Giant field fluctuations in dielectric metamaterial and Raman sensor

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ABSTRACT

New dielectric metamaterial based on the Bragg filter comprising ten dielectric bilayers was investigated. Each bilayer is the thin films of silicone dioxide (SiO_2) and another film of zirconium dioxide (ZrO_2). The surface of the multilayer film is profiled. It has a form of periodic system of rectangles separated by the open gaps. We use the computer simulation as well as analytical solution to find the reflectance of the multilayer as a function of the wavelength and electromagnetic (em) field distribution. The multilayer system reveals the enhancement of em fields at the surface. The considered Bragg filter was modified by Raman-active structure made of gold nanoparticles with chemically attached 3,3-thio-bis(6- nitrobenzoic acid) - (TNB). The high Surface Enhanced Raman Scattering (SERS) signal was detected.

Keywords: Dielectric metamaterial, field enhancement, SERS

1. INTRODUCTION

The optical response of metal nanostructures and its resonance effects, which are associated with surface plasmons (SP) excitation have attracted significant attention due to exciting practical applications in optical filters,[1] subwavelength optical waveguides,[2] SERS[3] et al. SERS being the most powerful analyte instrument for the effective chemical and biological analysis potentially results in the appearance of the high technological optical sensors.[7] Such sensors are based on the generation of different plasmon modes in the metal surfaces and further Raman scattering of these plasmons on molecules.The basic element of the detecting system is the SERS substrate, which typically is a matrix of the metallic inclusions fabricated from Au or Ag. The quality as well as absolute value of Raman signal strongly depend on the arrangement, shape, size and chemical composition of the substrate structure. Therefore the substrates based on dielectric resonators could decrease internal absorption and increase the efficiency of the sensors. The inclusions can be considered as nanoscaled antennas, which concentrate the incident radiation. The collective electromagnetic (em) field is excited as result of the interaction of the incident light with metallic and dielectric inclusions. The em field oscillations have several resonance frequencies and the local field is much enhanced with respect to the incident field. In this paper we investigate SERS active dielectric substrate fabricated from thin-film multilayer.

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2. BRAGG FILTER

2.1 Multilayer

Let us consider a thin-film multilayer comprising 10 bilayers characterized by index of refraction n_1, n_2, and thicknesses d_1, d_2, placed on semi-infinite substrate with refractive index n_0. The reflectance of the multilayer can be simply analytically solved from the Fresnel equations.[4] Figure 1 presents the calculated and measured reflectance spectra of the multilayer comprising 10 bilayers of zirconium dioxide (ZrO_2) and silicium dioxide (SiO_2) placed on aluminium substrate. The summarized thickness of the multilayer $\approx 2.6\,\mu$. Here n_1=n_{ZrO_2} is the refractive index of zirconium dioxide (ZrO_2), n_2=n_{SiO_2} - is the refractive index of silicium dioxide (SiO_2). The refractive index for aluminum was taken from.[5] The analytical reflectance shows the almost complete blockage of the incident wave at free-space wavelengths in the neighborhood of $600 - 820\,nm$. The experimental reflectance has a smaller amplitude due to the natural roughness and an absorption.[9]

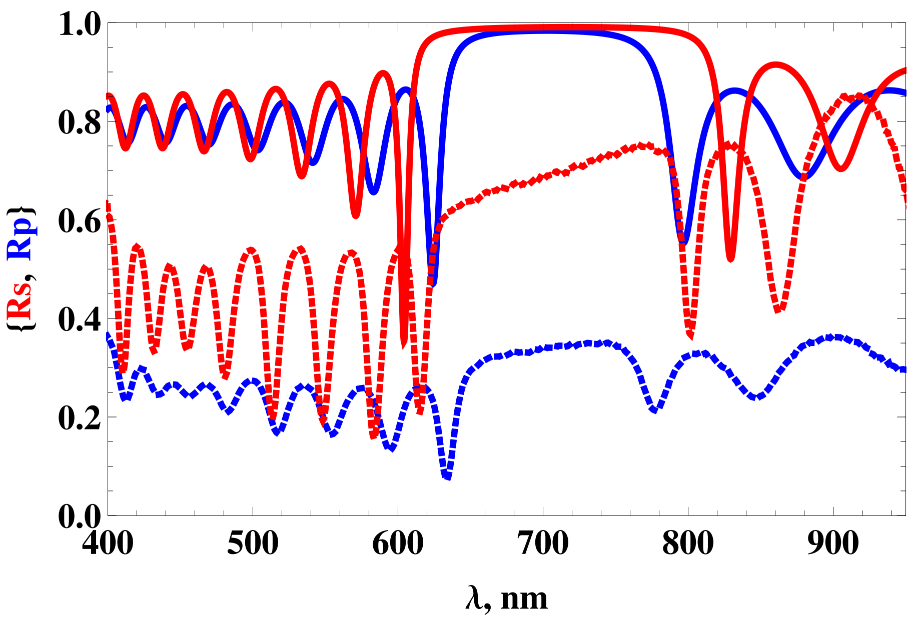

Figure 1. The calculated (solid lines) and measured (dotted) reflectance of the multilayer as a function of the free-space wavelength λ for angle of incidence ϕ=45 deg for s- (red) and p- (blue) polarized waves. The other parameters $d_1 = 97\,nm$, $d_1 = 129\,nm$, $n_{Zr} = 2.035$, $n_{Si} = 1.45376$.

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2.2 Surface periodic structure

The surface of the multilayer comprising 10 bilayers of silicone dioxide (SiO_2) and zirconium dioxide (ZrO_2) was modified so to create a periodic system of rectangle structures with width $1\,\mu$ segregated by the gaps with width $100\,nm$ and depth $\approx 1.5\,\mu$. The electrodynamics of periodic dielectric rectangles was modeled by using COMSOL package. Both the s- and -p polarization case are considered. The -s wave has the electric field component in the z direction, out of the modeling xy-plane. For the -p wave, the electric field vector is pointing in the xy-plane and perpendicular to the direction of propagation, whereas the magnetic field has only a component in the z direction.

The wavelengths involved in the model are sufficiently short compared to the grating constant, therefore the diffraction orders are presented. The criterion for positive interference is that the difference in optical path length along the two paths equals an integer number of vacuum wavelengths:

$$m\lambda = dn_\phi(sin\phi_m - sin\phi) \tag{1}$$

where ϕ - is the angle of incidence, ϕ_m is the reflected beam of diffraction order m, $m = 0, \pm1, ..\lambda$. It should be mentioned that most of optical devices require the normal incidence because of practical convenience. Thus, the calculated summarized reflectance for diffracted orders $m = 0, \pm1, \pm2$ for -p and -s polarized waves is shown in Fig. 2. The minima in the reflectance spectrum correspond to the frequencies of excitation of dielectric resonances where electric field is much enhanced (Fig. 3, 4). The value of the enhancement for -s polarization more than twice larger with respect to p- polarization.

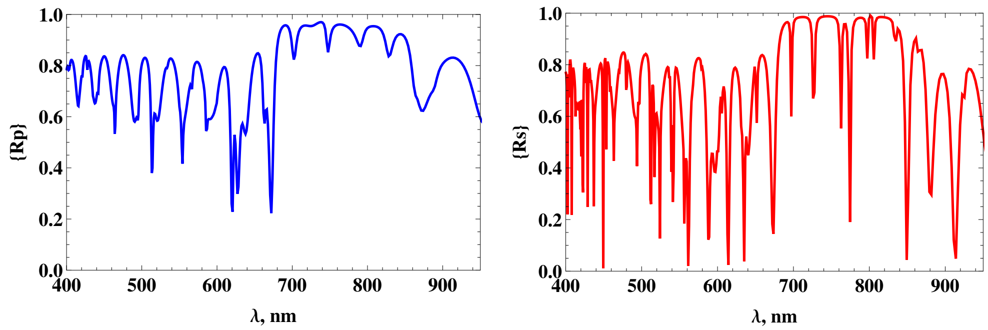

Figure 2. (a) Calculated reflectance as a function of the free-space wavelength λ for normal incidence (ϕ=0 deg) for p- (a) and s- (b) polarized wave. The other parameters: grating constant d=1100 nm, inter-gap spacing δ=100 nm, depth of the cavities l=1582 nm.

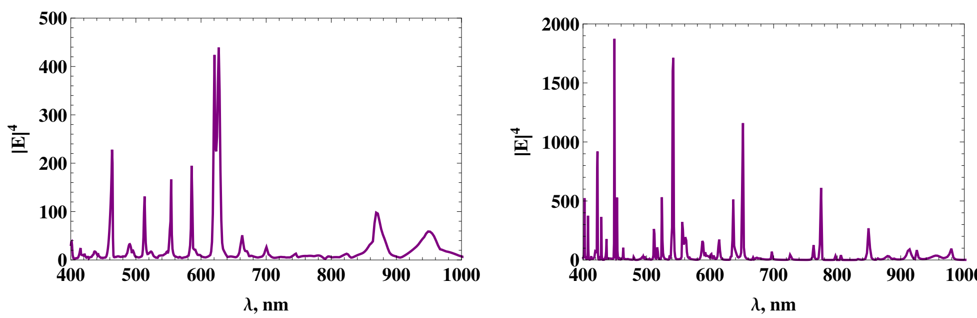

Figure 3. The maximum surface electric field $|E/E_0|^4$ as a function of free-space wavelength for normal incidence (ϕ=0 deg) for p- (a) and s- (b) polarized waves.

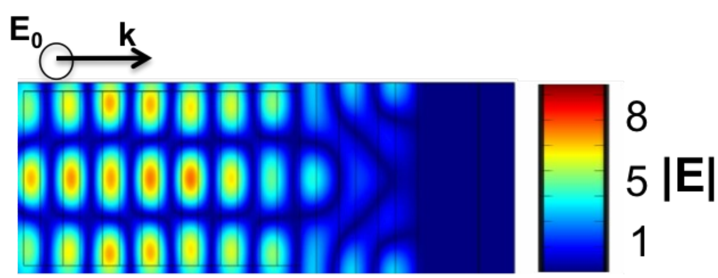

Figure 4. Electric field distribution $|E/E_0|$, $\lambda = 0.774\mu m$, $\phi = 0$ deg for -s wave in the unit cell.

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Our computer simulations show the surface structure result in the em field $G = |E/E_0|^4 \approx 10^3$ enhancement of due to excitation of dielectric resonances (Fig. 3).

3. SERS

3.1 SERS preparation

The surface of the multilayer comprising 10 bilayers of silicone dioxide (SiO2) and zirconium dioxide (ZrO2) was modified by FIB-assisted modification so to create a periodic system of rectangle structures with width

$1\,\mu$segregated by the gaps with width $100nm$ and depth $\approx 1.5\,\mu$. The morphology of the surface nanostructures was studied by scanning electron microscopy (SEM) using a Quanta microscope (FEI) with resolution near $5\,nm$ (Fig. 5). The periodic surface structures with summarized dimensional size $500 \times 250\,\mu$ were obtained by systematic etching with beam current 790 pA.

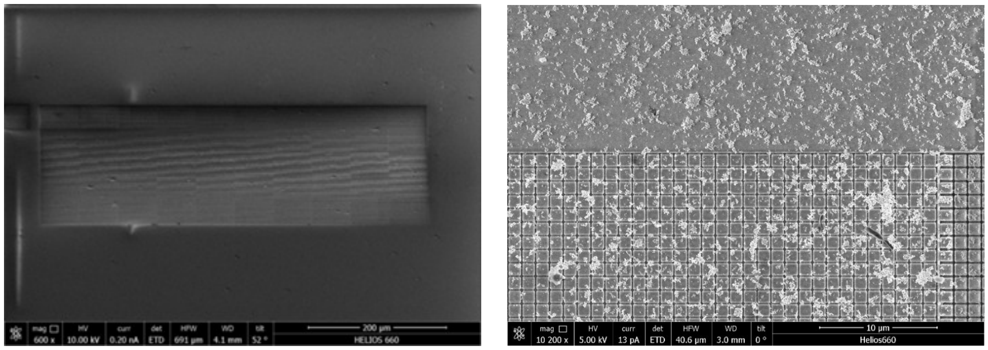

Figure 5. a) SEM images of the surface periodic structure. b) SEM images of surface periodic structure with immobilized Au-NP.

The gold nanoparticles (Au-NP) with average size $56\,nm$ were prepared by citrate method.[6] For the preparation of SERS active particles, Au-NPs were modified by 3,3-thio-bis(6- nitrobenzoic acid) - (TNB).[7] Au-NPs were adsorbed onto the surface periodic structure after deposition of polycation (poly(diallyldimethylammonium chloride)) according to the procedure described in the article[8] (Fig. 5)

3.2 SERS specta

A Raman spectrometer WITec with continuous-wave laser-785 (<250 mW) was used for the collection of spectra using an excitation wavelength of $785\,nm$. The excitation was performed in an epi configuration through a 100X objective (NA= 0.9) on a microscope. 1338 cm^{-1}. Raman scattering NO_2 band of thio 6-nitrobenzoic acid was used to investigate the SERS signal.The intensity distribution in the chosen band at the surface structure was compared with the intensity distribution at the neighboring area near the structure. Figure. (6) demonstrates the relative value of intensity of TNB Raman signal in the surface structure (red line) with respect to neighboring region (blue line). The optical mapping of the intensity distribution for band 1338 cm^{-1} is shown in Fig (7). We demonstrate huge enhancement of the intensity distribution in the surface structure with respect to neighboring region. To estimate the value of enhancement, the signal was normalized to the density of immobilized gold nanoparticles. It was shown that the enhancement of Raman signal at the structure area 2.5 times larger with respect to the neighboring area.

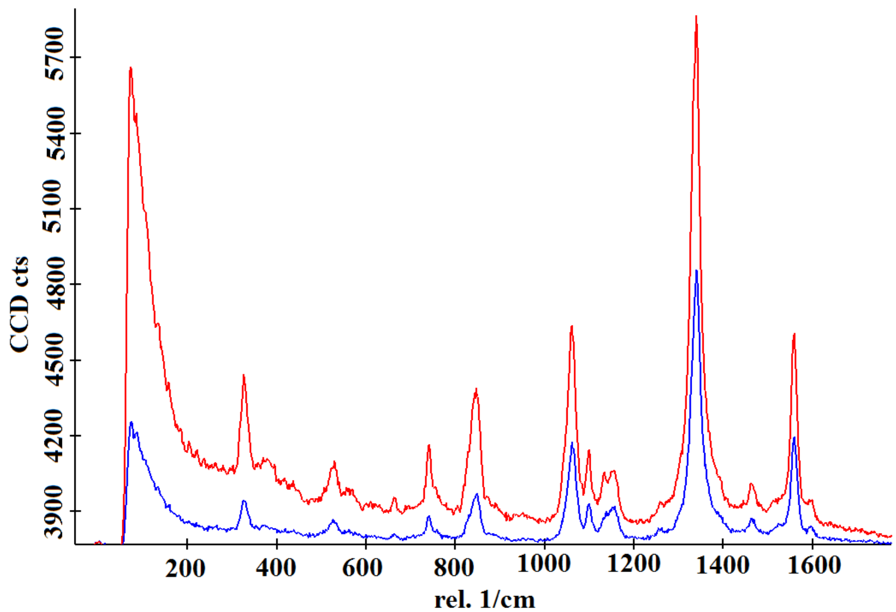

Figure 6. Raman signal of TNB for the surface structure (red line) and for the neighboring region (blue line).

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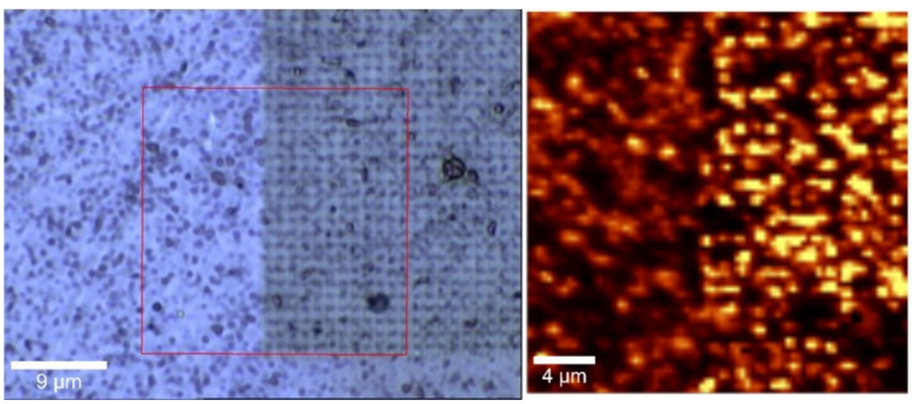

Figure 7. The optical mapping of the intensity distrubution for Raman band 1338 cm^{-1}. The parameters of mapping: scan dimensions 25mkm x 25 mkm, step of scanning $\approx 0.33\,\mu$. The excitation was performed in an epi configuration through a 100X objective (NA= 0.9) on a microscope WITec.

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4. CONCLUSION

The dielectric metamaterial fabricated from thin-film multilayer comprising 10 bilayers of silicone dioxide (SiO_2) and zirconium dioxide (ZrO_2) placed on aluminium substrate was investigated. The multilayer behaves as a good Bragg filter showing the almost complete blockage of an incident wave at free-space wavelengths in the neighborhood of $600 - 820\,nm$. The modified multilayer with cavities exhibits the enhancement of the em field in the surface structure due to excitation of dielectric resonances. The hot spots are localized at the face side of the surface. The SERS signal, characterized by factor G reaches the value $G = |E/E_0|^4 = 10^3$. The results of our analytical and numerical calculations are in a good agreement with the experimental results. It was shown from the mapping analysis that the SERS signal intensity from TNB is 2.5 times larger in the case of modified multilayer with gold nanoparticles that are immobilized on its surface. We suggest using the proposed metamaterial as a core of the high sensitive optical sensing device. The resonance frequencies can be tuned by variation of the shape of the surface.

REFERENCES

1. X. Lin and S. Lan, "Design of optical filtes with flat-on-top transmission lineshapes based on two-side-coupled metallic groves", *Plasmonics* **8**, pp. 283–287 (2013).
2. K. MacDonald, Z. Samson, M. Stockman and N. Zheludev, "Ultrafast active plasmonics", *Nat. Photonics* **3**, pp. 55–58 (2008).
3. J. Li, Y. Huang, Y. Ding, Z. Yang, S. Li, X. Zhou, F. Fan, W. Zhang, Z. Zhou, D. Wu, B. Ren, Z. Wang and Z. Tian, "Shell-isolated nanoparticle-enhanced Raman spectroscopy", *Nature Lett.* **464**, pp. 392–395 (2010).
4. E. Palik, "Handbook of optical constants", Elsevier Science, USA (1991).
5. O. Lecarme, Q. Sun, K. Ueno and H. Misawa, "Robust and versatile light absorption at near-infrared wavelengths by plasmonic aluminium nanorods", *ACS Photonics* **1**, pp. 538–546 (2014).
6. J. Turkevich, P. Stevenson and J. Hiller, "A study of the nucleation and growth processes in the synthesis of colloidal gold", *Discuss. Faraday Soc.* **11**, pp. 55–75 (1951).
7. I. Kurochkin, I. Ryzhikov, A. Sarychev, K. Afanasiev, I. Budashov, M. Sedova, I. Boginskaya, S. Amitonov and A. Lagarkov, "New SERS-active junction based on cerium dioxide facet dielectric films for biosensing", *Advanced Electromagentics* **3**, pp. 57–60 (2014).
8. M. Gromova, L. Sigolaeva, M. Fastovets, E. Evtushenko, L. Babin, D. Pergushov, S. Amitonov, A. Eremenko and I. Kurochkin, "Improved absorption of choline oxidase on a polyelectrolyte LBL film in the presence of iodine anions", *Soft Matter.* **7**, 7404–7409 (2011).
9. S.Kim, H. Ee, W. Choi, S. Kwon, J. Kang, Y. Kim, H. Kown and H. Park "Surface-plasmon-induced light absorption on a rough silver surface", *Appl. Phys. Lett.* **98**, 011109-1–011109-3 (2011).