completely blocked by Ag nanoparticles. Careful inspection of Fig. 2b reveals that the vapour-deposited silver forms a solid film on the top of the nanoporous ZrO₂ layer which is composed of Ag agglomerates. The Ag deposit seems to completely cover the oxide layer. Application of evaporation method leads to the formation of irregular voids and

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