SERS on Ag dendrites fabricated on porous aluminum oxide during anodizing of electrodeposited aluminum on silver

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Nanostructured silver has been widely investigated due to various fields of applications from biomedical to sensing [1]. Silver as a noble metal has been found to be especially important as an effective material for surface enhanced Raman spectroscopy (SERS) [2]. Latest trends in nanotechnology research provide enhancement of a weak Raman signal owing to the unique size effect achieved by synthesis of various nanomaterials with different shapes and morphologies as nanoparticles, nanowires and nanorods. Recently, attention has been paid on potential applications of three-dimensional open dendritic nanostructures showing catalytical effect [3]. Some recent studies show strong enhancement of Raman scattering on silver dendritic nanostructures bringing potentially remarkable prospects of application in several fields [2, 4].

Here we present an experimental set up to fabricate an efficient SERS substrate by introducing different experimental approaches resulting in formation of porous anodic aluminum oxide (AAO) template decorated with nanostructured Ag as shown in Fig. 1.

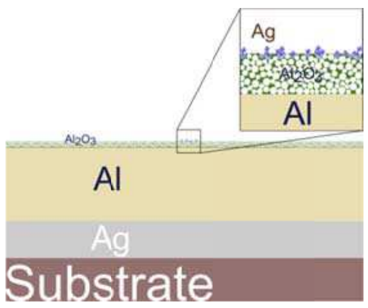

Fig. 1. Schematic representation of SERS substrate formation. Insert shows nanostructured silver dendrites formed during anodizing of Al layer.

At first, the alumina ceramic substrate was rendered electrically conductive with a special mixed bonded silver paste particularly developed for chip resistors.

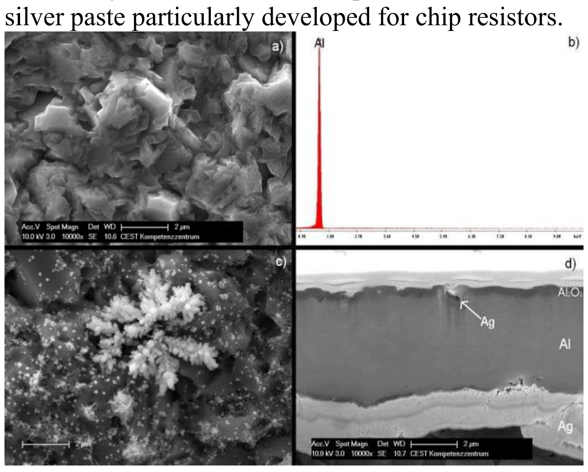

Fig. 2.a) SEM image of Al layer formed on Ag/ alumina ceramic substrate; b) EDX image of electrodeposited pure Al; c) SEM image of Ag dendrite on porous AAO fabricated after anodizing of Al layer and d) Cross-sectional SEM image of SERS substrate obtained by focused ion beam.

In the next step, aluminum was electrodeposited galvanostatically from an ionic liquid (1-ethyl 3-methylimidazolium chloride-aluminum chloride; BASF, Germany) at current density of 20 $mAcm^{-2}$ for 30 minutes. The temperature of the ionic liquid was set at 85°C and the thickness of obtained Al layer was around 6 µm. The morphology of the obtained layer consisted of pure Al as shown by EDX analysis is presented in Fig. 2.a. Final step includes anodizing in tartaric-sulfuric acid.

A porous AAO of around 500 nm thickness and 50 nm pore size was formed under anodizing experiments carried out at 37° C at constant voltage of 14 v for 20 minutes reached after 5 minutes voltage ramp. Under these operating conditions, migration and diffusion of silver led to fabrication of nanostructured silver on porous AAO (Fig.2.c-d). Morphology of such dendrites with an example of one (Fig.2.c) fabricated on AAO template and cross-section of the SERS substrate is presented in Fig. 2.d.

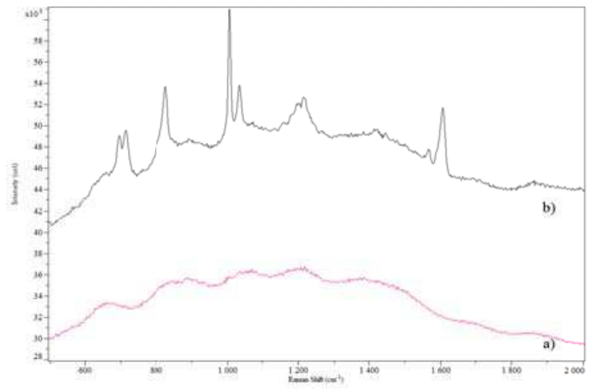

Fig.3. Raman spectra in the bulk state (a) in comparison to self-assembly monolayer formed on Ag dendrite (b) on porous anodic aluminum oxide template. The excitation wavelength is 633 nm.

SERS measurements of substrates fabricated as previously described were carried out after rinsing and sonication of a 100 µM of 1-phenylethyl mercaptan in methanol to ensure presence of monolayer only. Raman spectra show an enhancement when dendritic Ag is localized by optical focusing and compared to the rest of the substrate with nanostructured Ag distributed on porous AAO (Fig. 3). Thus lead to a conclusion that hot spots for SERS are three-dimensional dendritic structures causing strong field enhancement at the intersections of highly ordered branches.

References

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Acknowledgments

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