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Comparative analysis of SERS substrates of different morphology

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Abstract

In this work the surface enhanced Raman scattering (SERS) performance of gold coated patterned silicon surfaces of different morphology and period was investigated. Arrays of inverse pyramids, spheres and rounded pyramids of different sizes were fabricated by photolithography and selective etching. Thin layer of gold was sputtered onto the surface of the samples. The SERS performance of the substrates was tested using a highly dissolved organic solution.

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1. Introduction

Being a non-contact, fast and relatively easy materials characterization technique requiring no sample preparation Raman spectroscopy is finding many applications in biology and life sciences. However, Raman scattering is inherently weak, which prohibits its use for the analysis of low concentration analytes. Raman sensitivity can be improved by utilizing surface enhanced Raman scattering (SERS) [1], where the degree of achievable sensitivity can reach attomolar (10^{-18} M) concentrations, being observed in many cases [2]. As a spectroscopic tool SERS has the potential to combine the sensitivity of fluorescence with the structural information of Raman spectroscopy. During SERS the scattering takes place in close vicinity of nanostructures metallic surface (nanoparticle or some surface with nanoscopic morphology), and the interaction of the electromagnetic field of photons with the surface plasmons of the metal nanoparticles results in gain of the Raman signal, that can be several orders of magnitude. The key factor for successful SERS is to find appropriate SERS-active agents (nanoparticles or substrates) that will provide

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the required efficiency for a given excitation wavelength. In this work SERS active substrates of different size and morphology were prepared by lithographic technique from silicon with subsequent gold coating and tested for SERS enhancement performance using highly dissolved organic solution as test material.

2. Experimental

Arrays of inverse pyramids, spheres and rounded pyramids were prepared on polished silicon wafers using photolithographic technique. The surface was coated with an appropriate mask, in which shapes were created with 1x1 and 2x2 micron size and 3 micron period. Then isotropic and anisotropic etching and their combination were applied to the surfaces resulting in formation of arrays of hemispheres, inverse pyramids and rounded inverse pyramids, respectively. In the final step of the preparation the substrates were coated with a 40 nm thick sputtered layer of gold.

SERS measurements were carried out on a Renishaw 1000 micro-Raman spectrometer attached to a Leica DM/LM microscope. A 785 nm diode laser was used for the excitation and it was focused into a spot having diameter of 1 micron. Solution of benzene derivative (benzophenone) in isopropyl alcohol was used to test the SERS enhancement of the structures. The solution was dripped onto the array and the measurements were carried out after the evaporation of the solvent. Scanning electron microscopy was performed using a Jeol JSM-25 scanning electron microscope.

3. Results and discussion

Fig. 1 shows the scanning electron microscopic images of the prepared gold coated inverse hemispheres, rounded pyramids and pyramids, respectively. It can be seen that both the 1 and 2 micron base structures are of high uniformity. The isotropic and anisotropic etchings have different speed, resulting in structures of somewhat different size (especially in the case of the 1 micron samples), the largest inverse shapes were obtained with their combined application. The slowest etching was observed for the 1 micron inverse pyramids, where even no structures were formed on some areas of the silicon surface.

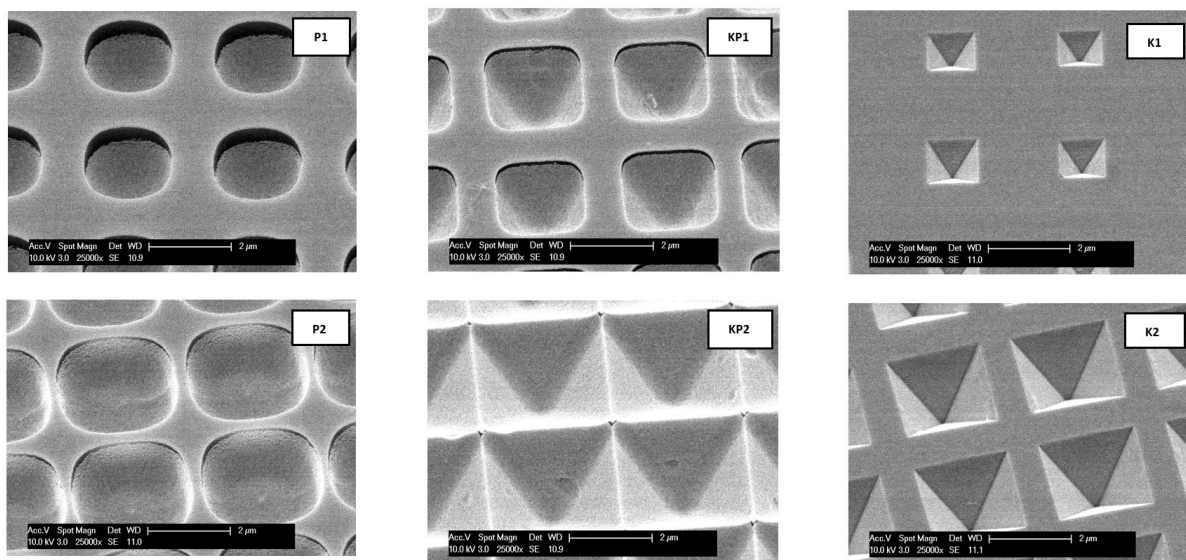


Fig. 1. Scanning electron microscopic images of gold coated inverse hemispheres (P1 and P2), rounded pyramids (KP1 and KP2), and pyramids (K1 and K2) etched from (upper row) 1x1 μm^2 and (lower row) 2x2 μm^2 opening windows.

The SERS spectra recorded on the samples are compared on Fig. 2. Some enhancement of the intensity was observed on all of the samples. The typical SERS enhancements, calculated from the intensity ratios of the same peak in the SERS and reference spectra were ranging from 10 to 100. However, this comparison with the reference spectrum does not reflect the exact SERS enhancement values, since the enhancement occurs only in the close vicinity of the metallic surface, but there is a significant non-SERS contribution from the part of the sample being out of the SERS enhancement region, which is present in both the SERS and the reference spectra and influences the intensity ratios and their comparison. Therefore, the SERS enhancements in Fig. 2 can be analyzed only relatively to each other.

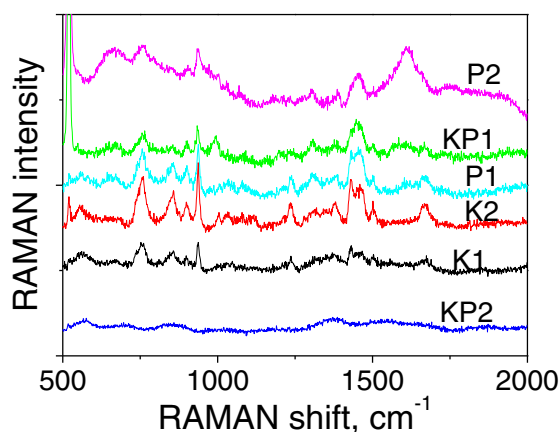


Fig. 2. Comparison of the SERS spectra recorded on different substrates with organic solvent of the same concentration. The spectra are baseline corrected.

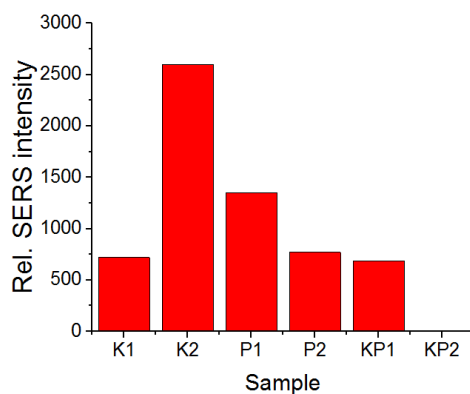


Fig. 3. Comparison of the relative SERS enhancements of the different SERS substrates. The y-axis represents the intensity of the 936 cm^{-1} peak in the SERS spectra of the test sample on different substrates.

Fig. 3 compares the relative SERS enhancements of the different substrates. It can be seen that the K2 sample has the highest efficiency, followed by the P1 with intensity being around half of the K2 substrate. The K1, P2 and KP1 surfaces have similar performance, while no SERS peaks were observed with the KP2 sample.

SERS spectra were also recorded on different parts of the inverse structures. It was found that the SERS efficiency has spatial dependence in these samples and higher enhancement was observed in the central parts of the inverse pyramids.

In some cases the spectra were dominated by strong photoluminescence (see KP2 on Fig. 2), overlapping the Raman bands. Interaction of the electromagnetic field of photons with the surface plasmons can enhance the photoluminescence, too. However, this effect is strongly distance-dependent and the photoluminescence is quenched near the metal surface [3], where the SERS has the highest efficiency. The strong photoluminescence and the lack of the Raman signal in these samples indicates the presence of some specific configuration and requires further investigations.

4. Conclusions

The SERS performance of gold coated patterned silicon surfaces of different morphology and size was investigated. Gold coated arrays of inverse pyramids, spheres and rounded pyramids of 1 and 2 micron base and 3 micron period were prepared and characterized. SERS enhancement was found on all of the samples, however, it was strongly dependent on the morphology and size of the SERS substrates.

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