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SYNTHESIS OF GOLD NANOSTRUCTURES USING WET CHEMICAL DEPOSITION IN SiO_2/Si TEMPLATE

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The size and interposition of particles is a key parameter for the practical application of metallic nanostructures which requires the development of a synthesis method with precise control over their parameters. In this work the method for the synthesis of gold nanostructures in the pores of silicon dioxide from a gold sulfite complex and a gold chloride solution via wet chemistry technique was proposed. The influence of deposition parameters, such as deposition temperature and electrolyte composition, on the deposit morphology was studied. It was shown that gold agglomerates were unevenly distributed over the silicon surface at high temperatures and practically uniformly distributed with temperature decrease. Addition of fluoric acid at the deposition stage defines the metal precipitation selectivity into the silicon oxide pores. The peculiarities of gold nanostructures formation mechanism were discussed.

Keywords: porous SiO_2/Si template, wet chemistry, growth mechanism, gold nanostructures
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1. Introduction

The steady increase in the number of publications devoted to nanostructures (NSs) and nanostructured materials is due to their unique properties, which are not typical for the bulk objects of the same composition [1, 2]. Particular attention is paid to NSs made of plasmonic metals, such as copper, silver and gold, exhibiting their unique optical properties in the visible wavelength range [3, 4]. When a light wave interacts with an NS with characteristic dimensions smaller than the wavelength of light, an oscillation of electronic cloud with plasmonic frequency ωp arises at the metal/dielectric interface (most often the dielectric is air) [5]. These areas are characterized by a high electrical field intensity – ‘hot spots’ [6]. This peculiarity makes it possible to use these structures as the basic element for signal enhancing in surface-enhanced Raman spectroscopy (SERS) for the study of substances with low concentrations [7].

The optical properties of plasmonic NSs strongly depend on the size, shape and type of metal [8]. These parameters determine the position and intensity of the plasmon resonance, the knowledge of which is required for laser type selection for SERS research. The shape and size of particles depend on the synthesis parameters, such as concentration and temperature of active solutions, deposition time, etc. [9, 10]. Using of the template synthesis method allows one to effectively control the deposition of NSs by varying the listed parameters [11–15]. Thus, in recent works we have demonstrated the possibility of obtaining copper [16] and silver NSs [17, 18] with a different size and shape in the pores of the ion-track SiO_2/Si template. Appearance of an oxide film on the silver and copper NSs surface limits their service durability due to blocking plasmonic effects. Considering the fact that gold based NSs are void of such problem [19–21], in this work an attempt of gold NSs selective deposition in the pores of the SiO_2/Si template is made. To obtain the NSs, the technique described in [22] was taken as the basis. Also, the first experiments on gold NSs deposition into a porous template from a solution of gold chloride were carried out. The deposition mechanism is not fully understood, especially with respect to Au cations and Cl anions. The authors proposed the gold NSs production in the pores of a polymer ion-track template by using a gold sulfite complex solution [23]. It should be noted that it is difficult to use systems with gold NSs in the polymer template pores for SERS application, since the polymer has a large number of molecular bonds, which introduce a lot of additional background peaks in SERS spectra. There are no difficulties with interpreting obtained results when silicon templates are used, since such substrates give only one strong vibration mode in the region of 520 cm^{-1}.

Thus, the possibility of synthesizing gold NSs in pores of silicon oxide from a gold sulfite complex and a gold chloride solution under various deposition conditions, as well as a detailed study of the obtained NSs are considered in the paper.

2. Methods

For deposition of gold NSs SiO_2/p-Si templates with pore sizes in the silica layer of about 550 nm were used. The features of obtaining such templates are described in detail in [24–27]. The deposition of gold into SiO_2 pores was carried out by the means of wet chemistry from the gold (I) sulfite complex $(Na)[Au(SO_3)_2]$ prepared according to the methods [22] and a gold chloride solution $AuCl_3{\cdot}H_2O$. The temperature of the solution was 0, 25 and 50°C. The deposition was carried out with the addition of a 5 M solution of hydrofluoric acid (HF) to the gold (I) sulfite complex and the gold chloride solution in a ratio of 1:1.

The primary attestation of the deposition results was carried out on a scanning electron microscope (SEM, *Hitachi* TM3030) with an attachment for energy dispersive X-ray spectroscopy studies (EDX, *Bruker* XFlash MIN SVE). A detailed analysis of the morphology of gold NSs was carried out on a SEM *JEOL* JSM-7500F.

3. Results and discussion

Figure 1 shows gold NSs deposited at various temperature conditions.

The increase of the gold amount on the surface of the SiO_2/Si template with electrolyte temperature decrease is clearly visible on SEM images (Fig. 1(a, d, g)) obtained from a large sample area. At 50°C single gold agglomerates are formed on the surface, and most of pores remain unfilled (Fig. 1(a, b, c). The temperature decrease down to 25°C leads to a metal amount increase on the surface of SiO_2, as well as to the formation of gold particles in the pores of SiO_2 (Fig. 1(d, e, f)). Sodium-containing crystals are also present on the surface. Gold NSs have characteristic sizes less than 100 nm and are randomly distributed on the template. Further temperature lowering down to 0°C causes an even greater increase in the metallic phase amount formed on the surface and in the pores (Fig. 1(g, h, i)). This gold deposit is formed both in the form of separate crystallites with sizes up to 200 nm, and their agglomerates. The analysis of EDX-maps and their corresponding spectra indicates the presence of only gold, silicon and oxygen (from SiO_2) in the studied systems.

Using a gold sulfite complex, deposition of gold in individual pores can be carried out provided that the temperature of the solution will be low. But because of the agglomerates formation on the surface it is not possible to achieve selectivity of the process. Therefore, when using a gold sulfite complex without additional activation of a silicon substrate localized on the bottom of pores in an oxide layer, the selectivity (exclusively in the pores) of the metal deposition process will be low.

For chemical activation of the silicon surface, hydrofluoric acid was added to the initial gold sulfite complex solution. When complex $Na_3[Au(SO_3)_2]$ and HF dissolve in water, they dissociate into cations and anions, including Au^{3+},

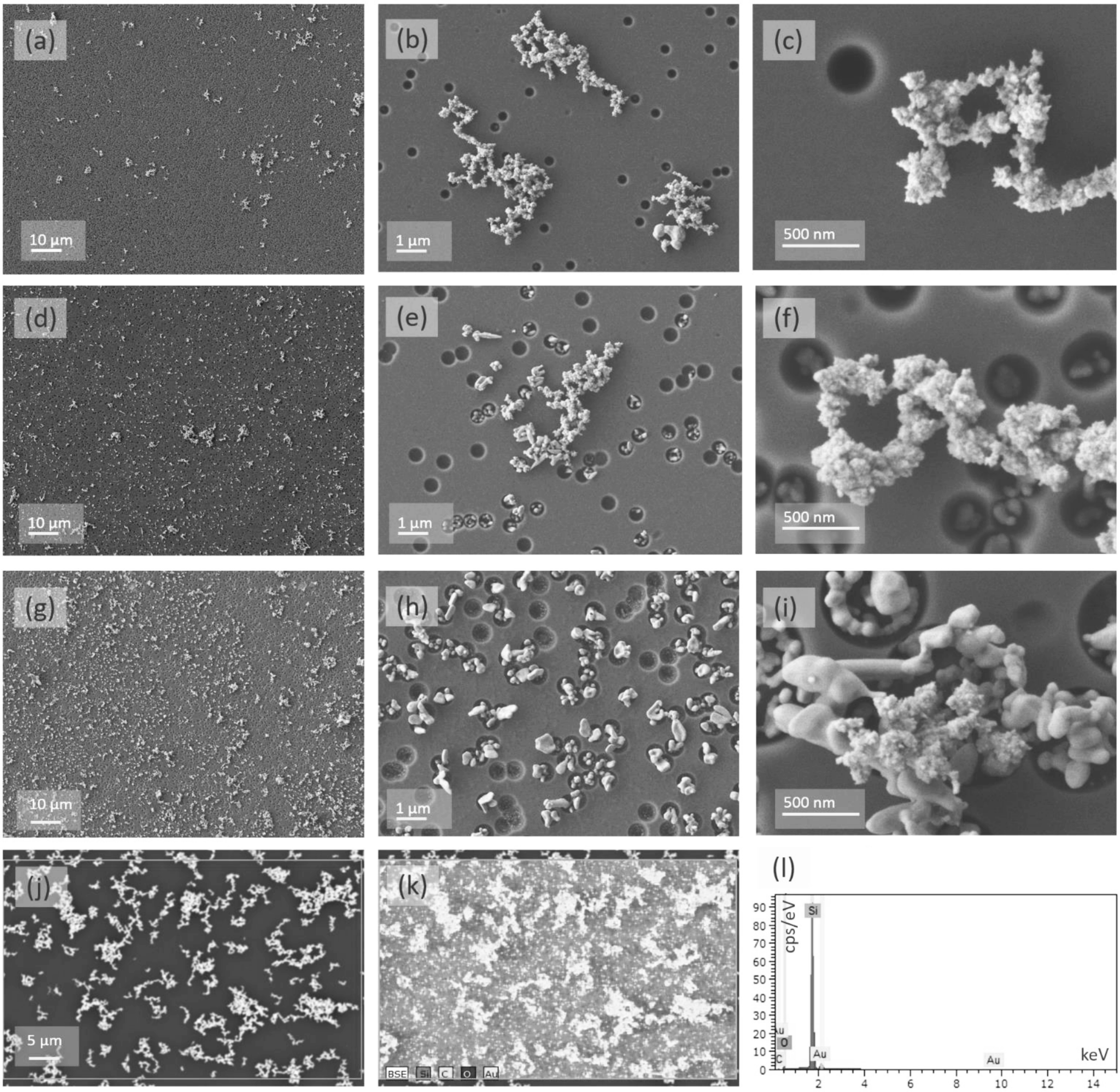


Fig. 1. SEM images of gold NSs on the SiO_2/Si template deposited from the gold sulfite complex solution at different temperatures: (a, b, c) 50°C; (d, e, f) 25°C; (g, h, i, j) 0°C; (k) EDX-map corresponding to the SEM image (j) in the gold detection mode; (l) EDX spectrum of the corresponding region.

H^+ and F^-, which participate in the following chemical reactions:

$$4Au^{+} + Si + 6F^{-} \rightarrow 4Au + SiF_6^{2-}, \quad (1)$$

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O. \quad (2)$$

From the analysis of chemical reactions (1, 2), it is obvious that the deposition of gold into the pores should occur with three simultaneous processes: electrochemical reduction of gold on silicon (1) with a simultaneous anodic process, Si passivation in acidic media to form a thin layer of SiO_2, and SiO_2 etching in hydrofluoric acid (2). This denotes the silicon surface activation by hydrofluoric acid. Electrons, participating in the reduction of gold cations to the metallic state in the electrolyte, are released from the silicon surface. The implementation of the processes near the silicon substrate will facilitate the selective metal deposition into the pores of the SiO_2/Si-template.

During the deposition from the gold sulfite complex without the addition of HF, the metal practically did not react at 50°C, and its amount was excessive at 0°C. Consequently for a better control of the process 25°C temperature was chosen for the deposition. The results of precipitation are shown in Fig. 2.

When dissolved in water, $AuCl_3$ and HF dissociate into cations and anions Au^{3+}, Cl^-, H^+, F^-, which participate in subsequent chemical reactions, schematically represented in Fig. 3(a). During the gold deposition in the pores, three processes simultaneously proceed: electrochemical reduction of gold on silicon with a simultaneous flow of anodic and cathodic processes, oxidation of silicon and etching of SiO_2 in fluorine acid (Fig. 3(a)).

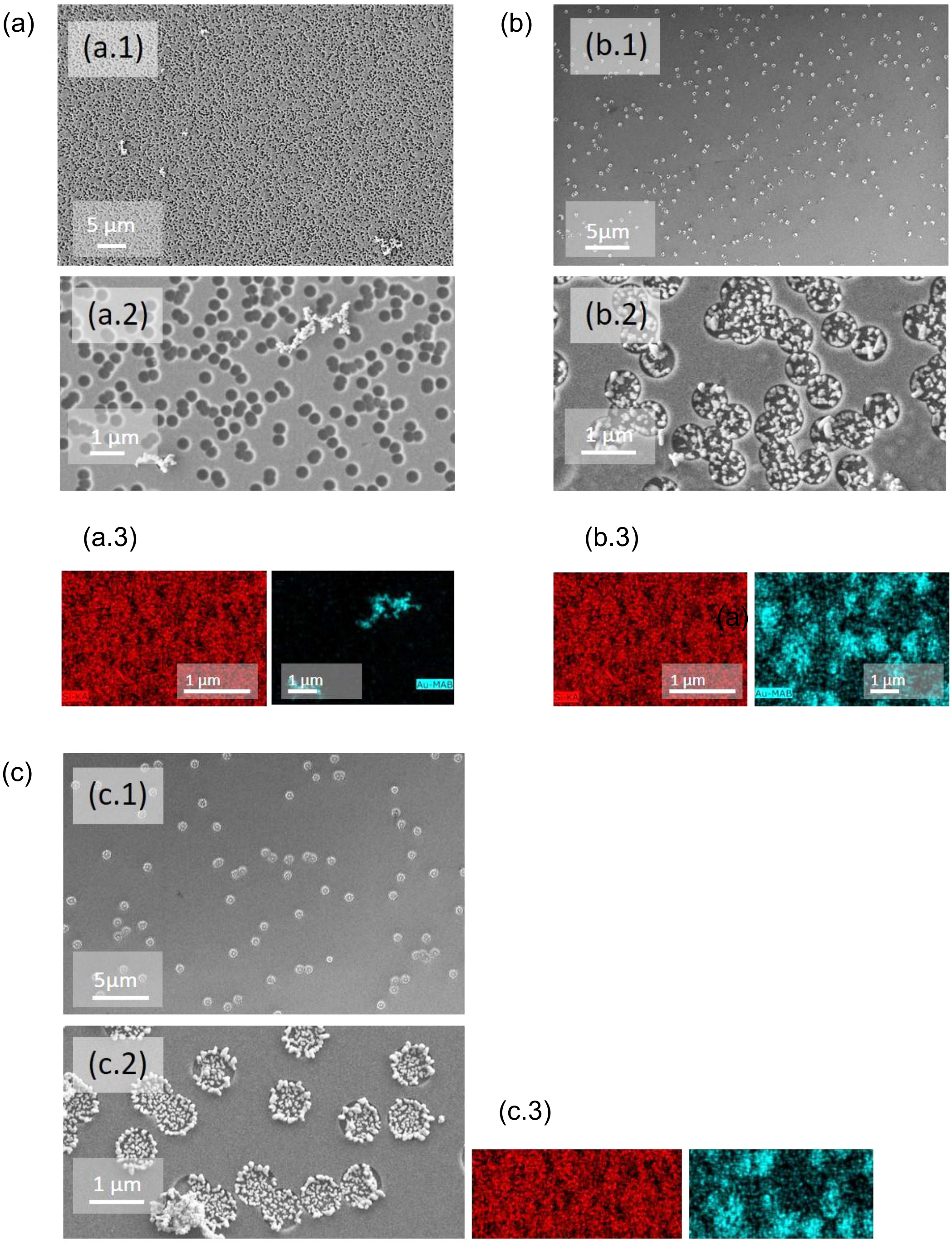


Fig. 2. SEM images of gold NSs from the complex $Na_3[Au(SO_3)_2]$ and HF on the SiO_2/Si template deposited at various temperatures: (a.1, a.2) 50°C; (b.1, b.2) 25°C; (c.1, c.2) 0°C; (a.3–c.3) their EDX-map corresponding to the SEM image (j) in the gold and silica detection mode, respectively.

Reduction

$4Au^{3+} + 3Si + 18F^{-} \rightarrow 4Au + 3SiF_6^{2-}$

Etching

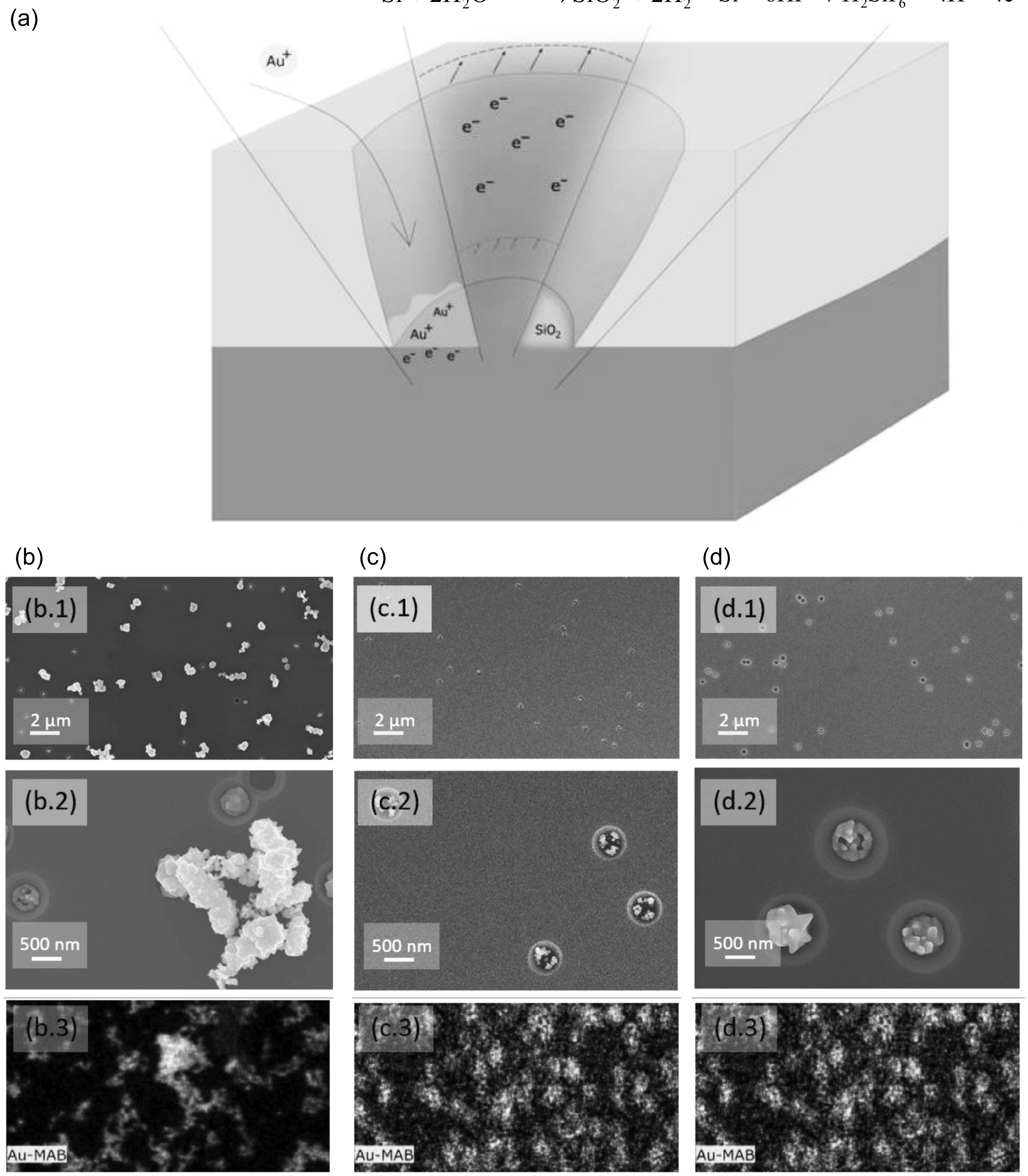
$Si + 2H_2O \rightarrow SiO_2 + 4H^{+} + 4e^{-}$

$Si + 2H_2O \xrightarrow{HCl} SiO_2 + 2H_2$

Oxidation

$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$

$Si + 6HF \rightarrow H_2SiF_6 + 4H^{+} + 4e^{-}$



Figs. 3(b)–(d) show the SEM images of 'in-between' shape structures (nanoparticles obtained at different deposition temperatures) obtained from the reaction solution of gold chloride, showing the morphological evolution of Au nanoparticles using different concentrations of hydrofluoric acid (1, 2.5 and 5%). Au nanoparticles begin to form along the lateral faces of the pore, turning into nanostructures of complex morphology with pointed tips (Fig. 3(d)). The change in shape and size indicates different rates of deposition with temperature, using different concentrations of hydrofluoric acid.

4. Conclusions

Series of experiments on the deposition of gold nanostructures into the pores of the SiO_2/Si ion-track template were carried out. It was shown that, during deposition from a gold sulfite complex, gold nanostructures were synthesized both in the silicon oxide layer pores and on the SiO_2 surface. It was demonstrated that the addition of a 5 M hydrofluoric acid solution to a gold sulfite complex solution stimulated the selective deposition of gold nanostructures in the SiO_2 template pores without gold deposit formation on the SiO_2 surface. In addition to gold, sodium-containing crystals were observed in some places on the template surface. This fact requires additional studies. The method is also proposed for the precipitation of gold chloride from a solution through the addition of hydrofluoric acid with processes of oxidation, etching and reduction, including substitution, between gold chloride and –OH groups on the defective portions of the silicon dioxide surface.

The sample regions, which have exclusively gold nanostructures in the template pores, can be interesting for SERS application.

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References

[1] A.D. Maynard, R.J. Aitken, T. Butz, V. Colvin, K. Donaldson, G. Oberdörster, M.A. Philbert, J. Ryan, A. Seaton, V. Stone, S.S. Tinkle, L. Tran, N.J. Walker, and D.B. Warheit, Safe handling of nanotechnology, Nature **444**, 267–269 (2006).

[2] E. Lindquist, K.N. Mosher-Howe, and X. Liu, Nanotechnology … What is it good for? (Absolutely everything): A problem definition approach, Rev. Policy Res. **27**, 255–271 (2010).

[3] B. Sharma, R.R. Frontiera, A.-I. Henry, E. Ringe, and R.P. Van Duyne, SERS: Materials, applications, and the future, Mater. Today **15**, 16–25 (2012).

[4] Y. Xia and N.J. Halas, Shape-controlled synthesis and surface plasmonic properties of metallic nanostructures, MRS Bull. **30**, 338–348 (2005).

[5] J. Langer, S.M. Novikov, and L.M. Liz-Marzán, Sensing using plasmonic nanostructures and nanoparticles, Nanotechnology **26**, 322001 (2015).

[6] H.J. Yin, Z.Y. Chen, Y.M. Zhao, M.Y. Lv, C.A. Shi, Z.L. Wu, X. Zhang, L. Liu, M.L. Wang, and H.J. Xu, Ag@Au core-shell dendrites: A stable, reusable and sensitive surface enhanced Raman scattering substrate, Sci. Rep. **5**, 1–9 (2015).

[7] K. Girel, E. Yantcevich, G. Arzumanyan, N. Doroshkevich, and H. Bandarenka, Detection of DNA molecules by SERS spectroscopy with silvered porous silicon as an active substrate, Phys. Status Solidi **213**, 2911–2915 (2016).

[8] H. Wei and H. Xu, Hot spots in different metal nanostructures for plasmon-enhanced Raman spectroscopy, Nanoscale **5**, 10794–10805 (2013).

[9] E. Kaniukov, A. Shumskaya, D. Yakimchuk, A. Kozlovskiy, I. Korolkov, M. Ibragimova, M. Zdorovets, K. Kadyrzhanov, V. Rusakov, M. Fadeev, E. Lobko, K. Saunina, and L. Nikolaevich, FeNi nanotubes: perspective tool for targeted delivery, Appl. Nanosci. 9, 835–844 (2019).

[10] A.L. Kozlovskiy, D.I. Shlimas, A.E. Shumskaya, E.Y. Kaniukov, M.V. Zdorovets, and K.K. Kadyrzhanov, Influence of electrodeposition parameters on structural and morphological features of Ni nanotubes, Phys. Met. Metallogr. **118**, 164–169 (2017).

[11] P. Apel, Swift ion effects in polymers: industrial applications, Nucl. Instrum. Methods Phys. Res. B **208**, 11–20 (2003).

[12] A.E. Shumskaya, E.Y. Kaniukov, A.L. Kozlovskiy, D.I. Shlimas, M.V. Zdorovets, M.A. Ibragimova, V.S. Rusakov, and K.K. Kadyrzhanov, Template synthesis and magnetic characterization of FeNi nanotubes, Prog. Electromagn. Res. C **75**, 23–30 (2017).

[13] D. Fink, A.V. Petrov, K. Hoppe, W.R. Fahrner, R.M. Papaleo, A.S. Berdinsky, A. Chandra, A. Chemseddine, A. Zrineh, A. Biswas, F. Faupel, and L.T. Chadderton, Etched ion tracks in silicon oxide and silicon oxynitride as charge injection or extraction channels for novel electronic

structures, Nucl. Instrum. Methods Phys. Res. B **218**, 355–361 (2004).

[14] E.Y. Kaniukov, D.V. Yakimchuk, V.D. Bundyukova, A.E. Shumskaya, A.A. Amirov, and S.E. Demyanov, Peculiarities of charge transfer in SiO_2(Ni)/Si nanosystems, Adv. Condens. Matter Phys. **2018**, 1–8 (2018).

[15] E.Y. Kaniukov, A.L. Kozlovsky, D.I. Shlimas, M.V. Zdorovets, D.V. Yakimchuk, E.E. Shumskaya, and K.K. Kadyrzhanov, Electrochemically deposited copper nanotubes, J. Surf. Invest. X-ray Synchrotron Neutron Tech. **11**, 270–275 (2017).

[16] E. Kaniukov, D. Yakimchuk, G. Arzumanyan, H. Terryn, K. Baert, A. Kozlovskiy, M. Zdorovets, E. Belonogov, and S. Demyanov, Growth mechanisms of spatially separated copper dendrites in pores of a SiO_2 template, Philos. Mag. **97**, 2268–2283 (2017).

[17] V. Sivakov, E.Y. Kaniukov, A.V. Petrov, O.V. Korolik, A.V. Mazanik, A. Bochmann, S. Teichert, I.J. Hidi, A. Schleusener, D. Cialla, M.E. Toimil-Molares, C. Trautmann, J. Popp, and S.E. Demyanov, Silver nanostructures formation in porous Si/SiO_2 matrix, J. Cryst. Growth **400**, 21–26 (2014).

[18] D. Yakimchuk, E. Kaniukov, V. Bundyukova, L. Osminkina, S. Teichert, S. Demyanov, and V. Sivakov, Silver nanostructures evolution in porous SiO_2/p-Si matrices for wide wavelength surface-enhanced Raman scattering applications, MRS Commun. **8**, 95–99 (2018).

[19] K.H. Su, Q.H. Wei, X. Zhang, J.J. Mock, D.R. Smith, and S. Schultz, Interparticle coupling effects on plasmon resonances of nanogold particles, Nano Lett. **3**, 1087–1090 (2003).

[20] F.H. Cho, Y.C. Lin, and Y.H. Lai, Electrochemically fabricated gold dendrites with high-index facets for use as surface-enhanced Raman-scattering-active substrates, Appl. Surf. Sci. **402**, 147–153 (2017).

[21] J. Fang, X. Ma, H. Cai, X. Song, and B. Ding, Nanoparticle-aggregated 3D monocrystalline gold dendritic nanostructures, Nanotechnology **17**, 5841–5845 (2006).

[22] A. Mashentseva, D. Borgekov, M. Zdorovets, and A. Russakova, Synthesis, structure, and catalytic activity of Au/poly(ethylene terephthalate) composites, Acta Phys. Pol. A **125**, 1263–1267 (2014).

[23] A.A. Mashentseva, D.B. Borgekov, D.T. Niyazova, and M.V. Zdorovets, Evaluation of the catalytic activity of the composite track-etched membranes for *p*-nitrophenol reduction reaction, Pet. Chem. **55**, 810–815 (2015).

[24] E.Y. Kaniukov, J. Ustarroz, D.V. Yakimchuk, M. Petrova, H. Terryn, V. Sivakov, and A.V. Petrov, Tunable nanoporous silicon oxide templates by swift heavy ion tracks technology, Nanotechnology **27**, 115305 (2016).

[25] D. Yakimchuk, V. Bundyukova, A. Smirnov, and E. Kaniukov, Express method of estimation of etched ion track parameters in silicon dioxide template, Phys. Status Solidi B Basic Solid State Phys. **256**, 1800316 (2018).

[26] V. Bundyukova, D. Yakimchuk, E. Shumskaya, A. Smirnov, M. Yarmolich, and E. Kaniukov, Post-processing of SiO_2/Si ion-track template images for pores parameters analysis, Mater. Today Proc. **7**, 828–834 (2019).

[27] V. Bundyukova, E. Kaniukov, A. Shumskaya, A. Smirnov, M. Kravchenko, and D. Yakimchuk, Ellipsometry as an express method for determining the pore parameters of ion-track SiO_2 templates on a silicon substrate, EPJ Web Conf. **201**, 01001 (2019).

AUKSO NANODARINIŲ SINTEZĖ SiO_2/Si MATRICOJE NAUDOJANT ŠLAPIĄ CHEMINĮ NUSODINIMĄ

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