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FOCUSED ION BEAM GRAPHENE PATTERNING AND NANOPARTICLE DEPOSITION FOR PLASMONIC APPLICATIONS

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Metal nanoparticles (NPs), especially those of coinage metals, attract a lot of attention for applications in sensing and imaging due to the phenomenon of localized surface plasmon resonance (LSPR) allowing to significantly increase the detection efficiency [1, 2]. For example, in surface enhanced Raman spectroscopy (SERS) an enhancement factor (EF) of 10^9-10^{10} can be reached using the matrixes with NPs, thus, pushing the detection limits to nano and pico mole concentrations of an analyte [2-4]. It was also shown that creation of so-called hot spots, the subwavelength regions of high electromagnetic field, further promotes SERS sensitivity [4, 5]. Therefore, a lot of research is currently focused on a design of plasmonic hot spots.

There are different approaches for formation of nanostructure arrays or aggregates enabling hot spots. One of the recent tendencies is to utilize graphene, a 2D material with a number of unique properties. It was shown that graphene is an excellent substrate for plasmonic NPs owing to its transparency and atomically thin nature [6]. There were several methods for deposition and anchoring of metal NPs developed also tuning the LSPR due to the interaction with graphene [7, 8]. An approach of the current paper authors proposes nanoscale modification of graphene by focused ion beam (FIB), formation of ordered arrays of defects (nanoholes), followed by deposition of size-selected silver NPs produced by gas-phase aggregation [9]. The gas aggregation method is known for the capability to synthesise very pure and monocrystalline NPs facilitating stability of their properties over long period of time [10, 11]. Randomly deposited NPs are tended to diffuse on atomically flat graphene surface until meeting the defect areas (holes) forming aggregates, which can serve as hot spots enhancing SERS. Preliminary results of this approach were published in [12] showing its efficiency. In the current work, further results on utilization of this approach are presented.

Commercial graphene (from Graphenea Semiconductor) grown by chemical vapour deposition on hBN/Si substrates was used. The patterns with arrays of nanoholes having periods of 170 and 300 nm were produced using focused Ga^+ ion beam with energy of 30 keV. Typical

atomic force microscopy (AFM) image of the pattern is shown in Figure 1. For comparison, the same patterns were also made on bare silicon surface. Silver NPs were produced utilising magnetron sputtering cluster apparatus (MASCA) [13], size-selected (approximately 15 nm in diameter) and soft-landed on both patterned Si and graphene. Size filtering was performed by electrostatic quadrupole mass selector. Therefore, the NPs under the deposition process were either positively or negatively charged. SERS properties were studied using Horiba LabRAM HR Evolution confocal Raman microscope utilizing laser with wavelength of 632.8 nm and power of 0.35 mW. The measurements were carried out on the samples kept in ambient atmosphere for 14 days after the fabrication, which were then covered by ethanol solution of Rhodamine 6G with 1 micromole concentration and dried under ambient conditions.

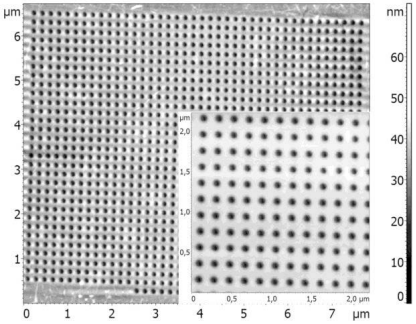

Figure 1. AFM image of hole array produced in graphene. Insert shows magnified area of the pattern.

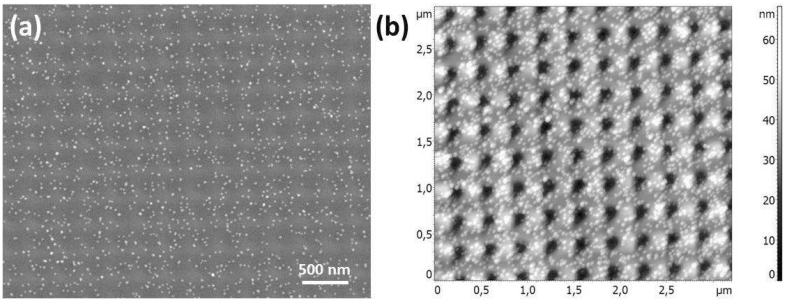

Figure 2. (a) Scanning electron microscopy (SEM) and (b) AFM images of Ag NPs on patterned Si.

As can be seen in Figure 2, the NPs deposited on patterned Si are located randomly with no gathering around the holes, i.e. not creating potential hot spots for SERS. For the case of graphene, an unexpected arrangement of the as-deposited NPs is found: the arrays of holes are

almost free of NPs while the surface around the patterns is densely covered by the NPs (Figure 3). The same phenomenon is found for both negatively and positively charged NPs. Thus, one can conclude that it is not related to a specific electrostatic charge, which could be created by the FIB treatment. The graphene areas modified by Ga^+ ions repel NPs of both polarities coming to the surface with so-called "thermal velocities", i.e. under the soft-landing conditions. The nature of this phenomenon is unclear and requires further investigation. Second round of deposition leads to an expected scenario; the NPs make aggregates in and around the holes within the patterned area while randomly located outside as can be seen in Figure 4(a). At room temperature, atomically flat graphene surface does not create significant diffusion barriers and Ag NPs can migrate over the distances of several tens nm becoming catch by the FIB-created defects.

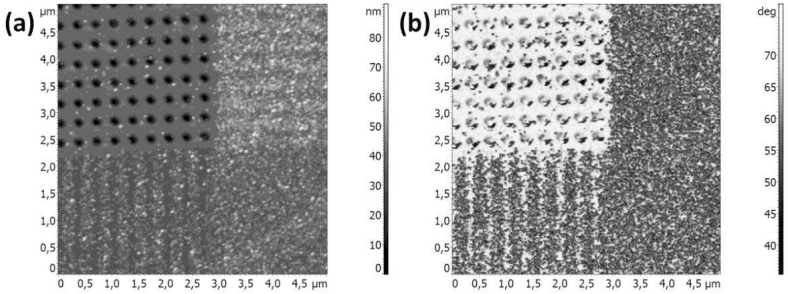

Figure 3. AFM (a) height and (b) phase images of Ag NPs on patterned graphene and around.

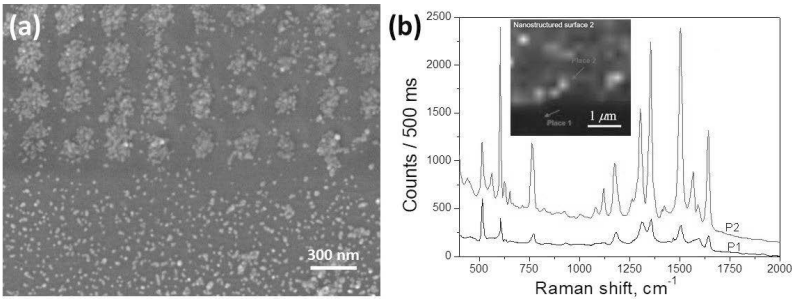

Figure 4. (a) SEM image of patterned graphene with Ag NPs aggregated in the holes (top) while randomly located outside the pattern (bottom) and (b) Raman spectra of Rhodamine 6G obtained from places outside P1 and inside P2 the patterned area. Insert shows SERS image for respective areas.

Typical SERS spectra obtained from the areas of unmodified graphene and nanostructured one both covered by Ag NPs are shown in Figure 4(b). For the unmodified graphene randomly

covered by the NPs (spectrum P1 in Figure 4(b)), the analytical EF [14] is estimated to be $\approx 4.7\times10^4$ compared to ordinary Raman measurements at the same experimental parameters, while for the area patterned by FIB with the NP agglomerates providing hot spots (spectrum P2 in Figure 4(b)) EF is calculated to be $\approx 2.8\times10^5$. The SERS image presented in insert of Figure 4(b) shows a considerable contrast between the patterned (top) and unmodified (bottom) graphene also indicating individual hot spots with very high intensity in the FIB-modified area.

In conclusion, the obtained results show that combining the graphene nanoscale modification using FIB with gas aggregated silver NP deposition provides an efficient way for the formation of matrixes with advanced plasmonic properties to be applied in sensing and imaging technologies.

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