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Thermostimulated processes of production of metal nanoparticles in oxide films formed by the sol-gel method

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Our study demonstrates that using the sol-gel method to form thin Me–SiO_2 films with composite sols containing nanoparticles of hydrous silica and silver/gold metal or germanium dioxide makes it possible to vary metal particle size (on reductive heat treatment in hydrogen for GeO_2) and size distribution, thus affecting optical characteristics of the films. Ge particles formed in GeO_2–SiO_2 system are smaller than those formed by reducing pure GeO_2 films. Silica sols produced with sodium metasilicate were found to stabilize the silver and gold nanoparticles formed by chemical reduction.

Key words: *sol-gel method; Me–SiO_2; system; thin film; nanoparticles*

1. Introduction

Nowadays, research in the field of physics and chemistry of nanodisperse and nanostructured systems is proceeding vigorously, the systems posessing a number of specific properties. Much attention is given to investigations of nanodisperse, chemically stable metals (silver, gold) and nanocrystals of various semiconductor compounds. They are of interest due to their unique optical, photophysical and other properties [1–6]. Their size-dependent optical properties make them usable as elements of optical devices with controllable parameters. Furthermore, they are of interest because they can provide a basis for production of superstructures such as colloidal crystals and two- and three-dimensional film systems with ordered nanoparticle arrangement (two- and three-dimensional superlattice).

Revealing non-linear optical characteristics of glasses doped with ultrafine noble metals (Ag, Au) has considerably increased interest in thin-film “metal-oxide” systems formed by the sol-gel method. This paper presents the results of the study of thermo-

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stimulated process yielding “metal-oxide” film systems based on composite sols. Using such sols considerably extends the possibility of controlling properties of the film systems, as compared to metal-ion-containing oxide sols used to form film systems.

2. Experimental

Thin-film “Me-oxide” (Me is for Ag, Au) systems were formed on the basis of respective composite sols produced by chemical reduction of metal ions incorporated in an oxide matrix. Stable silica sols (pH = 3–4 and pH = 8–9) were used. The sols were produced by acidic or alkaline hydrolysis of tetraethyl orthosilicate (TEOS) or from sodium metasilicate using an ionite. Sodium borohydride and hydrazine hydrate were used as reductants to produce silver nanoparticles in the oxide matrix, while sodium borohydride were used to produce gold nanoparticles, the mole ratios being Ag^+/BH_4^- ($N_2H_4 \cdot H_2O$) = 1/2; $AuCl_4^-/BH_4^-$ = 1/1, respectively. SiO_2 sols produced from sodium metasilicate are good stabilizers for metallic nanoparticles. Stable composite silica sols produced by TEOS hydrolysis are formed only in the presence of a stabilizer (hexadecanethiol, thioglycerol, $C = 10^{-6}$ $mol \cdot l^{-1}$). Metal atoms concentrations in all the composite sols were 10^{-3} $mol \cdot dm^{-3}$ with Me/Si atomic ratio of 0.0014. The table gives the particle size for silica phase in the oxide sols used to form Ag^0 and Au^0 nanoparticles.

Table. Properties of $Ag–SiO_2$ and $Au–SiO_2$ films depending on the heat treatment conditions

Reducing agent	Precursor of SiO_2 sol	Initial layer d_{av}/nm	Heated for 40 min at 500 °C	
			d_{av}/nm*	d_{av}/nm**
$Ag–SiO_2$ films				
$NaBH_4$	TEOS	30	50	23
$N_2H_4 \cdot H_2O$	TEOS	36	34	30
$NaBH_4$	Na_2SiO_3	7,5	16	10
$N_2H_4 \cdot H_2O$	Na_2SiO_3	24	50	10
$Au–SiO_2$ films				
$NaBH_4$	TEOS	30	35	50
$NaBH_4$	Na_2SiO_3	13	28	14

*In H_2.

** In air (for $Ag–SiO_2$ and $Au–SiO_2$) and then in H_2 (for $Ag–SiO_2$).

Composite $GeO_2–SiO_2$ sols were used as precursors to form $Ge–SiO_2$ films. The sols were formed either by simultaneous hydrolysis of TEOS and $GeCl_4$ in alcohol solutions with mole ratios TEOS/$GeCl_4$ = 5/1, TEOS/H_2O = 1/10 or by mixing onecomponent SiO_2 and GeO_2 sols, SiO_2/GeO_2 mole ratio being 5/1. The pure sols of SiO_2 (pH = 9) and GeO_2 (pH = 9) were produced by alkaline hydrolysis of TEOS and by the method based on solubility differences of hexagonal GeO_2 in aqueous ammonia of different concentrations [7], respectively.

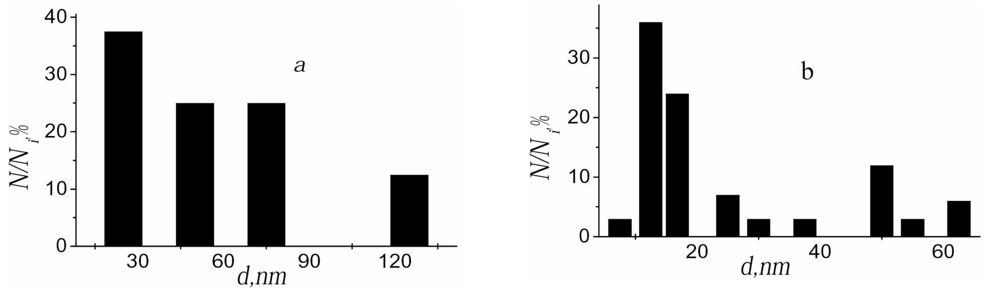
Ag–SiO_2 and GeO_2–SiO_2 films were formed via layer-by-layer spin coating of the respective composite sols on quarz glass substrates. Each layer deposition was followed by air-drying for 10 min at 150 °C. Au–SiO_2 films formed by the same method were of low optical density, therefore casting a composite sol on quarz glass substrates followed by air-drying for 10–12 h at room temperature was used instead. The dried Me–SiO_2 films were heated at 500 °C for 40 min either in the air or in hydrogen, as well as successively under both gases (40 min each). Temperature was raised by 5 °C per minute. The calculated thickness of the films was about 40 nm for double-layered Ag–SiO_2 and about 1 μ for Au–SiO_2 films. To produce Ge–SiO_2 films, the initial GeO_2–SiO_2 layers were reduced in hydrogen flow at 500 °C and 650 °C for 2 h. Four-layered Ge–SiO_2 films were 40 nm or 0.5 μ thick, depending on the method of the initial sol production (by TEOS and $GeCl_4$ co-hydrolysis or by mixing pure SiO_2 and GeO_2 sols).

Me–SiO_2 (Me is for Ag, Au, Ge) films formed were characterized by optical spectroscopy and electron microscopy (EM). Optical absorption spectra were recorded with a SPECORD M40 UV-VIS double-beam spectrophotometer in the wavelength range of 200–800 nm, particle size and shape in sols and films were determined using EM-125K electron microscope. IR spectra of GeO_2–SiO_2 powders separated from the sols were obtained with a Spectrum 1000 FT-IR spectrometer in the range of 400–4000 cm^{-1}. DRON-3 (CoKα radiation) was used for X-ray diffraction analysis.

3. Results and discussion

Ag(Au)–SiO_2 films

According to the EM data, acidic (pH = 3.5) silica sols produced by ion-exchange method from sodium metasilicate are composed of regularly shaped spherical particles with their sizes ranging from 5 to 40 nm, while those produced by alkaline hydrolysis of TEOS are composed of spheroidal particles 20–100 nm in size (Fig. 1a, 2a). Figures 1b, c and 2b, c give the data on sizes and size distributions of silver particles formed in the oxide sols, sodium borohydride and hydrazine hydrate being used as reductants. The silver particles produced are mostly smaller than those constituting the oxide matrix. The sizes of the former (ranging from 3,5 to 70 nm) depend on the types both of the precursors from which the oxide sols were produced and the reductants used. Optical spectra of the composite sols in the visible region differ both in the silver plasmon resonance maximum position (which varies from 390 to 415 nm) and in the absorption bandwidth. Powders separated from the sols are of various yellow-gray, gray and brown colours.



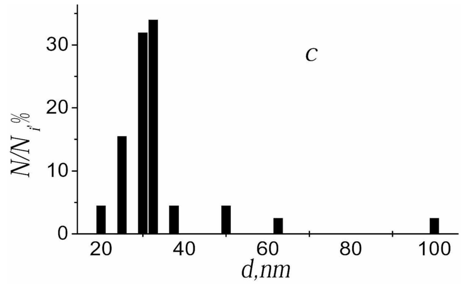
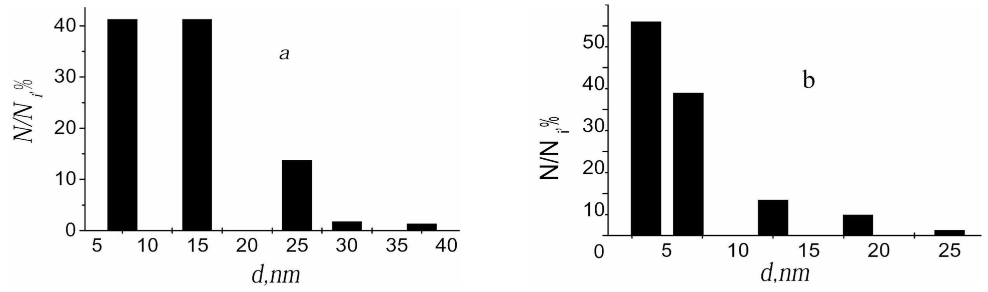


Fig. 1. Particle size distribution for: SiO_2 in the sol produced by alkaline TEOS hydrolysis (a) and silver in the composite sols (b, c). Reductants: b) sodium borohydride, c) hydrazine hydrate



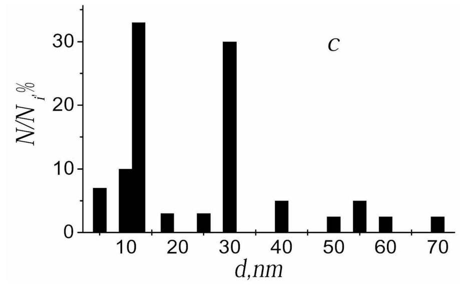


Fig. 2. Particle size distribution for: SiO_2 in the acidic sol produced by ion-exchange from sodium metasilicate (a), and silver in the composite sols (b, c). Reductants: b) sodium borohydride, c) hydrazine hydrate

Heating Ag–SiO_2 films in the air at 500 °C results in their discoloration, the temperature at which it occurs being little affected by the method of the sol production. Heating a discoloured sample in hydrogen (500 °C, 40 min) results in formation of silver particles accompanied by the nanocomposite colour reappearing. The sizes of the particles re-formed are either the same or 1,5–2 times smaller than those of the initial ones. When the particles become hermetically encapsulated, the composite looses its ability to discolour on further oxidative heating. Annealing the initial films in hydrogen results in the larger and polydisperse silver particles. The proportion of the small particles (5–20 nm) decreases and a fraction of the larger aggregates (up to 50–90 nm) appears (see Table). Optical properties of Ag–SiO_2 films formed from the composite sols differ significantly depending on the way of their production (with different sol precursors and reductants used) and heat treatment conditions (Fig. 3).

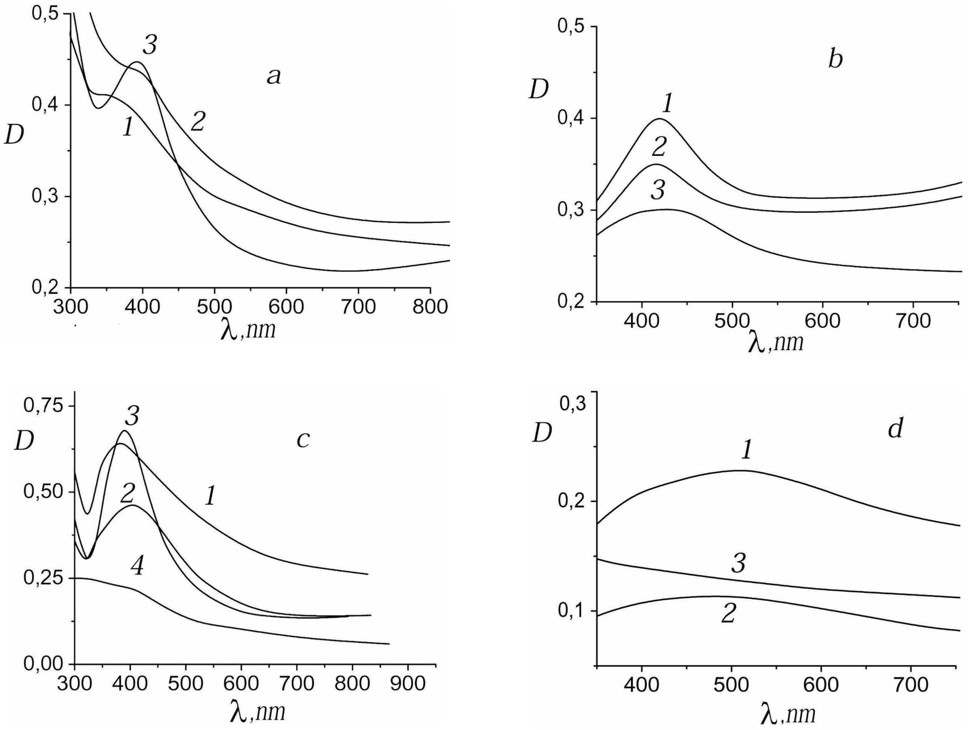


Fig. 3. UV-visible absorption spectra of silver-containing films formed from composite sols. Reductants: sodium borohydride (a, b), hydrazine hydrate(c, d). Matrices: alkaline SiO_2 sol produced from TEOS (a, c), acidic SiO_2 sol produced from sodium metasilicate (b, d).
Layers: 1) initial 2) heated in hydrogen 3) heated successively in the air and in hydrogen 4) air-heated

For the films formed from the composite sols produced with TEOS, heating in the “air-hydrogen” mode results in a sharper plasmon maximum with the optical density increasing. As for the films formed from the composite sols produced with sodium metasilicate as the silica sol precursor, the same heating mode results in the broader plasmon band and the optical density decreasing. For the films formed by heating in hydrogen (for both precursors of the oxide sol) there occurs a red shift of the silver plasmon absorption band due to an increase both in size and in polydispersity of the silver particles.

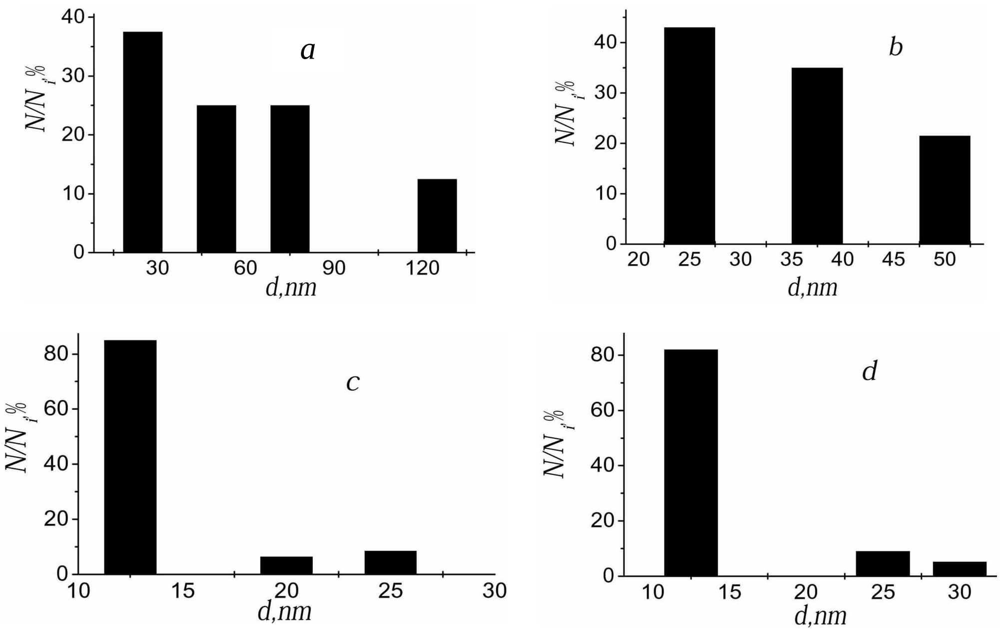


Fig. 4. Particle size distribution for SiO_2 in alkaline sols produced from TEOS (a) and sodium metasilicate (c), and for gold (b, d) in respective composite sols with sodium borohydride used as the reductant

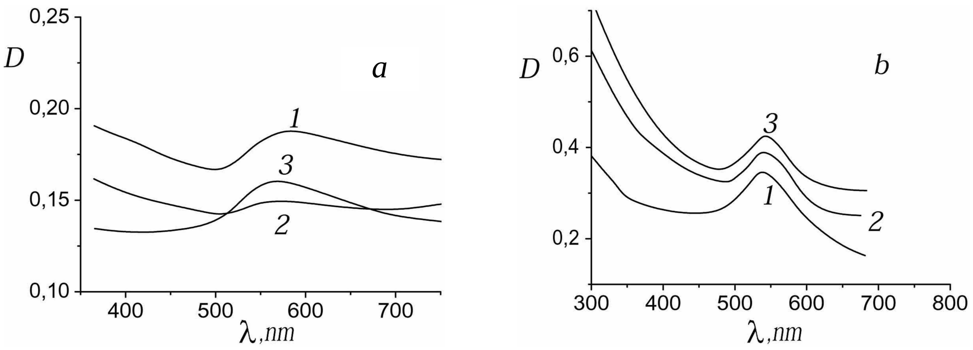


Fig. 5. UV-visible absorption spectra of gold-containing films formed from composite sols, sodium borohydride used as the reductant. Matrices: alkaline SiO_2 sols produced from sodium metasilicate (a), TEOS (b). Layers: 1) initial 2) air-heated 3) hydrogen-heated

The particles of gold in Au–SiO_2 films formed from respective composite sols used with particle sizes of 10–50 nm (Fig. 4b, d). In contrast to those of silver in the similar oxide matrices they do not oxidize when heated in the air. The particle size increases 1,5–2 times for different types of silica sols used (see Table). On heating Au–SiO_2 layers in hydrogen, larger gold particles are also formed by aggregation of the small ones. In spite of the particle size growth on heating, the shape of the optical absorption spectrum of the films remains essentially the same, the optical density only being slightly changed throughout the visible spectrum (Fig. 5). The changes in the optical density of both Au–SiO_2 and Ag–SiO_2 films on heating depend on the chemical nature of the oxide sol precursors. For the composite films based on sodium metasilicate, the decrease of the optical density observed on heating is due to their structurization resulting in the films becoming thinner. An increase in optical density is observed for the TEOS-based films, which can be related to the burnt remains of TEOS (particularly, carbon) contributing to the film absorption.

Ge–SiO_2 films

GeO_2 reduction with hydrogen in films formed from pure GeO_2 sols has previously been found to begin at 470–480 °C and to proceed with appreciable rate at 500 °C, the films turning red-brown because of ultrafine Ge particles formation [7].

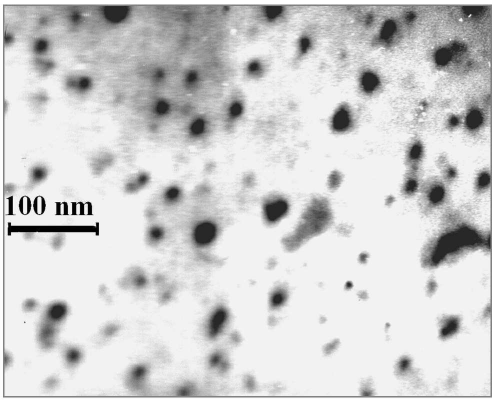


Fig. 6. TEM image of Ge-particles in Ge–SiO_2 film formed from GeO_2–SiO_2 sol produced by co-hydrolysis of TEOS and $GeCl_4$

The conditions of GeO_2 reduction to Ge in GeO_2–SiO_2 films under investigation differ significantly from those of pure GeO_2 films reduction. Heat treatment in hydrogen has been shown to be necessary to completely reduce GeO_2 in GeO_2–SiO_2 films formed from sols produced by co-hydrolysis. Virtually no reduction has been observed below 600 °C. The increased temperature of GeO_2 reduction to Ge in such films compared to that observed in films of pure GeO_2 may be explained by formation of mixed Si–O–Ge bonds in the sol produced by co-hydrolysis hindering GeO_2 reduction. IR-spectroscopy data confirm the presence of Si–O–Ge bonds. Absorption bands appear in GeO_2–SiO_2 powder spectrum (not shown) in the range of 600–700 cm^{-1} which are characteristic of the Si–O–Ge bond vibrations. The formation of such bonds is likely to explain the hindered GeO_2 crystallization in the GeO_2–SiO_2 system as opposite to that of pure GeO_2

(GeO_2 in SiO_2 matrix remains amorphous at the temperature of 500 °C, when the pure GeO_2 is already crystalline).

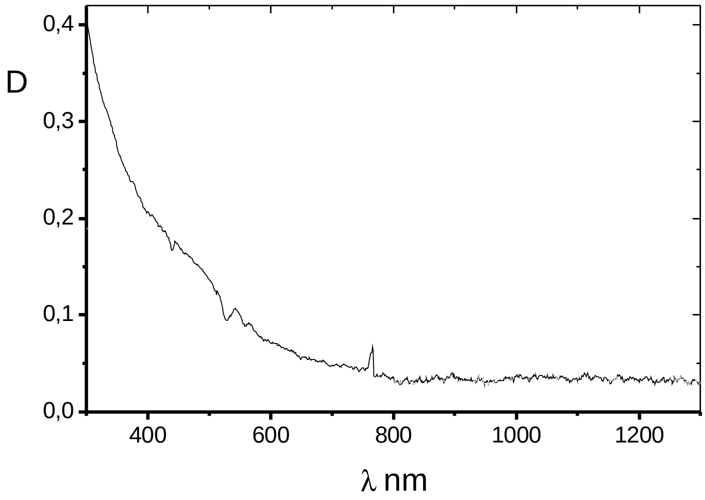


Fig. 7. Optical absorption spectrum of Ge–SiO_2 film prepared by reducing of GeO_2–SiO_2 layer in hydrogen

TEM-investigations have shown that spheroidal particles (5–15 nm in size) are formed in sols produced by co-hydrolysis of TEOS and $GeCl_4$. Particles of diamond-like germanium (10–15 nm in size) are formed in films produced from such sols and reduced at 650 °C for 2 h (Fig. 6). Optical absorption spectra of the reduced films are presented in Fig. 7 (GeO_2–SiO_2 precursor films do not absorb in that wavelength range). The films are characterized by an absorption edge (about 600–700 nm) blue-shifted from that of a bulk sample. Considering the above data concerning the Ge particle size in the films under study, it is unlikely that such a position of the absorption edge is related to the quantum size effect. It seems more likely that the shift observed is due to the light scattering on the assembly of particles, the size of it being smaller than the wavelength (according to the Mie theory) [8].

GeO_2 hydrogen reduction to Ge in GeO_2–SiO_2 films formed from the sols produced by mixing pure GeO_2 and SiO_2 sols proceeds at 500 °C. It is only the diamond-like germanium phase that is found in powders separated from the GeO_2–SiO_2 sols and heated at 500 °C for 2 h, indicating that heating in hydrogen for 2 h is enough to reduce GeO_2 to Ge in the films, too. According to the EM data, GeO_2–SiO_2 sols, prepared by mixing pure sols, contain spheroidal particles of sizes 10–25 nm for GeO_2 and 50–70 nm for SiO_2. In Ge–SiO_2 films produced from Ge particles of diamond-like structure are formed, of the sizes in the same range as those of GeO_2. Thus, there is no noticeable enlargement of the particles on reducing GeO_2 with hydrogen in SiO_2 matrix, in contrast to the reduction of pure GeO_2, for which a general trend of the particle size increase has been observed [9].

Thus, using the sol-gel method to form thin Me–SiO_2 films from composite sols containing nanoparticles of hydrous silica and silver/gold metal or germanium dioxide makes possible varying the metal particle sizes and size distribution, thus affecting optical characteristics of the films. Silica nanoparticles prevent aggregation of Ge particles formed in the Ge–SiO_2 system. Silica sols produced from sodium metasilicate were found to stabilize silver and gold nanoparticles formed by chemical reduction.

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