Coupling of plasmon and grating resonances for SERS enhancement

S A Scherbak\textsuperscript{1,2}, E S Babich\textsuperscript{2}, I V Reduto\textsuperscript{1,2,3}, A A Lipovskii\textsuperscript{1,2}

\textsuperscript{1}Department of Physics and Technology of Nanostructures, St. Petersburg Academic University RAS, St. Petersburg 194021, Russia
\textsuperscript{2}Institute of Physics, Nanotechnology and Telecommunications, Peter the Great St. Petersburg Polytechnic University, St. Petersburg 195251, Russia
\textsuperscript{3}Institute of Photonics, University of Eastern Finland, Joensuu 80101, Finland

Abstract. We used thermal poling structuring of glass samples followed by chemical etching and subsequent out-diffusion growth of silver nanoparticles to fabricate periodic arrays of grooves etched in the glass with silver nanoparticles at their bottom. A numerical modeling of optical properties of these periodic structures was performed. We demonstrated that they support both plasmon and grating resonances, which interaction provides additional enhancement of an incident electric field. This can increase surface-enhanced Raman scattering by such biresonant structure.

1. Introduction

Metal nanoparticles, being able to greatly enhance electromagnetic field of an incident light wave because of surface plasmon resonance (SPR) phenomenon [1], are under extensive studies during last decades. Particularly, they have become almost irreplaceable for single-molecule sensing based on surface-enhanced Raman scattering (SERS) [2]. Nanostructures, which supports two or more different optical resonances (so-called biresonant structures), can provide additional enhancement of local electric field and, therefore, sensing efficiency. E.g., these are metal core - dielectric shell nanoparticles [3], bimetal nanostructures [4, 5], periodically arrayed plasmonic [6, 7] or dielectric [8] nanoparticles. Recently, nanostructures combining a plasmon mode of a metal nanosiland film with a grating resonance (GR) of an array of dielectric pillars were proposed for Raman enhancement [9]. However, the authors of [9] admit that the nature of this enhancement is unclear: it can be due to either the interaction of the SPR and the GR or the SPR and the spatial dielectric resonance of each pillar separately.

In the present study, we consider a similar nanostructure: a periodic array of grooves etched in glass, few hundred nanometers in depth, with silver nanoparticles at their bottom. By the results of a numerical modeling, we univocally identify plasmon resonances and grating resonances. We estimate the enhancement of the local electric field provided by the nanostructures and discuss possibilities of their applications in sensing. Undeniable advantage of these structures is that they can be fabricated within a unified technological process based on thermal poling structuring of the glass and out-diffusion growth of the silver nanoparticles [10, 11].

2. Fabrication technology

The technology that is used for fabrication samples under discussion consists of four subsequent steps. First is silver-to-sodium ion exchange of soda-lime glass in AgNO\textsubscript{3}-NaNO\textsubscript{3} melt. This way, glass
samples enriched with Ag⁺ ions are obtained. Second, the samples are subjected to thermal poling using a periodically profiled anodic electrode. The applied electric field arranges the Ag⁺ ions distribution in the glass. Third, we etch the samples in a NH₄F:8H₂O solution. The poling also results in the decrease of the etching rate of the poled regions of the glass, therefore, we obtain periodical grooves in the glass. Fourth, the samples are annealed in H₂ atmosphere. Hydrogen reduces Ag⁺ ions, and this leads to the self-assembled formation of Ag nanoparticles at the grooves bottom via out-diffusion process. The detailed and graphical description of the fabrication steps can be found in our previous works [10-12].

Using the described technology we fabricated a series of test samples and estimated their morphological properties with scanning electron microscopy (SEM). In Figure 1 we demonstrate examples of the SEM images obtained.

![SEM images of a periodic array of grooves in glass with silver nanoparticles at the grooves bottom; the period of the structure ~600 nm.](image)

The images in Figure 1 demonstrate decent quality of the samples fabricated. The grooves are reasonably even and periodic. Estimated depth of the grooves is about hundreds of nanometers and depends on the etching time. The width of the ribs and grooves depends on the design of anodic electrode used in the poling. In the zoomed image (the right one in Figure 1) one can see the ensemble of silver nanoparticles at the grooves bottom, the average diameter of which is less than 10 nm. However, the size of the particles can be controlled by the time and the temperature of the hydrogen annealing step of the technology described above. The favorable size of nanoparticle is 40-60 nm, since its SPR wavelength coincides with the wavelength of the laser commonly used in SERS (532 nm) [13]. Optimal fabrication regimes and SERS measurements are the subject of further studies.

### 3. Modelling and discussion

To simulate optical properties of the periodic structures under consideration we used finite elements method in COMSOL Multiphysics environment. We considered a single particle in each groove and neglected the interaction of the particles inside the same groove for simplicity since the aim of this model is to demonstrate the SPR and GRs interaction.

A spherical metal nanoparticle, 50 nm in radius, was placed at the centre of the bottom of a groove in glass with sidewalls 250 nm in height (see Figure 2). We used Drude dielectric function ($\lambda_p=300$ nm, $\gamma=10^{14}$ sec⁻¹) for the nanoparticle, dispersionless dielectric permittivity $\varepsilon_{sub}=2.25$ for the glass and $\varepsilon_{up}=1$ for the upper media (air). The incident light wave was directed normal to the groove bottom and polarized normal to the grating layers. Using periodic boundary conditions allowed us to model only a single cell of the array (it is marked with a dotted line in Figure 2).
We varied the excitation wavelength, and calculated the electric field enhancement by a single isolated nanoparticle, see Figure 3a. Here and further by the enhancement of the electric field we mean resulting electric field averaged over the particle surface and normalized by the magnitude of the incident wave. Then we calculated the field enhancement by the periodic structures of different period with nanoparticles of the same size and the same dielectric function, and normalized these by the maximal enhancement calculated for the isolated nanoparticle. Thus, the results obtained are easily comparable with the enhancement by the single isolated nanoparticle. The field enhancement vs. the grating period ($P$) and the excitation wavelength ($\lambda$) is presented in Figure 3b.

In Figure 3b one can find regions of the field enhancement, which correspond to different optical resonances. The almost horizontal branch relates to the ordinary SPR (the same one is marked in Figure 3a), which wavelength is around ~530 nm for the particle of the considered size and having the abovementioned dielectric function. The slant branches labelled as I, II and I* correspond to different GRs. Branch I is the GR corresponding to the wave interaction through the glass substrate. This branch precisely coincides with the line $\lambda/n_{\text{sub}}=P$, where $n_{\text{sub}}=\sqrt{\varepsilon_{\text{sub}}}$ . Branch I* is the second order of this resonance and it coincides with the line $2\lambda/n_{\text{sub}}=P$. This GR is faint since it occurs at high periods when the particles in the lattice interact weakly, and its impact will not be considered further. Branch II matches with the GR corresponding to the interaction through the upper environment: $\lambda/n_{\text{up}}=P$. 

**Figure 2.** Scheme of the structure; the dotted line indicates a single period.

**Figure 3.** (a) Spectrum of the electric field enhancement by the single isolated nanoparticle (out of the grating). (b) The electric field enhancement in the periodic structure vs. the period ($P$) and the excitation wavelength ($\lambda$); The dependence is normalized by the maximal resonant enhancement of the electric field by the same nanoparticle.
where \( n_{\text{up}} \) is an effective refractive index of the upper medium that consists of glass layers and air spacers, therefore \( n_{\text{up}} \) is somewhere in between of \( n_{\text{sub}} \) and 1.0. Note that \( n_{\text{up}} \) depends on \( P \), and for periods much larger than the height of the glass layers (700-800 nm and more) \( n_{\text{up}} \) tends to 1.0. However, at such periods nanoparticles barely feel each other in the lattice, and for the considered periods \( n_{\text{up}} \) can be roughly estimated as \( n_{\text{up}} \approx (1.0+1.5)/2=1.25 \).

The combination of the resonances described above can be used to strengthen a SERS signal. When the SPR coincides with a GR (intersection of the SPR branch with branches I and II), the noticeable field enhancement occurs: about 1.6-fold for branch I and 1.3-fold for branch II. Note that this was calculated relatively to the maximum enhancement of the isolated particle, e.g. if the isolated particle at the SPR 10-fold enhances the electric field, then in the present cases the enhancement will be by 16 and 13 times, respectively. This can result in 3-5 times increase of the SERS efficiency compared to isolated metal nanoparticles.

The other way is, contrary, to spectrally separate these resonances to enhance the electric field at different wavelengths. This is relevant to nonlinear processes, in which light waves of different frequencies participate. Particularly, power of a SERS signal is defined by the enhancement of the electric field at the excitation wavelength and at the wavelength shifted by the Raman offset \( \Delta \lambda \):

\[
I_{\text{SERS}} \propto |E(\lambda)|^2 |E(\lambda+\Delta \lambda)|^2.
\]  

(1)

Commonly, only \( E(\lambda) \) is plasmon-enhanced, whereas \( E(\lambda+\Delta \lambda) \) is non-resonant. However, using such biresonant structures one can resonantly enhance both \( E(\lambda) \) and \( E(\lambda+\Delta \lambda) \), adjusting \( \lambda \) to \( \lambda_{\text{SPR}} \) and \( \lambda+\Delta \lambda \) to \( \lambda_{\text{GR}} \). The GRs only depend on the structure period and can be relatively easy tuned to the desired wavelength. Also, their magnitude is comparable to the one of the SPR (see Figure 3b). Therefore, this would greatly increase the selectivity of sensing and is applicable for SERS spectroscopy aimed at sensing of specific substances. The spectrum of the electric field enhancement by the structure with period of 510 nm is presented in Figure 4. The period \( P=510 \) nm was chosen for demonstration purposes to adjust the GR (branch II in Figure 3b) to the Raman-shifted wavelength of dye BPE (\( \Delta \lambda \approx 1640 \) cm\(^{-1} \)) – a well-known substance that is typical for gauge of SERS setups.

Figure 4. Spectrum of the electric field enhancement by a periodic structure with period \( P=510 \) nm (solid line); dashed line indicates single-resonant enhancement by the isolated particle.
According to Figure 4 $E_{\text{bires}}(\lambda+\Delta\lambda) \approx 1$, whereas $E_{\text{single}}(\lambda+\Delta\lambda) \approx 0.3$. Therefore, according to Eq. (1) and assuming that the isolated nanoparticle and the biresonant structure at ordinary SPR enhance the field approximately equally, the biresonant nanostructure provides about 10-fold increase of SERS signal ($|E_{\text{bires}}(\lambda+\Delta\lambda) / E_{\text{single}}(\lambda+\Delta\lambda)|^2 \approx 10$).

4. Conclusion
We proposed biresonant nanostructures that comprise arrays of metal nanoparticles in periodic grooves in glass. Test samples were successfully fabricated using the unified technological process based on thermal poling structuring of the glass and out-diffusion growth of silver nanoparticles. The morphological analysis with SEM demonstrated their descent quality.

Performed numerical modelling revealed different kinds of optical resonances the structures under discussion possess: the ordinary surface plasmon resonance that only depends on nanoparticles’ properties and the grating resonances that defined by the period of the nanostructures. The combination of SPR and GRs results in 1.3-1.6-fold increase of electric field enhancement compared to isolated nanoparticles. Therefore, such structures can be up to 3-5 times more efficient for SERS applications. Also, we demonstrated that in this biresonant structure the electric field at both fundamental and Raman-shifted wavelengths can be resonantly enhanced at the SPR and at the GR, respectively. This should provide at least more than an order of magnitude increase in SERS sensing of specific substances.

Acknowledgement
This study was funded by RFBR according to the research project № 18-32-00097

References
[1] Shahbazyan T V and Stockman M I 2013 Plasmonics : Theory and Applications (Dordrecht: Springer Netherlands)
[2] Prabowo B, Purwidyantri A and Liu K-C 2018 Surface Plasmon Resonance Optical Sensor: A Review on Light Source Technology Biosensors 8 80
[3] Scherbak S A and Lipovskii A A 2018 Understanding the Second-Harmonic Generation Enhancement and Behavior in Metal Core–Dielectric Shell Nanoparticles J. Phys. Chem. C 122 15635–45
[4] Babich E, Redkov A, Reduto I and Lipovskii A 2018 Self-Assembled Silver-Gold Nanoisland Films on Glass for SERS Applications Phys. status solidi - Rapid Res. Lett. 12 1700226
[5] Okuno Y, Nishioka K, Kiya A, Nakashima N, Ishibashi A and Niidome Y 2010 Uniform and controllable preparation of Au–Ag core–shell nanorods using anisotropic silver shell formation on gold nanorods Nanoscale 2 1489
[6] Zou S and Schatz G C 2006 Theoretical studies of plasmon resonances in one-dimensional nanoparticle chains: narrow lineshapes with tunable widths Nanotechnology 17 2813–20
[7] Khlopin D, Laux F, Wardley W P, Martin J, Wurtz G A, Plain J, Bonod N, Zayats A V, Dickson W and Gérard D 2017 Lattice modes and plasmonic linewidth engineering in gold and aluminum nanoparticle arrays J. Opt. Soc. Am. B 34 691-700
[8] Rendell R W, Shirey L, Long J P, Guo J, Glembocki O J, Caldwell J D, Owrtusky J C, Bezares F J and Kasica R 2013 Mie resonance-enhanced light absorption in periodic silicon nanopillar arrays Opt. Express 21 27587
[9] Kukushkin V I, Grishina Y V, Egorov S V, Solov’ev V V and Kukushkin I V 2016 Combined dielectric and plasmon resonance for giant enhancement of Raman scattering JETP Lett. 103 508–12
[10] Redkov A V, Zhurikhina V V and Lipovskii A A 2013 Formation and self-arrangement of silver nanoparticles in glass via annealing in hydrogen: The model J. Non. Cryst. Solids 376 152–7
[11] Zhurikhina V V, Brunkov P N, Melehin V G, Kaplas T, Svirko Y, Rutkaia V V and Lipovskii A A 2012 Self-assembled silver nanoislands formed on glass surface via out-diffusion for multiple usages in SERS applications Nanoscale Res. Lett. 7 1–5

[12] Redkov A, Chervinskii S, Baklanov A, Reduto I, Zhurikhina V and Lipovskii A 2014 Plasmonic molecules via glass annealing in hydrogen Nanoscale Res. Lett. 9 606

[13] Babich E S, Redkov A V, Reduto I V, Scherbak S A, Kamenskii A N and Lipovskii A A 2017 Raman enhancement by individual silver hemispheroids Appl. Surf. Sci. 397 119–24