Formation and SERS efficiency of periodic metal-dielectric nanostructures

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Abstract. We studied silver nanoparticles combined with periodic gratings on a glass surface.
The gratings were fabricated by selective etching of the glass slide patterned by thermal poling.
The nanoparticles were grown on the bottom of the gratings’ grooves by out-diffusion
technique. Obtained nanostructures supported both plasmonic and grating optical resonances
and demonstrated SERS enhancement two times higher than one of the pure plasmonic
structure.

1. Introduction
Surface enhanced Raman scattering (SERS) spectroscopy is an analytical tool widely used in chemical
biology and medical diagnostics to identify molecular species down to the lowest concentrations [1].
The identification is based on the detection of Raman scattering attributed to the molecule vibrations
and enhanced by optically excited metal nanoparticles (NPs). The maximal enhancement is achieved
when NPs are excited by a laser radiation at the NPs’ surface plasmon resonance (SPR) wavelength.
Therefore, metal nanostructures-based SERS substrates providing high-quality Raman signal from
analytes absorbed on their surface are being actively developed [2]. Additional increase of Raman
signal can be achieved by using biresonant nanostructures [3,4], which support two optical resonances.
Intensity of Raman signal is defined by the enhancement of electric field \( E \) at the excitation
wavelength \( \lambda_0 \) and at the wavelength shifted by the Raman offset \( \Delta \lambda \) for a particular \( \lambda_0 \):

\[
I_{\text{SERS}} \sim |E(\lambda_0)|^2 |E(\lambda_0 + \Delta \lambda)|^2.
\]

Thus, the resonances, being tuned to specific wavelengths, can provide enhancement of both exciting
(\( \lambda_0 \)) and scattered radiation (\( \lambda_0 + \Delta \lambda \)) increasing Raman sensitivity towards a specific molecule.

The present study is devoted to the fabrication and SERS performance of the biresonant structures
which are periodic grooves (gratings) on a glass surface with silver nanoparticles at their bottom.

2. Experiments
We fabricated biresonant structures using the four-step technique of soda-lime glass modification
described in detail in our previous work [5]. We used “Menzel” microscopic glass slides [6] and
subjected them to silver-to-sodium ion-exchange in 5wt.%AgNO₃-95wt.%NaNO₃ melt to enrich
subsurface layers with silver ions. Then we thermally poled the slides at 300V and 300°C for 5 min using an anodic electrode with grooves to form an accordant silica-like pattern and a silver ions distribution profile in the subsurface layer of the glass, for silica-like regions successfully prevent the penetration of silver ions into the glass. There were two sets (S1 and S2) of the grooves on the electrode surface: S1 with 250 nm deep 300 nm wide grooves periodically separated by 300 nm gap (grating with period 600 nm), and S2 with 400 nm wide grooves separated by 400 nm gap (grating with period 800 nm), the length of each groove was 2.5 mm. Sodium and silver ions in the regions of the glass brought in contact with the electrode (out of a groove) were drifted from the anodic surface to the bulk of the glass, and an ions-depleted (silica-like) glass layer was formed. It should be mentioned that the resulted silica-like pattern on the glass is not just an exact replica of the electrode relief but reflects spatial distribution of the applied DC electric field which is stronger near the edges of the grooves of the electrode [7]. The pattern was acid resistant, and the following etching for 10 min in 0.1wt.%HF-11.1wt.%NH₄F-88.8wt.%H₂O solution resulted in the formation of the gratings’ relief on the glass surface. The last step was annealing the samples in a H₂ atmosphere at 400°C for 10 min. Hydrogen reduced silver ions, and silver NPs were formed via out-diffusion process, partly in the glass bulk, but mainly at the bottom of the grooves.

The optical studies of the prepared nanostructures were performed using the normally incident light polarized parallel and perpendicular to the gratings’ grooves. SERS efficiency of the nanostructures was evaluated using the test analyte, BPE (1,2-Di(4-pyridyl)ethylene 97%), under excitation at \( \lambda_0=532 \) nm laser wavelength. The droplet of the analyte was dried on the surface of the nanostructures forming a thin layer of BPE with surface concentration \( \sim 10 \) nmol/mm².

3. Results and discussion

According to the modelling [4], biresonant structures under discussion demonstrate both plasmonic and grating [8] optical resonances. The spectral position of the grating resonance can be tuned by varying the grating period, while the SPR wavelength of silver NPs depends on their size. Thus, the highest enhancement of Raman BPE band at 1640 cm⁻¹ (\( \Delta \lambda \sim 50 \) nm) can be provided when the SPR wavelength coincides with the laser excitation wavelength \( \lambda_0 \) and the grating resonance wavelength is adjusted to the Raman-shifted wavelength (\( \lambda_0 + \Delta \lambda \)) (see equation (1)). The corresponding grating period is \( P=510 \) nm (groove depth 250 nm) and the radius of hemispherical silver NPs is \( R=50 \) nm. The prepared structures were the grating with period \( P=590\pm20 \) nm and hemispherical [9] silver NPs of average radius \( R=35 \) nm (S1), and the grating with \( P=780\pm45 \) nm and \( R=20 \) nm (S2). The depth of the gratings’ grooves on the glass surface was 250±10 nm. SEM images of the prepared structures are demonstrated in figure 1. Thus, S1 parameters were close to the modeled ones, while S2 was mismatched with the model. Therefore, S1 should provide an additional enhancement of Raman signal and significant increase of selectivity of BPE sensing, comparatively to S2.

![Figure 1](image_url). SEM images of the gratings on the glass surface with silver NPs at their bottom fabricated using the anodic electrode patterned as grating with period 600 nm S1 (a) and 800 nm S2 (b). The measured grating period, \( P \), and the average NPs’ radius, \( R \), are denoted.

We illuminated the samples with the white light polarized perpendicular (“perpendicular polarization”) and parallel (“parallel polarization”) to the gratings’ grooves, collected corresponding extinction spectra and compared the responses. The extinction was higher in the case of the
“perpendicular polarization”, since the interaction between the periods in the grating is stronger than in the “parallel polarization” case and the periodic properties are more pronounced. We subtracted the “parallel polarization” spectra from the “perpendicular” ones. The resulted differential spectra are shown in figure 2. Each spectrum demonstrates two resonant peaks. The short-wavelength peaks at 496 nm and 446 nm in S1 and S2 spectra, respectively, correspond to the SPR of the silver NPs on the glass surface (at the bottom of the grooves) [10]. The long-wavelength peaks at 618 nm and 830 nm are attributed to the grating resonances in accordance with the equation:

$$\lambda_{GR} = d \cdot n_{eff},$$

where \(d\) is the grating period and \(n_{eff}\) is effective refractive index of the grating. Basically, equation (2) is the condition of diffraction in the lateral plane. The effective refractive index of the fabricated structures was evaluated as follows:

$$n_{eff} = n_{glass} \cdot (1 - x) + 1.0 \cdot x.$$  (3)

where \(x\) is the ratio of the groove width to the period and \(n_{glass} = 1.5\) is the glass refractive index. Since the silica-like pattern on the glass did not exactly repeat the electrode relief, the etched grooves were wider than gaps between them, so the glass made up less than a 50% share of the grating structure. The effective refractive index for both S1 and S2 was \(~1.2\pm0.1\).

We conclude that sample illumination with light polarized perpendicular to the grooves results in the grating resonance excitation and additional enhancement of the SPR. The increase in the grating period (see S2 in figure 2) results in red-shift of the grating resonance wavelength and a significant decrease in the SPR enhancement. We suppose that random distribution of NPs inside the broad grooves (due to the larger grating period) degrades grating properties.

![Figure 2. Extinction spectra of the gratings with different periods on the glass surface with silver nanoparticles in the gratings’ grooves. The periods (P), the surface plasmon resonances (SPR) and the grating resonances (GR) are denoted.](image)

We compared the Raman enhancement provided by S1 and S2 in different excitation configurations (see figure 3). SERS spectra were measured under excitation by “perpendicular” and “parallel” polarized laser radiation. Note, that Raman enhancement in the case of “parallel polarization” is provided by the silver nanosiland film on the glass surface at the bottom of the grooves, which supports only the SPR, while at the “perpendicular polarization” the grating resonance is excited as well. The Raman integral intensities were calculated through numerical integration over BPE band of fixed width 11 cm\(^{-1}\) at 1640 cm\(^{-1}\) (see table 1). S1 demonstrates two times higher Raman enhancement when both plasmon and grating resonances are excited (“perpendicular polarization”). The signal-to-noise ratio in SERS spectra is also higher for the “perpendicular polarization” (see figure 3). Thus, S1 demonstrates sensing selectivity towards BPE that corresponds to performed modelling of the biresonant structure with similar parameters.

The sample with the larger grating period (S2), which parameters mismatched with the model, demonstrated no difference in Raman integral intensities collected under “parallel” and “perpendicular polarization” (see table 1). Thus, as expected, there were no additional enhancement of Raman
scattering due to the excitation of the grating resonance and related selectivity towards BPE molecules.

![Figure 3. SERS spectra of S1 collected using light polarized parallel (blue dotted line) and perpendicular (red solid line) to the grating grooves. Excitation wavelength is 532 nm. Inset: scheme of electric field orientation relative to grating.]

**Table 1.** Integral intensity of the BPE Raman band at 1640 cm$^{-1}$ obtained for S1 and S2 under excitation by laser radiation polarized perpendicular and parallel to the gratings’ grooves.

|       | “Perpendicular polarization” | “Parallel polarization” |
|-------|------------------------------|-------------------------|
| S1    | 1187 a.u.                    | 675 a.u.                |
| S2    | 1477 a.u.                    | 1450 a.u.               |

It should be noted, the increase in the grooves’ width in S2 results in the formation of the silver nanoisland film with morphology (average radius, size dispersion, density, etc.) different from one observed in S1 (see figure 1). Therefore, the comparison of Raman enhancement provided by S1 and S2 is out of the question.

We acknowledge that the fabrication technique, being based on self-assembly, has a reproducibility issue. This issue is currently under study.

**4. Conclusion**

It is experimentally demonstrated that the gratings on a glass surface combined with silver nanoparticles support two optical resonances: the surface plasmon resonance of the silver nanoparticles and the grating resonance. These biresonant structures are two times more SERS-efficient than a similar one-resonance plasmonic system due to the increased sensing selectivity towards specific molecules.

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