Optical absorption and HRTEM characterization of metallic nanoparticles produced by MeV ion implantation

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Ion implantation has attracted considerable interest as a method to modify the optical properties of insulators in order to produce materials with nonlinear optical properties. In this work we describe the synthesis of metallic nanoparticles in silica by MeV ion implantation using the IFUNAM’s Pelletron accelerator. Several factors such as the ion fluence, the radiation damage induced by the ion implantation, and the subsequent thermal annealing conditions (temperature, atmosphere, etc.) can determine the shape, size and distribution of the clusters in the sample. High-purity silica samples were implanted at room temperature with Cu, Ag or Au ions at various fluences up to $6 \times 10^{16}$ ions/cm$^2$. The samples were then annealed in either a reducing or an oxidizing atmosphere at temperatures ranging from 300 to 900°C. The samples were characterized by optical absorption and HRTEM. Rutherford Backscattering Spectrometry was used to determine the concentration of the implanted ions and their depth distributions in the samples. Changes in the optical properties of the samples arise from nanometer-sized metallic clusters produced as a result of implantation and/or annealing. The metallic nanoclusters strongly absorb optical radiation at the surface plasmon resonance wavelength (∼560 nm for Cu, ∼400 nm for Ag, ∼520 nm for Au). Reducing and oxidizing annealing atmospheres affect in a different way the nucleation and growth of Cu, Ag and Au nanoparticles. The implications and the possible mechanisms concerning this behavior are discussed in this paper.

Keywords: Metallic nanoparticles; optical properties; silica; absorption; ion implantation.

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1. Introduction
The exceptional properties of silica such as high transparency in a wide spectral region (visible, UV, vacuum-UV) and low conductivity, in combination with favorable mechanical characteristics, have led to its widespread utilization in many technological applications [1]. Hardness, fracture and corrosion resistance originate from the strong covalent bonding between Si and O atoms, while the transparency and the low conductivity arise from the high energy gap (approximately 9 eV) from valence to conduction band. Recently, metal ion implantation has been widely used to introduce foreign ions into pure bulk silica to produce metallic nanoparticles, at the near-surface region of the samples, after an additional thermal annealing [2-4]. Moreover, the composites formed by metallic nanostructures embedded in glass matrices exhibit large optical nonlinearities, as their high third-order dielectric susceptibility $\chi^{(3)}$, and therefore these materials are particularly promising candidates for technological applications in the fields of nonlinear integrated optics, photonics and in all optical switching technology [2]. The nonlinear optical properties depend on the size and shape of the clusters, and on the interaction of the metallic clusters with the host matrix. Because of the interest for optoelectronic applications, most of the recent papers in literature deal with implantation of metals with very weak reactivity, i.e. mainly copper, silver and gold, in silica [5-11]. These metallic nanoparticles can be synthesized within silica glasses by ion implantation followed by thermal annealing [2-5]. However, not only the implanted ions, but also the defects generated during the implantation and the subsequent heat treatment can modify the optical properties of the implanted silica. Therefore, it is also very important to assert if the modification of the optical properties in silica is due to defects or to the implanted ions [12]. The present work

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High-purity silica glass plates (16×16×1 mm³), with OH content less than 1 ppm and impurity content less than 20 ppm (with no individual impurity content greater than 1 ppm), were implanted at room temperature with 2 MeV Cu, Ag and Au ions at various fluxes up to 6×10¹⁶ ions/cm². After implantation, all the samples were cut into identical small pieces (5×8 mm²) and thermally annealed in either a reducing (N₂+H₂) or an oxidizing (air) atmosphere at various temperatures up to 1100°C for 1 hour. The ion depth distributions and fluxes were determined by RBS measurements using a 3 MeV ⁴He⁺ beam. Ion implantation and RBS analysis were performed at the 3 MV Tandem accelerator (NEC 9SDH-2 Pelletron) facility at the Instituto de Física (UNAM). HRTEM was performed using a JEOL JEM-2010F FasTEM microscope operating at 200 kV (0.19 nm point-to-point resolution) and equipped with a GATAN digital micrograph system for image acquisition (version 3.7.0). The sample preparation procedure includes mechanical polishing and Ar⁺ ion beam milling from the glass substrate side to generate a cross-section sample. The final thickness of the sample is <100 nm, to be transparent to the electron beam. High-resolution images were obtained at the optimum focus condition (Scherzer condition) [23]. Also, nanoparticle image simulation was performed with the SIMULATEM software [24]. Optical absorption spectra were obtained at room temperature using a Perkin-Elmer 330 double-beam spectrophotometer in the wavelength range 190-900 nm.

2. Ion implantation and the creation of defects in silica

It is well known that ion implantation is widely used in the fabrication of devices with industrial applications because the implanted species allow the modification of the physical properties of the material [3,13,14]. High-energy positive-ion implantation meets other attractive demands: deep level ion implantation, 1-2 μm in silica with MeV ions, three dimensional modification of materials, good controllability of doping levels and spatial distribution of impurity [13,15]. Also, ion bombardment induces complex microstructural changes, such as point defects and amorphous regions, in the near-surface region of a crystalline solid. Thus, the mechanisms concerning damage production by ion implantation have been a very attractive subject of study for many years. Defects encountered in radiation or implantation damage studies are characterized by their influence on the physical properties of semiconductors, metals or oxides [16,17].

The presence of defects in fused silica, generated either during fabrication or by external treatments, degrades its features of transparency and low conductivity since the difference between the electronic states localized in defects is less than the energy gap from valence to conduction band in pure silica [18]. To our knowledge, little work has been done on optical emission of ion-implanted silica in order to establish the evolution of defects in ion-implanted silica after thermal annealing [12]. Moreover, the OH content in SiO₂ can affect the formation of defects and/or the transformation of existing defect precursors in SiO₂ [19]. It has been observed that swift ions in SiO₂ produce point defects, like E’ and B₂ centers, generated by oxygen displacements [20]. An oxygen vacancy can generate two kinds of defects depending on its electronic charge: the E’ and B₂ centers, which are considered the most typical defects in SiO₂. The E’ and B₂ centers have well-known absorption bands at 214 and 248 nm, respectively [12,20]. The paramagnetic characteristic of the E’ center, allows the use of Electron Paramagnetic Resonance (EPR) analysis to study the E’ defects in ion-implanted silica [21,22].

3. Experimental

High-purity silica glass plates (16×16×1 mm³), with OH content less than 1 ppm and impurity content less than
rent density of the implanted ions, as well as on the matrix material itself.

According to our previous experience, nanoclusters may get formed or not even during the implantation process depending on the ion beam current and they may get formed or modified by subsequent thermal treatments [5,6,27]. Figure 2 shows the optical absorption spectra of the silica samples implanted with 2 MeV Ag ions at three different fluences, after the annealing at 900°C in either a reducing or an oxidizing environment. At this temperature occurs a significant increase in the surface plasmon resonance intensity compared with that observed at lower temperatures, in particular for the samples annealed in a reducing atmosphere. The surface plasmon resonance associated with the formation of metallic Ag nanoparticles appears at around 400 nm and increases with the ion fluence. It is clearly greater in magnitude for the samples annealed at 900°C in a reducing environment in comparison with those annealed in air, for the same fluence.

Our results suggest that the formation of Ag nanoclusters is enhanced favorably by the annealing in the reducing atmosphere. We consider that the reducing atmosphere is more favorable to the formation of larger Ag nanoclusters because the presence of hydrogen atoms during the annealing allows the passivation of defects such as Si- or O- broken bonds, which may act as nucleation centers for Ag nanocluster formation. Then, in the case of annealing in a reducing atmosphere, the concentration of nucleation centers should be lower compared with that expected in an oxidizing environment. While the Ag nanoclusters can grow larger in a reducing atmosphere, they could be smaller but numerous after the annealing in air [5]. Therefore, the higher intensity in the optical resonance peak of the samples annealed in a reducing atmosphere compared to the ones annealed in air is due to their larger cluster size and in some samples greater cluster number. Also, it is important to take into account that the mobility of Ag atoms in silica is very high [5,8], especially at high temperatures, allowing the formation of larger Ag clusters in the samples implanted with higher fluences. Then, the increase in the absorption peak intensity with the annealing temperature is due to the increase in the volume fraction of silver precipitates in the implanted samples. Also, a red-shift is observed for increasing nanoparticle size and simultaneously a broadening of the resonance occurs, for a given annealing atmosphere. On the other hand, not only particle parameters such as size and shape influence the plasmon resonance energy, but also the refractive index of the surrounding medium. Increasing refractive index of the medium leads to a red-shift of the resonance, and this red-shift is due to the shielding of the surface charges by the polarization of the embedding medium [14]. This effect must be studied in detail and we will address this behavior in a future work.

Figure 3 shows the optical absorption spectra of the silica samples implanted with 2 MeV Cu ions at $3 \times 10^{16}$ Cu/cm$^2$, and the corresponding ones annealed at 900°C in a reducing or an oxidizing atmosphere. In the case of metallic Cu nanoparticles, the surface plasmon resonance appears at $\sim$560 nm, but it is clearly less intense than the Ag plasmon resonance. Again, it seems that the annealing in a reducing atmosphere favors the formation of the Cu nanoparticles. One can also observe, especially in the as-implanted sample, the absorption band at 248 nm associated with the B$_2$ centers. In the case of Au implantation, higher annealing temperatures were required to induce the formation of the Au nanoparticles. Figure 4 shows the optical absorption spectra of the silica samples implanted with 2 MeV Au ions at three different fluences, after the annealing at 1100°C in either a reducing or an oxidizing atmosphere. The surface plasmon resonance associated with the formation of metallic Au nanoparticles appears at around 520 nm and increases with the ion fluence. Our results indicate that for the same fluence, the formation of larger Au nanoclusters is enhanced favorably by the annealing in the oxidizing atmosphere. According to the previous discussion concerning the formation of nucleation centers, in the case of annealing in a reducing atmosphere the concentration of nucleation centers should be lower compared with that expected in an oxidizing environ-
ment. Therefore, due to the low mobility of Au atoms in silica, it is expected that Au nanoclusters will grow larger and numerous in an oxidizing atmosphere, because in the case of annealing in a reducing atmosphere the potential nucleation centers are more isolated from each other.

Figure 5a shows a typical low magnification TEM micrograph from a cross-section view of a 2 MeV Ag-implanted silica sample after an annealing in a reducing atmosphere. This kind of micrographs allows us to study the polydispersity of the nanoparticle sizes. For a fluence of $6 \times 10^{16}$ ions/cm$^2$ and after an annealing at 600°C in a reducing atmosphere, micrographs containing about 200 Ag nanoparticles were analyzed and a narrow size distribution with an average size of 5.9±1.0 nm was obtained. The crystalline nature of these nanoparticles was studied by high-resolution TEM. Figure 5b shows a typical HRTEM image of a ~4 nm diameter Ag nanoparticle and its corresponding Fast Fourier Transform.

**Figure 3.** Optical absorption spectra from 1 mm thick silica glass plates implanted with 2 MeV Cu ions at a $6 \times 10^{16}$ Cu/cm$^2$ fluence and annealed at 900°C in either an oxidizing (solid line) or a reducing atmosphere (dashed line). The spectrum corresponding to the as-implanted sample is also included (dotted line).

**Figure 4.** Optical absorption spectra from 1 mm thick silica glass plates implanted with 2 MeV Au ions at various fluences and annealed at 1100°C in either an oxidizing (solid line) or a reducing atmosphere (dashed line).

**Figure 5.** TEM micrographs from a cross-section view of a 6×$10^{16}$ Ag/cm$^2$-implanted sample after an annealing at 600°C in a reducing atmosphere: a) low magnification image; b) HRTEM image of a ~4 nm diameter Ag nanoparticle and its corresponding Fast Fourier Transform.
Figure 6. HRTEM micrograph of a truncated decahedra shape corresponding to a 5 nm diameter Ag nanoparticle from a $6 \times 10^{16}$ Ag/cm$^2$-implanted sample after an annealing at 600$^\circ$C in a reducing atmosphere: a) original HRTEM image; b) its corresponding Fast Fourier Transform; c) model used in the simulation; d) simulated HRTEM micrograph obtained using the multislice method.

zone axis orientation. A majority of the particles were found to have well defined polyhedral shapes. Besides single crystalline particles (fcc Ag nanoparticles and cuboctahedral shapes), non-crystalline structures such as truncated decahedral shapes were observed. Figure 6 shows an example of a $\sim$5 nm diameter Ag nanoparticle with a truncated decahedral shape, together with its FFT image, the model used and the simulated HRTEM micrograph.

In the case of Cu-implanted silica we have obtained by HRTEM not only direct evidence for the formation of metallic Cu nanoparticles, but also for the existence of copper oxide nanoparticles in the samples, especially in the ones annealed in air [27]. This result was also confirmed by X-ray photoelectron spectroscopy (XPS) studies [27]. The size distribution of the metallic Cu nanoparticles was estimated to be about 4.5$\pm$0.85 nm for the samples annealed in the reducing atmosphere, and 3.5$\pm$1.4 nm for those annealed in the oxidizing atmosphere. Thus, smaller nanoparticles and narrower size distributions are obtained after the annealing in a reducing atmosphere. On the other hand, the Cu nanoparticles exhibit also well defined polyhedral shapes, such as cuboctahedral and pyramidal structures. These results will be discussed in detail in a forthcoming paper.

5. Conclusions

The synthesis of metallic nanoparticles in silica by MeV ion implantation using the IFUNAM's Pelletron accelerator was described. 2 MeV Cu, Ag and Au ions were implanted in fused silica glasses with different fluences and annealed between 300 and 1100$^\circ$C to study the effect of thermal treatments on the nanoparticles formation. We have determined a correlation between the experimental parameters (fluence, annealing temperature, reducing or oxidizing atmospheres) and the intensity of the surface plasmon resonance of the metallic nanoparticles. It seems that a thermal treatment in a reducing atmosphere has several advantages compared with an oxidizing one, especially in the case of Ag- and Cu-implanted silica. Narrower size distributions are obtained with the reducing atmosphere annealing, and this seems to be related with the diffusion of hydrogen, which interacts with the ion-beam induced defects, avoiding their annihilation during the heating process and therefore creating nucleation centers that allow the growth of more monodisperse nanocluster distributions. On the other hand, in the case of Cu-implanted silica, besides the formation of metallic Cu nanoparticles, copper oxides nanoparticles were also observed. Finally, HRTEM images revealed the existence of metallic nanoparticles with well defined polyhedral shapes. Further studies are in progress in order to determine not only the actual size distribution of the different nanoparticles, but also the shape distribution, because these two characteristics are fundamental for the potential technological applications.

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