Conference materials
UDC 53.097
DOI: https://doi.org/10.18721/JPM.161.228

Bottom-up approach to the formation of bi-resonant glass-metal nanocomposite

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Abstract. We demonstrate the bottom-up approach to the formation of a glass-metal nanocomposite. The approach is based on simultaneous diffusion of different metal ions in glass and the self-assembly of the reduced ions with the formation of metal nanoparticles. In particularly, the approach includes: sputtering of silver and gold thin films on the surface of the glass, embedding of silver and gold ions in glass via field-assisted ion-exchange (applying DC voltage to metal films) and annealing of the ions-enriched glass at the temperature above the glass transition temperature. The formed nanocomposite is glass substrate with the buried layers of gold and silver nanoparticles, which is characterized by two distinct optical resonances (bi-resonant nanocomposite). The influence of the parameters of the ion exchange (thickness of metal films, ratio of the metals, and applied voltage) and annealing (temperature and duration) on the formation of silver and gold nanoparticles and optical properties of the glass-metal nanocomposite is considered.

Keywords: glass-metal nanocomposite, field-assisted ion-exchange, nanoparticles

Funding: This study was supported by the Russian Science Foundation (agreement 22-22-20005 dated 23.03.2022) and St. Petersburg Science Foundation (agreement 04/2022 dated 13.04.2022).

Citation: Babich E.S., Lubyankina E.A., Reduto I.V., Bottom-up approach to the formation of bi-resonant glass-metal nanocomposite, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (1.2) 2023 185–190. DOI: https://doi.org/10.18721/JPM.161.228

Материалы конференции
УДК 53.097
DOI: https://doi.org/10.18721/JPM.161.228

Подход «снизу-вверх» для формирования бирезонансных стеклометаллических нанокомпозитов

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Аннотация. Мы продемонстрировали подход «снизу-вверх» для формирования бирезонансных стеклометаллических нанокомпозитов, представляющих собой стекло с золотыми и серебряными наночастицами в объеме. Подход заключается во внедрении ионов серебра и золота в стекло посредством электростимулированной диффузии металлов из тонкопленочных многокомпонентных электродов, и в восстановлении ионов и кластеризации атомов с образованием наночастиц при последующей высокотемпературной обработке. В рамках работы изучено влияние параметров диффузии и высокотемпературной обработки на процесс формирования наночастиц и оптические свойства стеклометаллических нанокомпозитов.

Ключевые слова: стеклометаллические нанокомпозиты, электростимулированная диффузия, наночастицы

Финансирование: Работа выполнена за счет гранта Российского научного фонда (соглашение № 22-22-20005 от 23.03.2022) при софинансировании Санкт-Петербургским научным фондом (соглашение № 04/2022 от 13.05.2022).

Ссылка при цитировании: Бабич Е.С., Лубянкина Е.А., Редуто И.В. Подход «снизу-вверх» для формирования бирезонансных стеклометаллических нанокомпозитов // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 1.2. С. 185–190. DOI: https://doi.org/10.18721/JPM.161.228

Introduction

Media containing metal nanoparticles receive a significant attention due to their unique optical properties related to the phenomenon of localized surface plasmon resonance (LSPR) in the nanoparticles [1]. Engineering spectral position and intensity of LSPR allows enhancement of light emission [2], optimizing photovoltaic structures [3], optical nonlinearity effects [4] and transmission spectra [5], etc. LSPR strongly depends on material, shape and size of nanoparticles, and numerous studies are devoted to the manipulation of fine features of the nanoparticles and precise nanofabrication to adjust LSPR position [6, 7]. Another approach is to combine several LSPRs and, thus, modify/expand the spectral range in which the properties of a material as a whole are significantly affected by the plasmonic properties of the embedded nanoparticles. This possibility has been confirmed by formation of core-shell [8] and alloyed nanoparticles [9], or joining of different types of nanoparticles on a substrate [10]. In this work, we present an approach to manipulate optical properties of a glass embedded with metal nanoparticles that is glass-metal nanocomposite (GMN), which is based on simultaneous diffusion of different metal ions in glass and the self-assembly of silver and gold nanoparticles with the formation of a bi-resonant structure.

Materials and Methods

Two series of GMNs have been made and optically characterized using SPECORD 50 spectrometer. The depth distribution of the formed nanoparticles was characterized via monitoring absorption spectra of GMN during it step by step etching in HF solution (5 μl HF: 5 g NH_4F: 40 g H_2O) and measuring thickness of etched glass layer with mechanical profilometer Ambios XP-1.

First series

We embedded gold ions in glass by applying DC voltage, +250 or +1000V, to 50 nm-thick gold film sputtered on the glass surface. During this procedure the glass slide was heated to 300 °C to accelerate diffusion of the ions (field-assisted ion-exchange) [11]. The procedure continued until current flowing through the glass slide decreased down to ~0.1 mA. To form gold nanoparticles, we annealed the glass slide for 30 min at 650 °C.

Second series

Both, silver and gold ions were embedded in glass by the field-assisted ion-exchange. The surface of the glass slide was covered with gold and silver films, each 50 nm thick, and topped with 10 nm-thick gold layer to protect silver from oxidation. We applied DC voltage of +250 or +1000 V to the bi-layer film at elevated temperature of 300 °C until current flowing through the glass slide decreased down to ~0.1 mA and annealed the obtained samples for 30–60 min at 650–700 °C. The bi-layer anode with different ratio of thicknesses of silver/gold layers was also tested. In particular, DC voltage of 1000+ V was applied to the surface of the glass slide covered with 50 nm-thick gold and 30 nm-thick silver films; the glass slide was annealed for 60 min at 700 °C.

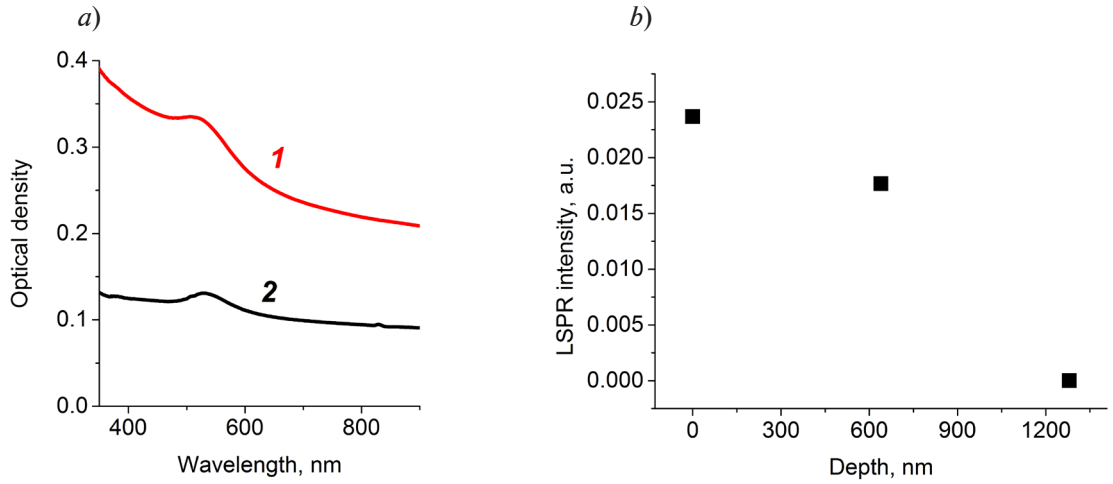

Fig. 1. Optical absorption spectra of GMN (first series) obtained under 1000 V (*1*) and 250 V (*2*) (*a*). Dependence of the intensity of gold LSPR in the spectrum of GMN on thickness of etched glass (the GMN was obtained under 250 V) (*b*)

Results and Discussion

The absorption spectra of the samples of the first series are presented in Fig. 1,*a*. One can see, gold doping of glass by field-assisted ion-exchange combined with the high-temperature annealing results in the formation of a structure with LSPR at ~525 nm which is characteristic for gold nanoparticles [12]. The concentration of gold nanoparticles is higher in the sample obtained under 1000 V comparatively to the one obtained under 250 V, which follows from the noticeable difference in the LSPR intensity. Note, ultrasonic cleaning of the samples' surface in acetone did not affect the spectra, which evidences formation of gold nanoparticles in the glass bulk that is GMN. To characterize depth distribution of the nanoparticles we step by step etched GMN in HF solution, measured thickness of etched glass and GMN absorption spectra (see section 2 for details). The results for the sample obtained under 250 V are presented in Fig. 1,*b*. Evidently, a thin, ~1300 nm, layer of GMN is formed in anodic subsurface region.

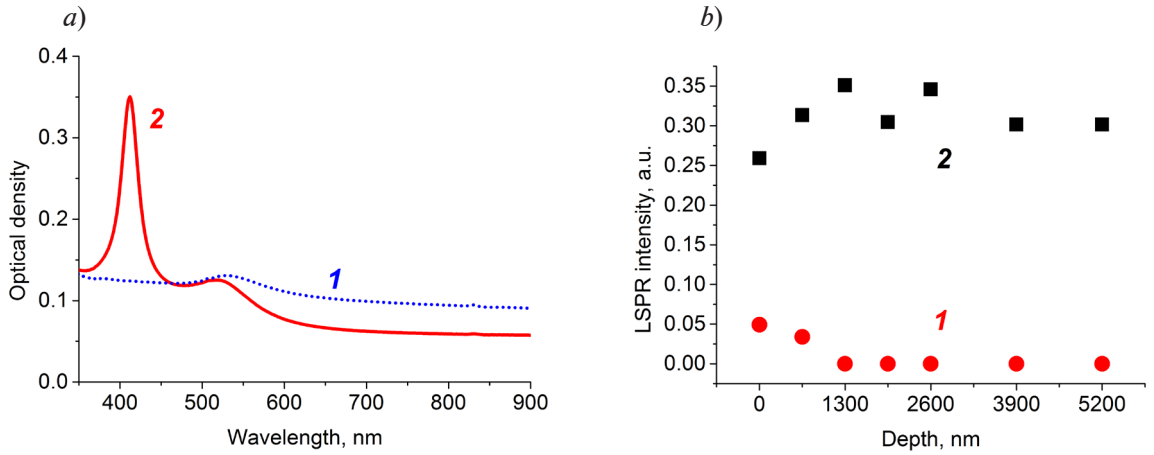

Fig. 2. Comparison of optical absorption spectra of GMN (*1*, first series) and bi-resonant GMN (*2*, second series) obtained under 250 V (*a*). Dependence of the intensity of gold (*1*) and silver (*2*) LSPRs in the spectrum of bi-resonant GMN on thickness of etched glass (*b*)

The absorption spectrum of the sample in the second series obtained under 250 V and annealing for 30 min at 650 °C is presented in Fig. 2,*a* and compared with the spectrum of the sample in the first series obtained under the same conditions. The spectrum of the sample in the second series demonstrates two optical resonances at ~410 and ~525 nm, and does not change after ultrasonic cleaning of the sample surface in acetone. Thus, both silver and gold ions diffused into the glass in the course of the field-assisted ion-exchange with the bi-layer anode, and the high-temperature annealing resulted in reduction of the ions and formation of nanoparticles in the glass bulk that is a bi-resonant GMN. The difference in silver/gold LSPR intensities supposedly indicates a difference in concentrations of silver and gold nanoparticles in the GMN.

Intensity and spectral position of the longer-wavelength LSPR coincide well with ones of LSPR in the GMN formed by the field-assisted ion-exchange with single-layer gold anode and hence presence of silver does not essentially influence gold diffusion and clustering (see Fig. 2,*a*). We assumed that silver nanoparticles form separately from the gold ones.

To determine the burial depth of gold and silver nanoparticles we repeated the step by step etching. The results for the 250 V sample are presented in Fig. 2,*b*. One can see, gold LSPR vanishes from the GMN spectrum when ~1300 nm of glass is etched off, which corresponds with the results of the etching of the sample obtained using single-layer gold anode (see Fig. 1,*b*). Silver LSPR remains in the spectrum, even when ~5000 nm of glass is removed. Note, silver LSPR disappeared from the spectrum when ~15 μm of glass was removed. The results clarify process of ions diffusion in the course of the field-assisted ion-exchange with bi-layer gold-silver anode: the concentration of silver ions in glass increase faster than gold one due to higher mobility of silver ions [13, 14]. However, since ions continue to move from glass surface towards bulk under the electric field, silver ions go deeper in the glass, which results in spatial separation of gold and silver ions. The high-temperature annealing results in reduction and clustering of the ions and formation of bi-resonant structure represented as layered GMN: gold nanoparticles in the subsurface glass layer of the thickness of ~1 μm and silver nanoparticles-containing layer buried deeper in glass by ~ 15 μm.

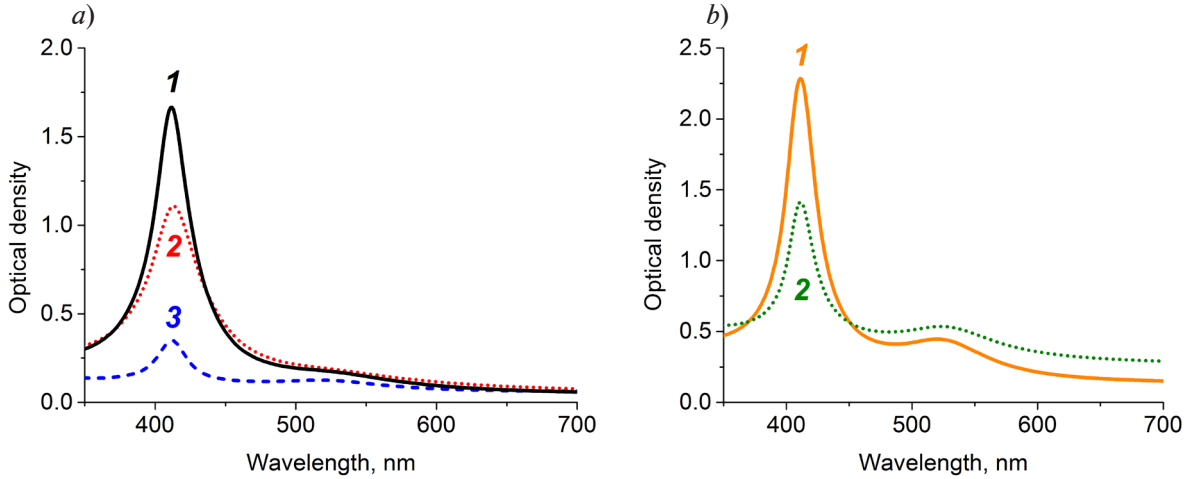

Fig. 3. Optical absorption spectra of bi-resonant GMNs obtained under different applied voltage and annealing duration: 1000 V and 60 min (*1*), 1000 V and 30 min (*2*), 250 V and 30 min (*3*); annealing temperature 650 °C (*a*). Spectra of GMNs obtained under 1000 V, 700 °C and 60 min using bi-layer anodes with different ratio of thicknesses of gold/silver layers (Au:Ag): 1:1 (*1*), 1.5:1 (*2*) (*b*)

The ratio of silver/gold LSPR intensities in the formed bi-resonant GMN can be varied by the ratio of thicknesses of silver/gold layers in bi-layer anode, the applied voltage, temperature or duration of the annealing. For example, increase in the voltage from 250 V to 1000 V or the annealing duration from 30 to 60 min results in the intensification of silver LSPR (Fig. 3,*a*), while increase in the annealing temperature from 650 to 700 °C or decrease in thickness of silver layer in bi-layer anode from 50 to 30 nm results in the intensification of gold LSPR (Fig. 3,*b*).

Conclusion

Two-step bottom-up approach is demonstrated for fabrication of bi-resonant GMN. The approach includes applying DC voltage to bi-layer gold-silver film sputtered on glass surface and annealing of the glass at 650–700 °C. Obtained GMN contains gold nanoparticles in ~1 μm thick subsurface region and silver nanoparticles in an essentially thicker region. The GMN is characterized by two resonances which spectral positions correspond to LSPR in silver and gold nanoparticles. It is demonstrated that the ratio of silver/gold LSPR intensities can be adjusted by varying the applied voltage, temperature or duration of the annealing.

Acknowledgments

This study was supported by the Russian Science Foundation (agreement №22-22-20005 dated 23. 03. 2022) and St. Petersburg Science Foundation (agreement №04/2022 dated 13. 04. 2022), project № 22-22-20005.

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Received 21.10.2022. Approved after reviewing 08.11.2022. Accepted 08.11.2022.