FORMATION OF METAL NANOCLUSTERS IN SILICATE GLASSES FOR NONLINEAR OPTICAL APPLICATIONS

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Abstract

Silver nanoclusters have been formed in light waveguides obtained by Ag⁺-Na⁺ ion-exchange process in glass, by either irradiating with low-mass ion beams or by heating in hydrogen atmosphere at temperatures varying in the range 100-250°C. Metal nanocluster-silica composites have been also obtained by the sol-gel technique. Nanocluster modifications induced by pulsed laser irradiation have been investigated, and annealing behavior of nanoclusters synthesized by the sol-gel has been studied. Composites were characterized by Secondary Ion Mass Spectrometry and Rutherford Backscattering Spectrometry, in order to determine concentration depth-profiles, and by Transmission Electron Microscopy for the nanocluster detection and size evaluation. Optical analyses were performed to evidence linear and nonlinear properties.

I. INTRODUCTION

Nonlinear optical materials are essential components of functional photonic devices for optical communications, sensing, and computing [1-3], as -for example- all-optical switching devices [2]. Understanding the correlation between material processing and nonlinear optical properties is especially critical for the development of advanced nonlinear optical materials for photonic devices. The material properties for applications in such devices include picosecond or shorter response times, low power switching threshold, wavelength tunability, thermal stability, low two-photon absorption, high threshold for laser-induced damage, and THz recycling frequency.

In the last few years, composite glasses formed by embedding semiconductor or metal nanoclusters in glass have attracted much attention as promising materials for optoelectronics. In particular, metal nanocluster-doped glasses, i. e., glasses which contain crystallites of metals, show an enhanced third-order susceptibility, whose real
part is related to the intensity-dependent refractive index [2]. This technological interest is strengthened by the general interest in strongly quantum-confined electronic systems which exhibit quite a number of striking effects deriving from the increased electronic density of states near the conduction-band edges. This suggested the introduction for metal nanoclusters-doped composites of the term metal quantum-dot composites (MQDC) in analogy to multiple-quantum-well devices. Glass researchers have employed various ways to prepare metal nanocluster-doped glasses, namely, sol-gel processes, quenching and heat-treatments and processes which use porous glasses. More recently, ion implantation has attracted a large interest for the possibility to pattern the materials, to overcome the doping solubility limits, and to introduce virtually any element in the glass substrate [4-8]. Several material-related aspects of the above mentioned metal colloids have been studied and we believe that, in addition to the development of the preparation techniques and of the chemical, structural and optical characterization, we should begin to consider the so-called architecture of systems for optical information processing.

In this paper we present the results obtained by our group, in cooperation with external laboratories, on metal (particularly silver) nanocluster formation in glasses obtained by sol-gel as well as low-mass ion irradiation or annealing in hydrogen atmosphere of light waveguides prepared by the ion-exchange technique. Results on thermal stability and modifications induced by pulsed-laser irradiation will be also reported.

II. EXPERIMENTAL

The composition of the glass utilized for the fabrication of ion-exchanged waveguides is (wt %): 69.6 SiO₂, 15.2 Na₂O, 1.8 Al₂O₃, 6.5 CaO, 5.1 MgO, 1.1 K₂O, 0.4 S0₃, 0.2 TiO with trace-amounts of Fe₂O₃, As₂O₃ and Cs₂O. Glass samples were ion-exchanged in a molten salt bath of 0.1 % mol. AgNO₃ in NaNO₃. Exchange temperature of 320 °C and processing time of 30 minutes were set to obtain penetration depths of about 5 µm. Two different experiments were performed on ion-exchanged samples. Some waveguides were irradiated by He⁺ or N⁺ ions at energies varying from 100 keV to 2 MeV. Other waveguides were heat-treated in a quartz tube with H₂ flux at a pressure slightly greater than atmospheric one. Treatments times were between 2 hours and 12 hours and temperatures in the range 120 °C to 250 °C. Furthermore, some samples, as-exchanged and after He⁺ irradiation, were irradiated by using a Q-switched Nd:YAG laser operated at both 1064 nm and 532 nm of wavelength. Pulse duration was about 10 ns.

The sol-gel method was used for the synthesis of metal (copper or silver or copper-silver mixture) doped silica films deposited on silica glass substrates with a procedure described in [9-10]. The sol-gel coatings were heat-treated in different atmospheres (argon, air, 5%H₂-95%N₂) at different temperatures, in the range 500-1100°C, using soaking periods for each step in a cumulative heating procedure.

In the case of ion-exchanged waveguides, subsequently treated with the above described methodologies, silver and sodium profiles were determined by Rutherford Backscattering Spectrometry (RBS), while the hydrogen profile was obtained by
Elastic Recoil Detection Analysis (ERDA). In both techniques, a \(^{4}\text{He}^{+}\) beam at the energy of 2.2 MeV was used at National Laboratories INFN-Legnaro. Secondary Ion Mass Spectrometry (SIMS) analyses were also performed, using a CAMECA IMS-4f spectrometer. Refractive index profiles of the waveguides were reconstructed by an inverse WKB method from the set of effective indices corresponding to the guided modes. The effective indices were determined by m-lines spectroscopy. Optical absorption spectra were recorded in the wavelength region from 250 to 600 nm, by a Cary UV-VIS-NIR dual-beam spectrophotometer. Samples for transmission electron microscopy (TEM) were prepared by cutting 3 mm diameter discs with a slurry drill, mechanical grinding of the disc from the backside to a thickness of about 20 mm. The final thinning to the electron transparency was achieved by planar backthinning by ion milling with an Ar gun at 5 keV. To minimize ion damage, samples were cryogenically cooled during ion milling. The prepared samples were examined in a Philips CM30 TEM, operating at 300kV. Finally, nonlinear refractive index was obtained by Z-scan measurements, performed using a mode-locked cavity-dumped dye laser with pulse duration of 6 ps and in the wavelength range from 570 to 590 nm.

III. RESULTS AND DISCUSSION

A. Annealing of waveguides in hydrogen atmosphere

Annealing causes a near-surface precipitation of metallic silver to form nanometer-size clusters with good uniformity in size and spatial distribution, as shown in Figure 1, where we reported the cross-sectional TEM photograph of the sample annealed at 250 °C for 5 hours. Here, from the surface to a depth of about 270 nm, it is evident the presence of silver clusters, of spheroidal shape, with fcc structure, randomly oriented with diameters in the range 4-6 nm. The optical absorption spectra of annealed samples display a band peaked at about 410 nm, typical of absorption in metallic silver nanoclusters, due to the surface plasmon resonance (SPR) [11-13]. The SPR frequency depends on metal-particle size through the dielectric response function of the metal, and in this case the absorption band is consistent with predictions of the Mie theory for silver nanoclusters having radius of the order of a few nanometers.

![TEM micrographs (cross section) of silver nanoclusters, formed after annealing in hydrogen atmosphere for 5 hours at 250 °C.](image)
In Figure 2 the hydrogen and silver concentration profiles are reported after annealing in hydrogen atmosphere for 5 hours at 180°C, together with a corresponding typical absorption spectrum, showing the characteristic peak due to metallic silver nanoclusters. In a study of this process [14] we reached the conclusion that the hydrogen permeation and ion-exchange between hydrogen and sodium (remaining in the glass matrix after silver-for-sodium exchange) are steps of annealing process. A further step is the diffusion of silver towards the surface, with an activation energy, 22 kcal/mole, close to that measured for silver-sodium interdiffusion in glasses of similar composition. Silver migration cannot be simply ascribed to a direct interaction with hydrogen, but to a more complex process involving a charge balancing mechanism during hydrogen-sodium ion-exchange. An activation energy of about 15 kcal/mole was obtained for the hydrogen permeation in the glass.

![Figure 2. Hydrogen and silver depth concentration profiles (left) and optical absorption spectrum (right) for samples annealed at 180°C.](image)

B. Low-mass ion irradiation of ion-exchanged waveguides

The formation of silver nanoclusters was also obtained by irradiation of ion-exchanged samples with He⁺ or N⁺ ions. The irradiation current and time were varied in order to study the role of deposited energy rate and processing time [15].

TEM micrograph for a 100 keV, 2x10¹⁶ cm⁻² nitrogen-irradiated sample is reported in Figure 3. The inset shows the selected area electron diffraction pattern indicating the presence of randomly oriented silver crystals. The clusters radius in the irradiated region is about 2-3 nm.
Figure 3. TEM micrograph (cross section) of silver nanoclusters, formed after 100 keV, 2x10^{16} cm^{-2} nitrogen irradiation of an ion-exchanged waveguide.

We have reported elsewhere [16] that the irradiation current density is a critical parameter for the precipitation process. At present, it is not possible to separate the contributions to the silver precipitation, of thermal effects due to local heating, and of radiation-enhanced diffusion. Certainly the silver diffusivity, the deposited energy distribution and defect migration would play an important role in determining the final concentration distribution of precipitates.

Third-order susceptibility measurements for these samples gave positive values of the intensity-dependent refractive index n_2 up to 10^{-13} cm^2/W, that turn into negative values after repeated measurements. This peculiar behavior indicates that, when exposed to high optical power densities, silver in the nanoclusters tends to modify the chemical environment, possibly changing permanently its oxidation state. Ion-irradiated samples were laser-treated by using a Q-switched Nd:YAG laser operated at both 1064 and 532 nm of wavelength, with a pulse duration of about 10 ns. After a single pulse irradiation above a threshold value of 0.3±0.1 J/cm^2 for \( \lambda = 532 \) nm and 5±1 J/cm^2 for \( \lambda = 1064 \) nm, the irradiated region becomes nearly transparent and the SPR optical absorption peak is dramatically reduced. The TEM micrograph of a helium irradiated silver-exchanged soda-lime glass sample, before and after irradiation by a laser pulse at \( \lambda = 532 \) nm and \( E = 0.5 \) J/cm^2, is reported in Figure 4.

Figure 4. TEM views of an ion-exchanged/ion-irradiated sample before (left) and after (right) laser irradiation with 0.5 J/cm^2 at \( \lambda = 532 \) nm.
A reduction of the cluster diameter from the value of about 5 nm before to a value of about 2.5 nm after laser irradiation is evident. This is accompanied by a corresponding increase in the number of clusters, being the total silver concentration constant, as determined by RBS analysis. The increasing ratio between the number of surface and bulk atoms with decreasing cluster size favours the formation of silver-oxygen interactions with respect to silver-silver bonds. This was evidenced by X-ray photoelectron spectroscopy (XPS) and X-ray excited Auger-electron spectroscopy (XE-AES) measurements [17]. After laser irradiation the silver α parameter (binding energy of XPS Ag3d_{5/2} and kinetic energy of AES AgM_{5}NN peak) changes from 720.3±0.2 eV, close to the value of metallic silver (720.5±0.2 eV), to 719.1±0.2 eV, in agreement with the value measured for an Ag_{2}O standard. Besides the fragmentation of the silver clusters formed in the ion-irradiated region, we observe that the laser irradiation is also effective in promoting cluster formation in as-exchanged region, where are present few small clusters with a mean diameter of about 1.5 nm. In these regions the laser irradiation causes the formation of small nanocluster, about 2.5 nm in diameter. In this case, laser light induces nucleation and growth depending on different mechanisms [18].

C. Metal nanoclusters in silica matrix synthesized by the sol-gel technique

Metal (copper or silver or copper-silver mixture) doped silica films were deposited on silica glass substrates by the sol-gel dip-coating method [9-10]. In the case of silver nanocrystal-doped silica films, two types of clusters with different diameters were observed in the coatings heat-treated at 300 and 450 °C, with respective average diameter of about 1 nm and 15 nm, the latter composed by much few clusters, both with an fcc structure. At 500 °C and 550 °C, the densification of the silica matrix favours a new precipitation step for silver, with a final particle diameter distribution of 3±1 nm. The clusters formed at and above 500°C are stable and do not exhibit any degradation of their optical properties with aging. The copper-containing films were first heated in air up to 550 °C to burn out organic compounds. A broad absorption band at about 740 nm indicate the presence of Cu^{2+} ions. Subsequent annealing in reducing atmosphere (5%H_{2}-95%N_{2}) induces the formation of Cu nanoclusters, evidenced by a broad Cu-SPR absorption band at about 570 nm, at 700 °C; however, the absorption band in the range 600-800 nm indicates that Cu^{2+} was not yet completely reduced. As the temperature raised at 800 °C, a clear SPR absorption peak grew at about 568 nm. At this temperature, the increase of the annealing time causes a sharpening of the SPR absorption band and its blue-shift to 562 nm. TEM analysis shows nearly spherical particles with an average diameter of about 8 nm and an fcc structure. In the case of Ag and Cu co-doped silica films, films were prepared with Cu/Ag molar ratio of 1.2 and 3 at constant (Ag+Cu)/SiO_{2} molar ratio of 0.175. After annealing in reducing atmosphere, at 700 °C, separated Ag and Cu nanoclusters are formed in the silica matrix, with clearly visible SPR bands of both Ag and Cu. Both Ag and Cu SPR peaks are shifted with respect to SPR of single-metal doped silica. The size of the clusters and their distribution turn out to be dependent on the film
composition. Bright-field TEM of lAg3Cu sample, annealed at 700 °C, is shown in Figure 5.

In the lAg1Cu sample small clusters of about 5 nm in diameter and bigger clusters of 40-50 nm in diameter coexist. A narrower size distribution with diameters from 5 to 35 nm is observed in the lAg2Cu film. Clusters become spherical with a more homogeneous distribution (5-20 nm in diameter) in the case of lAg3Cu sample. Z-scan measurements [10] were performed for a laser pulse duration of 6 ps and in the wavelength range from 570 to 590 nm. For sample lAg1Cu and pure Cu the measured value of nonlinear refractive index are both of the order of $10^{-13} \text{ m}^2/\text{W}$ at $\lambda=590\text{ nm}$. A study of nanocluster annealing behavior has been performed in different annealing atmospheres. Cluster growth and dissolution, as well as migration of metal atoms towards the sample surface, with a subsequent evaporation, were observed to occur at temperatures which depend on the annealing atmosphere. In particular, in the mixed silver-copper system, the formation of Ag-Cu phase separated clusters was observed.

IV. CONCLUSIONS

Metal nanoclusters are formed in silica and soda-lime glasses by using different methods. From the point of view of nonlinear optical material fabrication, the investigated techniques promise to be suitable for designing nonlinear devices with performances based on nonlinear metal-doped glasses. Extended research activity is necessary in particular for reaching the control of the cluster size uniformity and of the cluster stability during high-power laser irradiation.

REFERENCES