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Size variation and optical absorption of sol-gel Ag nanoparticles doped SiO_2 thin film

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Abstract

In this research, we have focused on the formation of Ag nanoparticles dispersed in SiO_2 matrix using sol-gel method. The influences of the metal concentration on the size variation of Ag nanoparticles and the size effect on the surface plasmon absorption have been studied. Sol-gel silica thin films containing Ag particles were synthesized by dip-coating on soda-lime glasses. The molar ratio of Ag/Si was chosen from 0.2% to 8%. All films were dried in air at 100 °C for 1 h. Using X-ray photoelectron spectroscopy, the Ag/Si ratios in the prepared films have been measured. In addition, it was shown that the prepared matrix was a stoichiometric composition as SiO_2, and the synthesized nanoparticles were mainly in the metallic state. Size and distribution of the nanoparticles were measured by high resolution scanning as well as transmission electron microscopy and also atomic force microscopy analyses for low and high Ag concentrations, respectively. We have found that by decreasing the Ag/Si ratio from 8 to 0.2 mol%, the particle size reduces from 95 to 4 nm with a nearly spherical shape. UV-visible spectrophotometry showed that the size reduction of the Ag nanoparticles for the Ag/Si molar ratios ranging from 8 to 0.2 mol% leads to an intensity reduction of the absorption peak and a blue shift from 460 to 410 nm.

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Keywords: Nanoparticles; Silver; Sol-gel; Silica matrix

1. Introduction

Formation of metal nanoparticles dispersed in solid dielectric materials, which can result in novel optical properties, has been of increasing interest due to their potential applications in nonlinear optics [1,2]. Optical properties of the nanoparticles depending on the surrounding medium have special worth [3]. Recently, various techniques such as laser ablation, sputtering, and sol-gel methods have been used to fabricate such composite thin films (especially transparent matrix thin films containing nanoparticles). Among them, the sol-gel synthesis is one of the most useful methods for preparation of metallic nanoparticles in an oxide transparent matrix such as SiO_2 or TiO_2. Meantime, different metal particles such as gold [4–7], copper [8,9], platinum [10,11], and silver [12–16] were introduced in glassy matrices by the sol-gel method.

It is well known that the properties of such composite films are dependent on their microstructure, e.g. size, shape, composition, and also spatial distribution of the particles in the film [17,18]. Therefore, in order to describe the relationship between the optical properties and microstructure of the composite thin films, it is necessary to obtain the composite films with well-defined microstructures. Recently, the effect of some parameters controlling nano-silver growth in silica sol-gel films has been investigated [16].

In this investigation, we report a facile and fast route for synthesis of SiO_2 thin films containing Ag nanoparticles by using the sol-gel technique. The influences of the metal concentration on the size variation of Ag nanoparticles, and so, on the surface plasmon absorption of the films have been studied. Moreover, the surface concentration of nano-silver and the chemical state of the grown matrix as well as the nanoparticles located on its surface have been determined.

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2. Experimental

Sol-gel silica thin films containing silver nanoparticles were synthesized by dip-coating on soda-lime glass microscope slides. The SiO_2–Ag sol was prepared using tetraethyl orthosilicate (TEOS), ethanol, distilled water, nitric acid, and silver nitrate. The solution was prepared by mixing TEOS and ethanol in equal volume. After stirring for 30 min, we added distilled water to the solution drop by drop while stirring at room temperature. Then, different amounts of $AgNO_3$ and HNO_3 (to adjust pH of the solution about 2) were added to the solution. The assumed molar ratios of TEOS/C_2H_5OH/H_2O/$AgNO_3$ are 1, 3.8, 4, and n, respectively. The n is nominal molar ratio of Ag/Si which was chosen as 0%, 0.2%, 0.4%, 0.6%, 0.8%, 1.2%, 1.6%, and 8%. Following preparation of the solutions containing Ag colloids, the sols were left for aging until the viscosity reached approximately the range of 2–4 cP. The coatings were performed by 60 s dipping of the glass slides in the solution with a pulling rate of 1 mm/s. All films were dried in air at 100 °C for 1 h which lead to obtaining transparent light brown color films. Meantime, for silica films containing 0.2 and 8 mol% Ag, we have considered an additional heat-treatment at 200 °C in air for 2 h.

The surface roughness and topography of the films as well as grain size and size distribution of the Ag nanoparticles on the films were studied by atomic force microscopy (AFM) in air with a silicon tip of 10 nm radius in contact method. A Philips-CM200 high resolution transmission electron microscopy (HRTEM) was used at 200 kV to determine size of the nano-silver particles and also particle size distribution for the film containing 0.2 mol% Ag which was annealed at 200 °C in air for 2 h. The surface morphology of the films was examined by a Philips-XL30 High resolution scanning electron microscopy (HRSEM). A Jascow-V530 UV-visible spectrophotometer was used to determine the optical absorption of the films in the wavelength range of 300–1100 nm. Moreover, using the optical method, the film thickness was measured in the range 140–190 nm, as a typical thickness of the dried films for all the silver concentrations. X-ray photoelectron spectroscopy (XPS) equipped with an Al–K_α x-ray source was employed to study the surface atomic concentration and chemical state of the silica films doped by silver nanoparticles. All binding energy values were determined by calibration the C(1s) line to 284.6 eV. Both survey scans and individual high-resolution scans for Ag(3d), Si(2p), C(1s) and O(1s) peaks were recorded.

3. Results and discussion

AFM images of the silica films containing 0, 0.8, 1.6 and 8 mol% Ag have been shown in Fig. 1. For the silica film with no Ag concentration, as our reference morphology, a uniform surface (with no special feature on it) is observed (Fig. 1a). By increasing the Ag concentration to 0.4 mol%, some particle-like features with 18 nm average size were observed on the surface (not shown here). At 0.8 mol%, AFM images show a considerable amount of spherical particles on the silica surface with diameters ranging from 10 to 50 nm and average size of about 28 nm, as can be seen in Fig. 1b. AFM images of the dried films containing higher Ag concentrations showed that surface concentration and also average size of the particles are increased by raising the Ag concentration. The average size of the particles was measured about 48 and 65 nm for 1.2 and 1.6 mol% Ag concentrations, respectively. By increasing the Ag concentration to 8 mol%, AFM images showed that the thin

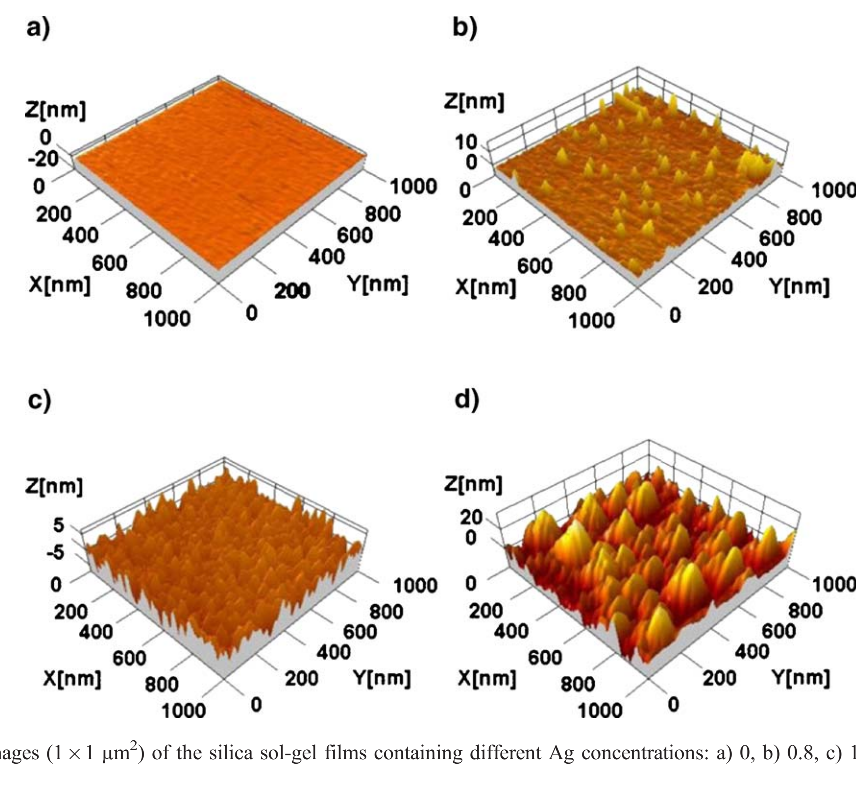

Fig. 1. AFM images (1 × 1 μm^2) of the silica sol-gel films containing different Ag concentrations: a) 0, b) 0.8, c) 1.6 and d) 8 mol%.