CONDENSED-MATTER SPECTROSCOPY

Metal Clusters and Nanoparticles in Dielectric Matrices: Formation and Optical Properties

I. A. Gladskikh* and T. A. Vartanyan

ITMO University, St. Petersburg, 197101 Russia
*e-mail: 138020@mail.ru
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Abstract—The optical properties of thin dielectric films with metal inclusions and their dependence on thermal and laser annealing are studied experimentally. Metal clusters (Ag, Au, and Cu) in dielectric materials (Al_2O_3 and SiO_2) are obtained by simultaneous vacuum deposition of metal and dielectric on the surface of a corresponding dielectric substrate (sapphire and quartz). It is shown that, depending on the deposited dielectric material, on the weight ratio of deposited metal and dielectric, and on the subsequent thermal treatment, one can obtain different metal structures, from clusters with a small number of atoms to complex dendritic plasmonic structures.

INTRODUCTION

It is a distinguishing feature of nanostructures that their properties can be precisely adjusted by changing their size and shape. It remains important to determine the size dependences of the electronic structure of such objects. A metal cluster consisting of several atoms can be separated into an individual group. The optical properties of these clusters are close to the properties of molecules due to their discrete electronic structure [1, 2]. These properties considerably change with addition or removal of one atom or with a change in the cluster shape. In addition, due to a discrete electronic structure, metal clusters possess luminescent properties, which is characteristic neither of bulk metals [3] nor of metal nanoparticles with sizes exceeding the characteristic sizes of clusters (of the order of a nanometer).

An increase in the number of atoms in a nanoparticle enhances the role of collective excitations of conduction electrons responsible for the appearance of intense absorption bands well-known as localized surface plasmon resonance bands. The plasmon resonance frequency depends both on the size and shape of nanoparticles and on the permittivity of the surrounding material [4]. Under resonance conditions, the incident electromagnetic field near a metal nanoparticle is multiply amplified and localized. These effects find important applications in enhanced Raman scattering and in spectroscopy of single nanoobjects.

The methods of obtaining metal clusters in the form of colloidal solutions are based on chemical synthesis [5]. Clusters can also be formed by ion exchange in glasses or by deposition of clusters into solid-state matrices from inert gases [6, 7]. However, these methods hardly can be used to create nanophotonic devices based on metal clusters. There is also no universal method for obtaining clusters of various metals.

In the present work, clusters were formed by physical deposition of metal vapors in vacuum. However, it seems impossible to obtain metal clusters by ordinary deposition of metals on substrates because, even at a relatively small amount of deposited metal, the formed metal nanoparticles are rather large and possess plasmonic properties [8], while investigation of extremely small amounts of matter is a hard technical problem. To avoid formation of large particles, a dielectric material consistent with the material of the substrate was deposited simultaneously with metal. The samples produced by this method represented dielectric matrices with embedded metal particles. This method allows one to vary the size and, hence, optical properties of clusters by changing the ratio of metal and dielectric deposition rates. The advantages of this method include the possibility of creating multilayer structures with different optical properties.

EXPERIMENTAL RESULTS

Thin Al_2O_3 and SiO_2 films with nanosized metal inclusions of Ag, Au, and Cu were obtained by simultaneous deposition of one of the above-mentioned dielectric materials and one of the metals on the surface of sapphire and quartz substrates in a PVD-75 (Kurt J. Lesker) vacuum chamber at a residual vapor pressure of $\sim 10^{-6}$ Torr. Figure 1a shows the schematic of the setup. As an evaporator for metals, we used a
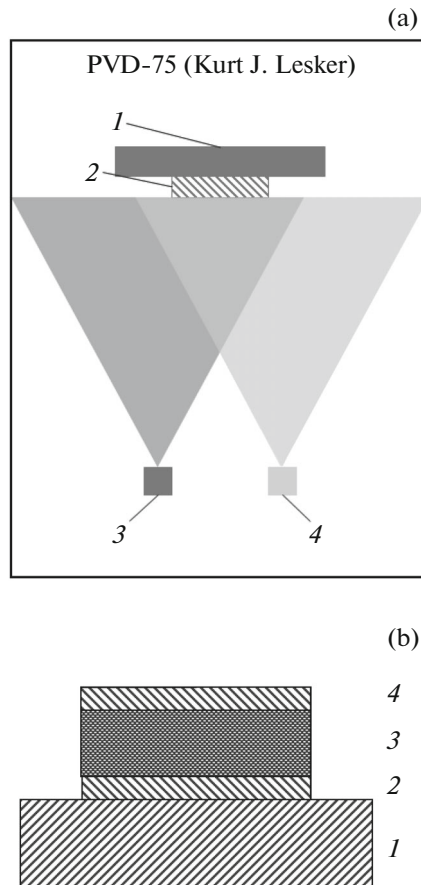
Fig. 1. (a) Schematic of the experimental setup: (*1*) manipulator, (*2*) substrate, (*3*) thermal evaporator for metals, and (*4*) electron-beam evaporator for dielectric materials. (b) Sample scheme: (*1*) substrate, (*2*) and (*4*) pure dielectric layers, and (*3*) dielectric layer with metal inclusions.

Fig. 2. Optical density spectra of (a) a SiO_2 film on a quartz substrate and (b) an Al_2O_3 film on a sapphire substrate: (*1*) substrate spectrum, (*2*) spectrum of the substrate with a freshly deposited film, and (*3*) spectrum of the substrate with the film 96 h later.

tungsten boat heated by passing current. The dielectrics were deposited using an electron-beam evaporator. The amount of deposited materials was controlled by a quartz thickness detector. The metal and dielectric deposition rate varied from 0.1 to 0.5 Å/s. The metal and dielectric were deposited simultaneously, except for the first and the last 30 Å, which consisted solely of the dielectric material. The thickness of the metal-containing layer was 270 Å.

Thus, the samples obtained have a sandwich structure consisting of a substrate and a dielectric layer with metal inclusions sandwiched between thin layers of the pure dielectric material (Fig. 1b).

After deposition, the films were irradiated by the third harmonic of a pulsed Nd:YAG laser (with a pulse duration of 10 ns and an energy density of 75 mJ/cm^2) and thermally treated at 200°C for 1 h. The optical density spectra of samples were measured on an SF-56 (LOMO) spectrophotometer.

To determine the effect of dielectric materials on the optical properties of substrates, we deposited pure
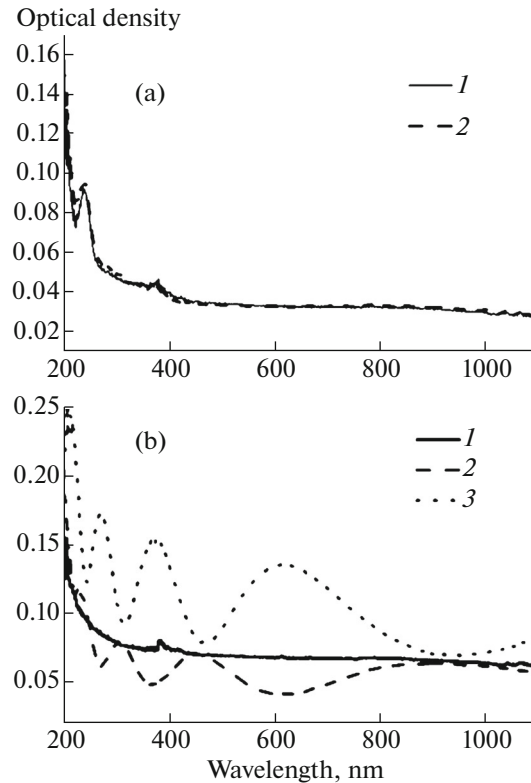
Al_2O_3 and SiO_2 films 300 Å thick on the substrates of the same materials (Fig. 2). A thin SiO_2 film caused almost no changes in the quartz substrate spectrum, while the Al_2O_3 film deposited on a sapphire substrate decreased its optical density at wavelengths of 272, 365, and 620 nm. After several days, we observed an opposite effect; i.e., this coating increased the optical density at the same wavelengths.

In the case of simultaneous deposition of silver and dielectric, the extinction spectra exhibit narrow absorption lines in the near UV region (Fig. 3). The films were produced with ratios of the silver and dielectric deposition rates of 1 : 5 and 1 : 1. The as-deposited Al_2O_3 film with silver has one absorption band, which shifts to longer wavelengths with increasing concentration of silver. Thermal annealing and laser irradiation also cause a long-wavelength shift.

The film obtained at the ratio of Ag and Al_2O_3 deposition rates of 1 : 5 (Fig. 3a) has the absorption maximum at wavelength $\lambda = 354$ nm. This film was rather stable, and its optical properties almost did not change for two weeks (thin curve in Fig. 3a). After annealing, the maximum slightly shifted to $\lambda = 362$ nm. The laser radiation most strongly affected the absorption maximum position. After irradiation, the
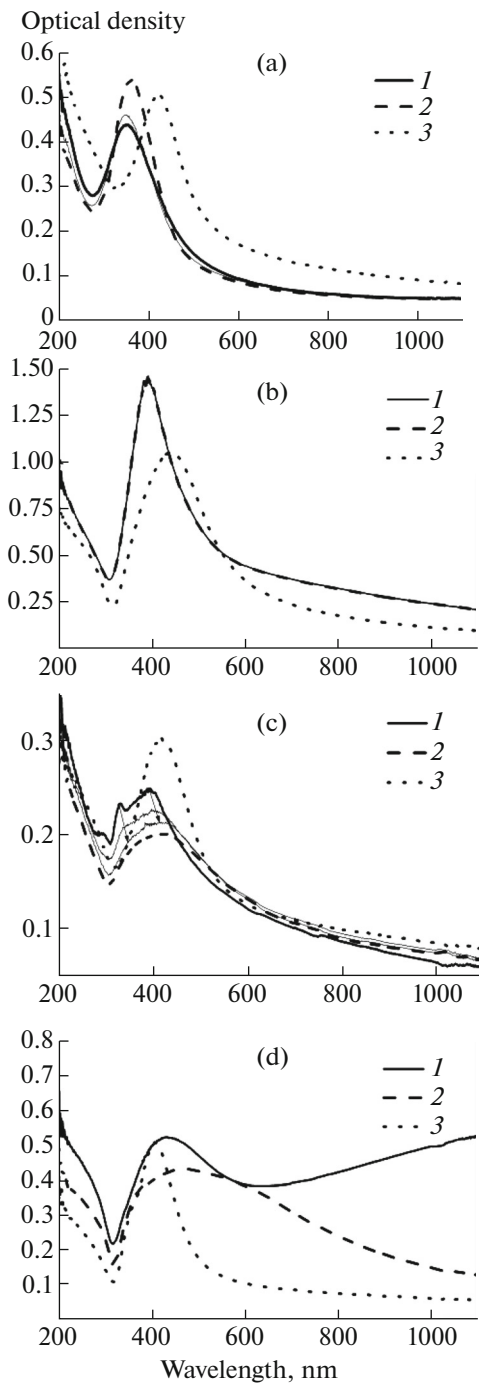
Optical density

Fig. 3. Optical density spectra of dielectric films with metal inclusions (a, b) for Ag and Al_2O_3 synthesized with deposition rate ratios of (a) 1 : 5 and (b) 1 : 1, as well as (c, d) for Ag and SiO_2 synthesized with deposition rate ratios of (c) 1 : 5 and (d) 1 : 1. Curves *1* show the spectra after deposition, curves *2* are the spectra after thermal annealing, and curves *3* are the spectra after laser irradiation.

absorption band maximum shifted to $\lambda = 422$ nm. For the Al_2O_3 film with silver deposited with a deposition rate ratio of 1 : 1 (Fig. 3b), the absorption peaks after deposition and after laser treatment lie at $\lambda = 393$ and

440 nm, respectively. Thermal annealing caused no noticeable changes in the extinction spectra.

The optical density spectra of SiO_2 films synthesized under the same deposition conditions were drastically different. The optical density spectra of the structure obtained by deposition of Ag and SiO_2 with a deposition rate ratio of 1 : 5 (Fig. 3c) contain three peaks at wavelengths $\lambda_1 = 293$, $\lambda_2 = 333$, and $\lambda_3 = 394$ nm. This structure was nonequilibrium; i.e., we observed a red shift and a decrease in the optical density with time (the spectra measured 24 and 48 h after deposition are shown by thin solid curves), the short-wavelength peaks decaying faster than the long-wavelength maximum. Annealing shifted the peaks further to the red, and, finally, the optical density spectrum contained only one broad peak at $\lambda = 420$ nm. Further laser irradiation of the film increased its extinction approximately by 1.5 times and did not change the maximum position.

The extinction spectra of the sample produced by simultaneous deposition of Ag and SiO_2 with a deposition rate ratio of 1 : 1 (Fig. 3d) exhibits a maximum at wavelength $\lambda = 430$ nm and a monotonic increase in absorption at wavelengths exceeding 600 nm. Annealing of the film led to a considerable decrease in the long-wavelength extinction, which completely disappeared after laser treatment. The short-wavelength peak became much narrower after laser annealing.

Similar experiments were performed with Al_2O_3 films containing gold and copper. Figure 4 presents the spectra of optical Al_2O_3 films with gold particles. Gold clusters are characterized by the existence of a broad absorption band extended from the near-UV region to 600 nm with a shoulder at about 400 nm. Thermal annealing leads to a red shift of the shoulder to approximately 450 nm. The extinction spectra of films after irradiation exhibit a pronounced maximum at a wavelength of 540 nm, which is especially clearly seen in the difference spectrum.

The extinction spectra of the Al_2O_3 films deposited simultaneously with copper (Fig. 5) also show a broad absorption band in the wavelength region below 600 nm. Thermal annealing decreases the optical density in the short-wavelength spectral region and increases it in the long-wavelength region. Like in the case of films with gold, laser treatment leads to the formation of a peak in the difference spectrum at $\lambda = 600$ nm, though it is less pronounced.

DISCUSSION OF RESULTS

The results obtained are as follows. Simultaneous vacuum deposition of metal and dielectric materials results in the formation of dielectric films with metal nanoparticles absorbing in the near-UV and visible regions, which is typical for metal cluster consisting of a small number of atoms. Annealing of films leads to a red shift of extinction peaks. High-power laser irradi-
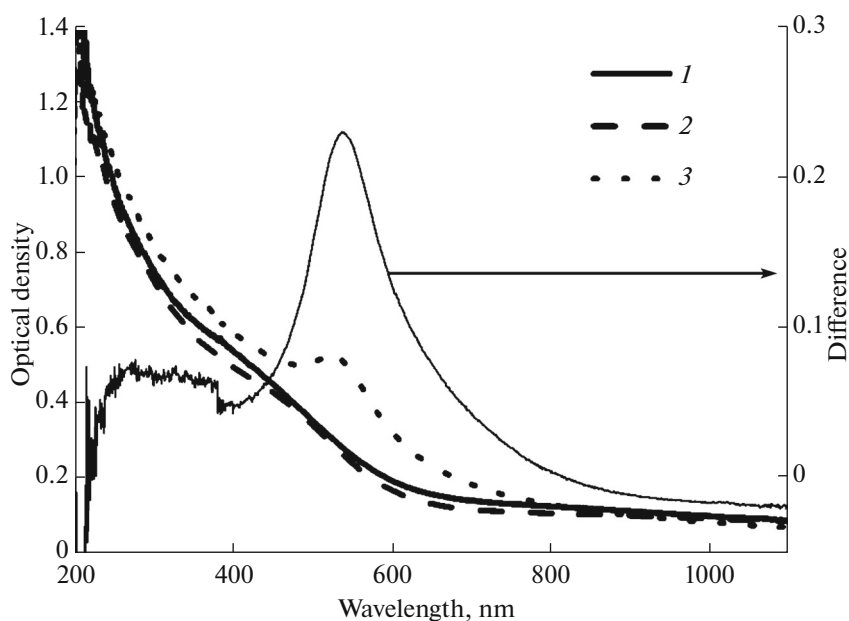
Fig. 4. Optical density spectra of Al_2O_3 films with gold inclusions obtained at a ratio of Al_2O_3 and gold deposition rates of 1 : 1: (*1*) after deposition, (*2*) after thermal annealing, and (*3*) after laser irradiation.
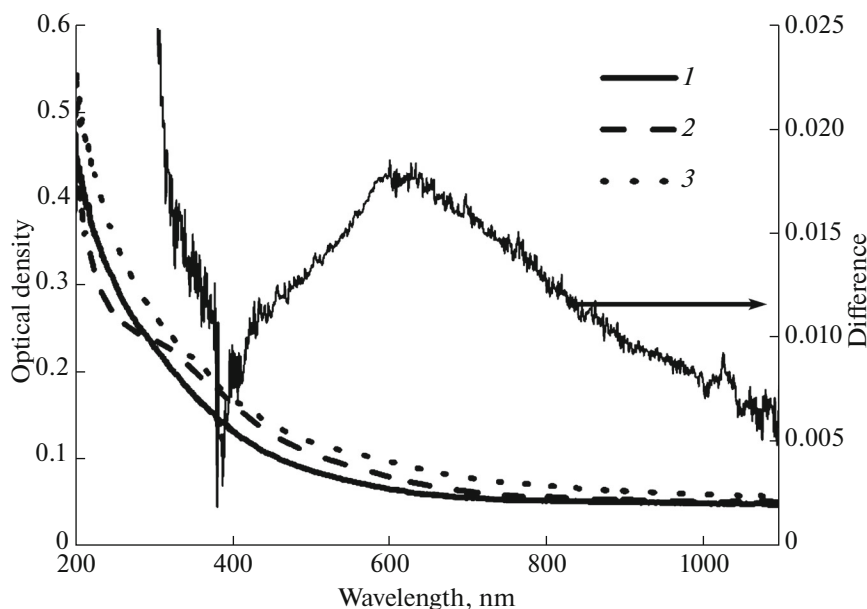

Fig. 5. Optical density spectra of Al_2O_3 films with copper inclusions obtained at a ratio of dielectric and gold deposition rates of 1 : 2: (*1*) after deposition, (*2*) after thermal annealing, and (*3*) after laser irradiation.

ation causes the appearance of narrow absorption bands.

The extinction spectra of silver clusters in Al_2O_3 and SiO_2 films deposited at identical deposition rate ratios are strongly different, which we relate to the structure of the dielectric films.

Deposition of Al_2O_3 on a sapphire substrate results in the formation of a film with a refractive index lower than that of the substrate, which can occur due to the

formation of a porous structure. With time, this film may condense water, which leads to a change in the refractive index of the film and, hence, in the extinction spectrum. The SiO_2 film on a quartz substrate does not affect its optical properties, which allows us to conclude that quartz is deposited in the form of a dense homogeneous layer.

Thus, with identical amounts of silver and dielectric, the clusters formed in Al_2O_3 films (Fig. 3a), due

to a porous structure in which silver atoms can rather freely move, can be larger than the clusters formed in the case of simultaneous deposition of Ag and SiO_2 (Fig. 3c). It was shown in [9] that silver clusters with the number of atoms $n \leq 12$ have several narrow absorption bands within the range of 3−5 eV, while larger clusters exhibit one broad absorption band, which lies within the range of 3.2−3.8 eV depending on the cluster size. The presence of several maxima in the extinction spectra of silver clusters can be also related to their shape. It was shown that spherical particles with number of atoms $n > 13$ have one absorption peak, while the absorption spectra of biaxial and triaxial particles of the same size contain two and three peaks, respectively [10]. However, due to self-organization of metal clusters deposited in vacuum, it seems impossible to obtain structures of complex shape.

The samples containing gold and copper exhibit broad absorption bands in the visible range, which is related to a larger number of transitions in this spectral region in clusters of these metals than in silver clusters [11].

The temporal changes in the optical density spectra of samples after thermal and laser annealing is related to thermal conversion of clusters into larger metal particles [12]. Moreover, while thermal annealing leads to a small red shift of the absorption, the particles formed after laser annealing exhibit pronounced plasmon resonance at wavelengths of 420−440 nm (silver particles), 550 nm (gold particles), and 600 nm (copper nanoparticles). These wavelengths are close to the positions of plasmon resonance localized in spherical particles of corresponding metals in a medium with a refractive index of 1.5.

The optical density spectrum of the film of SiO_2 with Ag synthesized at a deposition rate ratio of 1 : 1 (Fig. 3d) strongly differs from the spectra of all the other samples studied in this work. The given deposition conditions probably allow formation of complex dendritic plasmonic structures [13, 14]. The action of annealing and laser radiation on such a structure is similar to the thermal action on thin unannealed metal films formed by deposition on a cold substrate, i.e., causes formation of individual particles of regular shape [8].

CONCLUSIONS

A rather simple method for obtaining metal clusters and nanoparticles in dielectric matrices is proposed. It is shown that simultaneous deposition of metal and dielectric materials results in the formation of metal clusters with a small number of atoms. Thermal and laser annealing lead to an increase in the size of clusters, which manifests itself in the red shift of the absorption band and in the appearance of a well-pronounced plasmon resonance in the extinction spectra of films.

This method allows one to produce both metal clusters with a small number of atoms and complex dendrite structures. This method can be used in the future to produce multilayer structures in the form of dielectric films with metal clusters and different refractive indices.

ACKNOWLEDGMENTS

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