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Relationship between the Ag depth profiles and nanoparticle formation in Ag-implanted silica

J C Cheang-Wong, A Oliver, J Roiz, L Rodríguez-Fernández, J M Hernández and A Crespo-Sosa

Instituto de Física, Universidad Nacional Autónoma de México, AP 20-364, México, DF 01000, México

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Abstract

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, high-purity silica samples were implanted at room temperature with 2 MeV Ag ions at various fluences (0.5, 2.4 and 5.3×10^{16} ions/cm^2). The samples were then annealed in either a reducing or an oxidizing atmosphere at temperatures ranging from 300 °C to 1100 °C. The samples were characterized by optical absorption and Rutherford backscattering measurements. Changes in the optical properties of the samples arise from nanometre-sized metallic clusters produced as a result of implantation and/or annealing. The Ag nanoclusters strongly absorb optical radiation at the surface plasmon resonance wavelength (∼400 nm). The Rutherford backscattering spectrometry results indicate that the Ag concentration in the samples decreases with increasing annealing temperatures and then influences the optical properties. Indeed, it seems that at relatively high temperatures the Ag nanoclusters can melt and become atomically dispersed silver within the glass. As the mobility of these Ag atoms increases, they migrate not to the sample surface, but mainly laterally through the sample, and eventually the Ag material is lost by the borders of the sample. A correlation was found between the Ag depth profiles and the formation of the surface plasmon resonance as a function of the annealing temperature. The implications and the possible mechanisms concerning this behaviour are discussed in this paper.

1. Introduction

Composites formed by nanometre-sized metallic clusters embedded in glass matrices exhibit interesting nonlinear optical properties, and are promising candidates for applications in the fields of nonlinear integrated optics, photonics, sensing and computing. For example, hybrid optoelectronic devices use electrical signals to modulate the phase of a lightwave

in a guide. Also, optical switching circuits at THz frequencies and waveguide media with intensity-dependent refractive indices are being developed. Most of the papers concerning the formation of metallic nanoclusters dealt with implantation of metals with very weak reactivity, i.e., copper, gold and silver, in silica [1, 2]. These metallic nanoparticles can be synthesized within silica glasses by ion implantation followed by thermal annealing [3, 4]. Several factors such as the ion fluence, the radiation damage induced by the ion implantation, the subsequent thermal treatment conditions (temperature, atmosphere, etc) can determine the shape, size and distribution of the clusters in the sample. Also, the interaction of the metallic cluster with the host matrix affects the optical properties of the ion-implanted silica glass. In particular, the nonlinear optical properties of the material are caused by optical absorption due to the surface plasmon resonance frequency, which depends on the index of refraction of the host substrate and the electronic properties of the metal colloids. In the case of Ag implantation in silica, the surface plasmon resonance associated with the formation of Ag nanoparticles appears approximately at 400 nm (3.1 eV) [5].

In this work, we investigate the formation of Ag nanoparticles in silica by 2 MeV ion implantation and correlate the optical absorption at the surface plasmon resonance wavelength with the Ag concentration depth profiles determined by Rutherford backscattering spectrometry (RBS). In our case, the Ag-implanted samples were annealed in either a reducing or an oxidizing atmosphere at temperatures ranging from 300 °C to 1100 °C. In Ag ion implantation, however, relatively large Ag particles can be obtained without subsequent annealing even at low implantation fluences ($\sim 10^{16}$ ions/cm^2) [5, 6]. This suggests that Ag has a relatively high mobility in silica glass. Also, it has been observed that the size of the Ag particles increases with the annealing temperature [6]. However, most of these reports are related to Ag implantations at energies below 300 keV, and to our knowledge there are few papers concerning the MeV Ag implantation in silica [7, 8]. On the other hand, in the case of keV Ag implantations it was observed that implanted Ag migrates to the sample surface during thermal annealing at temperatures of 200 °C and above, and remains there until it begins to disappear from the surface at temperatures higher than 400 °C [6]. In our case, it seems that at relatively high temperatures (>900 °C) the Ag nanoclusters can melt and become atomically dispersed silver within the glass. The high mobility of these Ag atoms allows them to migrate not to the sample surface, but mainly laterally through the sample, and eventually the Ag material is lost by the borders of the sample. Therefore, we consider that it is important to understand how the formation of silver clusters in silica is affected by the annealing temperature, as well as by the annealing atmosphere, and how the optical absorption at the surface plasmon resonance wavelength is modified.

2. Experimental details

High-purity silica glass plates ($16 \times 16 \times 1$ mm^3), 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 Ag^+ ions at various fluences (0.5, 2.4 and 5.3×10^{16} ions/cm^2). After implantation, all the samples were cut into identical small pieces (5×8 mm^2) and thermally annealed in either a reducing ($70\%N_2 + 30\%H_2$) or an oxidizing (air) atmosphere at 300, 600 and 900 °C for 60 min. Additional thermal treatments were performed sequentially only on the sample implanted with the intermediate fluence (2.4×10^{16} Ag/cm^2), in the reducing environment in the temperature range of 925–1100 °C for 30 min per step at intervals of 25 °C. Optical absorption spectra were obtained at room temperature using a Perkin-Elmer 330 double-beam spectrophotometer in the wavelength range of 190–900 nm. The Ag distributions and doses 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 of the University of Mexico.

3. Results and discussion

3.1. Optical properties

Spontaneous cluster formation took place even during Ag implantation only in the case of the silica sample implanted with the highest fluence (5.3×10^{16} Ag/cm^2), because the as-implanted sample presented at ∼395 nm the surface plasmon resonance associated with the formation of Ag nanoparticles. No additional features were observed in the absorption spectra before the annealing. After thermal annealing at 300 °C in either the reducing (70%N_2 + 30%H_2) or the oxidizing (air) atmosphere only the sample implanted with the highest fluence exhibits at ∼395 nm the surface plasmon resonance associated with Ag nanoparticles. Moreover, the intensity and width of the surface plasmon resonance of this sample are practically the same, independent of the annealing atmosphere.

After the 600 °C treatment, the surface plasmon resonance appears in all the samples, except for that implanted with the lowest fluence (0.5×10^{16} Ag/cm^2). Also, the surface plasmon resonance is slightly greater in magnitude for the samples annealed in an oxidizing atmosphere compared with those annealed in a reducing environment, for the same fluence. Furthermore, the plasmon resonance maximum presents a shift with respect to its position after the 300 °C annealing (∼395 nm). Whereas the plasmon resonance is peaked at ∼391 nm for the sample implanted with the highest fluence, it appears at ∼375 nm for the sample implanted with the intermediate dose.

Figure 1 shows the optical absorption spectra of the silica samples implanted with 2 MeV Ag ions at three different fluences, after annealing at 900 °C in either a reducing or an oxidizing environment. At this temperature a significant increase in the surface plasmon resonance intensity occurs compared with that observed at lower temperatures, in particular for the samples annealed in a reducing atmosphere (figure 1(b)). In contrast to the 600 °C annealing, the surface plasmon resonance 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. Therefore, our results suggest that the formation of Ag nanoclusters is enhanced favourably by the annealing in the reducing atmosphere. We consider that the reducing atmosphere is more favourable 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 centres for Ag nanocluster formation. Then, in the case of annealing in a reducing atmosphere, the concentration of nucleation centres should be lower compared with that expected in an oxidizing environment. Therefore, while the Ag nanoclusters can grow larger in a reducing atmosphere, they could be smaller but numerous after the annealing in air.

In the case of the sample implanted with the lowest fluence, the surface plasmon resonance only appears after annealing in the reducing atmosphere at 900 °C (figure 1(b)). It seems that the minimum fluence required for the formation of Ag nanoclusters is around 0.5×10^{16} ions/cm^2 for an annealing at 900 °C in a reducing atmosphere and $\sim 2 \times 10^{16}$ ions/cm^2 for an annealing at 900 °C in an oxidizing atmosphere. In particular, the thermal treatment in the reducing atmosphere (70%N_2 + 30%H_2) seems to favour in a better way the formation of larger Ag nanoclusters in comparison with the annealing in air. According to our experience, the minimum Ag fluence that ensures the formation of Ag nanoparticles depends on several parameters, such as the ion fluence and the temperature and atmosphere of the annealing.

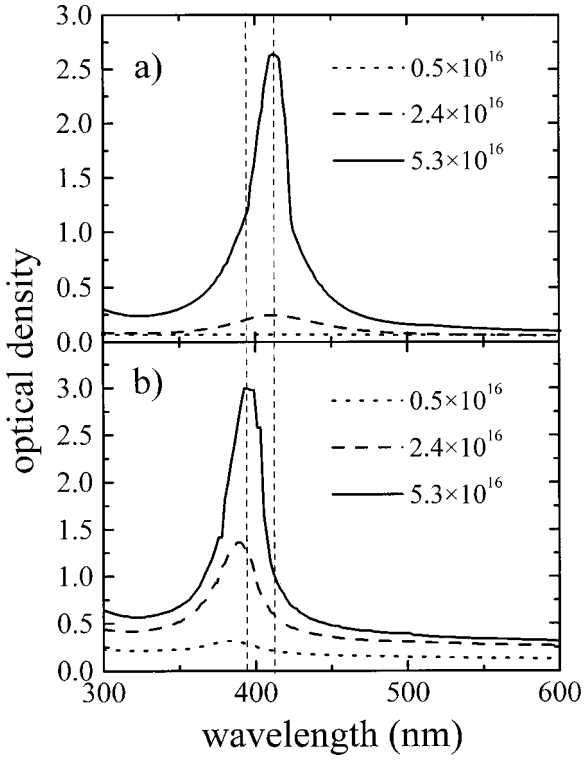

Figure 1. Optical absorption spectra from 1 mm thick silica glass plates implanted with 2 MeV Ag ions at various doses and annealed at 900 °C in either: (a) an oxidizing (air) atmosphere or (b) a reducing (70%N_2 + 30%H_2) atmosphere. The vertical dashed lines are just a guide for the eye.

However, another important factor is the Ag mobility in the implanted matrix, and this parameter also depends on the type of silica (silica quality, OH content, impurity content, presence of defects, etc).

Concerning the shift of the surface plasmon resonance peak, it seems to depend not only on the Ag fluence, but also on the annealing atmosphere. Indeed, the maximum appears at around 390–394 nm after annealing in a reducing atmosphere (figure 1(b)), and at 411–413 nm in the case of annealing in air (figure 1(a)). Connecting this behaviour with some reports that show that the peak position of the surface plasmon resonance shifts towards larger wavelengths with the increase of particle size [6], this would indicate that annealing in an oxidizing environment allows the formation of larger nanoparticles in comparison with those produced by annealing in a reducing atmosphere, in agreement with the results of other authors [8]. These authors associated a 20 nm shift with an increase of about 50 nm in the particle radius [6]. In our case, however, the magnitude of the change in cluster size is found to be too small to account for such a surface plasmon resonance shift. Therefore, the increase in the Ag particle size cannot be invoked to explain such a large shift in the surface plasmon resonance peak after annealing in an oxidizing environment. Additional studies are in progress in order to elucidate this behaviour.

Our results indicate that thermal annealing enhances the Ag mobility in the temperature range of 300–900 °C, allowing the formation of larger Ag clusters. Then, the increase in the

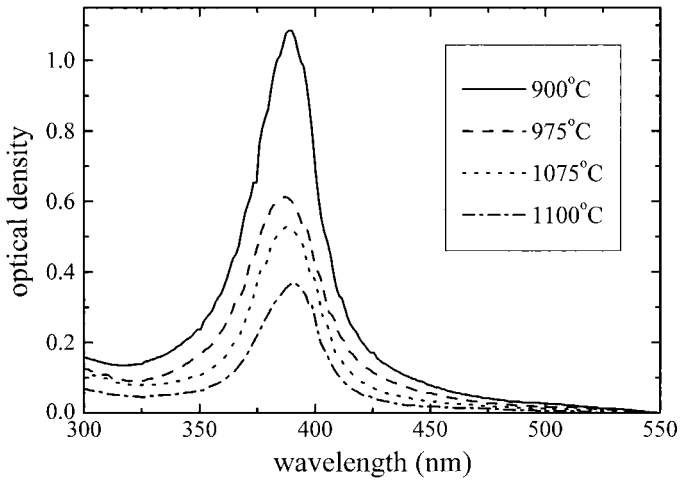

Figure 2. Optical absorption spectra corresponding to the sample implanted with the intermediate fluence (2.4×10^{16} Ag/cm^2) and annealed in a reducing atmosphere (70%N_2 + 30%H_2) in the temperature range 900–1100 °C.

absorption peak intensity with the annealing temperature is due to the increase in the volume fraction of silver precipitates in the implanted sample. Moreover, the position, bandwidth and shape of the surface plasmon resonance depend on the size, shape and concentration of the particles [3]. In order to study the effect of higher temperatures on the behaviour of the Ag nanoparticles, additional thermal treatments in a reducing environment were performed sequentially on the sample implanted with the intermediate fluence (2.4×10^{16} Ag/cm^2) in the temperature range 925–1100 °C for 30 min per step at intervals of 25 °C. Optical absorption and RBS spectra were obtained after each annealing temperature.

Figure 2 shows the optical absorption spectra corresponding to some of the samples annealed in a reducing atmosphere in the temperature range 900–1100 °C for 30 min. One can observe the evolution of the surface plasmon resonance as a function of temperature. Indeed, at 600 °C the surface plasmon resonance begins to appear and it reaches its maximum intensity at approximately 900–925 °C. Then, it decreases almost continuously with temperature, and finally the surface plasmon resonance completely disappears after annealing at 1100 °C for 60 min (not shown). Figure 3 shows the surface plasmon peak intensity as a function of the temperature after annealing in the reducing atmosphere for the sample implanted with 2.4×10^{16} Ag/cm^2, showing that the peak height decreases continuously with temperature. No significant variations are observed in the peak position of the surface plasmon resonance as a function of the annealing temperature. The plasmon peak positions just vary from 388 nm to 392 nm, and are also plotted in figure 3. The intensity and the position of the surface plasmon resonance remain constant in the temperature range of 975–1050 °C. For higher annealing temperatures, the plasmon position shifts to larger wavelengths whereas the peak intensity decreases continuously. Experiments are being conducted concerning a detailed study as a function of the temperature on samples annealed in the oxidizing atmosphere.

This behaviour suggests that for temperatures higher than 925 °C the existing Ag nanoclusters are dissolved or shrunk because under these conditions there is a possibility of melting small Ag particles. Indeed, it has been shown theoretically [9] as well as experimentally [10, 11] that the melting temperature T_m of nanoparticles with radius r is lower than the bulk melting point T_b. All the phenomenological theories lead to the relationship

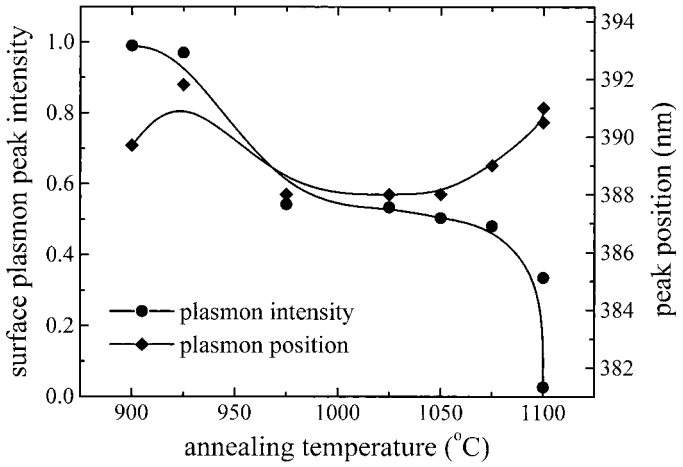

Figure 3. The intensity and the position of the surface plasmon resonance as a function of the temperature after annealing in a reducing atmosphere for the sample implanted with 2.4×10^{16} Ag/cm^2. The solid lines are just a guide for the eye.

$1 - T_m/T_b \propto 1/r$, i.e., the melting temperature is inversely proportional to the radius of the nanoparticle [11]. Thus, the melting temperature of small nanoclusters is drastically decreased to ∼400 °C for particle radius <2 nm and to ∼600 °C for particle radius ∼3 nm, compared with the Ag bulk melting point (962 °C) [10]. Actually, it is important to correlate this gradual decrease of the surface plasmon resonance intensity (mainly due, in principle, to the diminution in the amount of Ag nanoclusters with sizes smaller than a given size) with the Ag concentration depth profiles measured by RBS, because Ag atoms seem to become dissolved from the clusters and move away from the sample, as we will discuss below.

3.2. Ag concentration depth profiles

In order to determine both the Ag content and the concentration depth profile of the implanted ions, the RBS spectra were simulated using the RUMP code [12]. Figure 4 shows the 3 MeV $^4He^+$ RBS spectrum of the 2.4×10^{16} Ag/cm^2 as-implanted sample together with the RUMP simulation. The RBS spectra obtained after annealing in a reducing atmosphere are also shown in the inset of figure 4 for three different temperatures (975, 1025 and 1100 °C). From the RBS spectra, it is clear that both the Ag content and the distribution of Ag atoms in silica as a function of depth are modified by the annealing. Figure 5 shows the Ag concentration determined by RBS as a function of the annealing temperature. One can observe that the Ag content remains constant for thermal anneals up to 900 °C, and then it decreases systematically for higher temperatures. This behaviour indicates that high-temperature treatments not only induce the dissolution of small nanoclusters as explained above, but enhance the mobility of Ag in silica, allowing the diffusion of the Ag atoms away from the initial implanted location. In our case, the Ag content decreases from $\sim 2.4 \times 10^{16}$ Ag/cm^2 at 900 °C to $\sim 1 \times 10^{16}$ Ag/cm^2 at 1100 °C, and the Ag concentration depth profile becomes sharper and non-Gaussian, as discussed below. Therefore, high-temperature annealing in a reducing atmosphere causes a loss of ∼60% of the entire Ag content, presumably by evaporation of silver by the borders of the sample, as discussed below.

The inset in figure 5 shows that the Ag concentration depth profile of the as-implanted sample can be correctly simulated using a Gaussian distribution, centred at

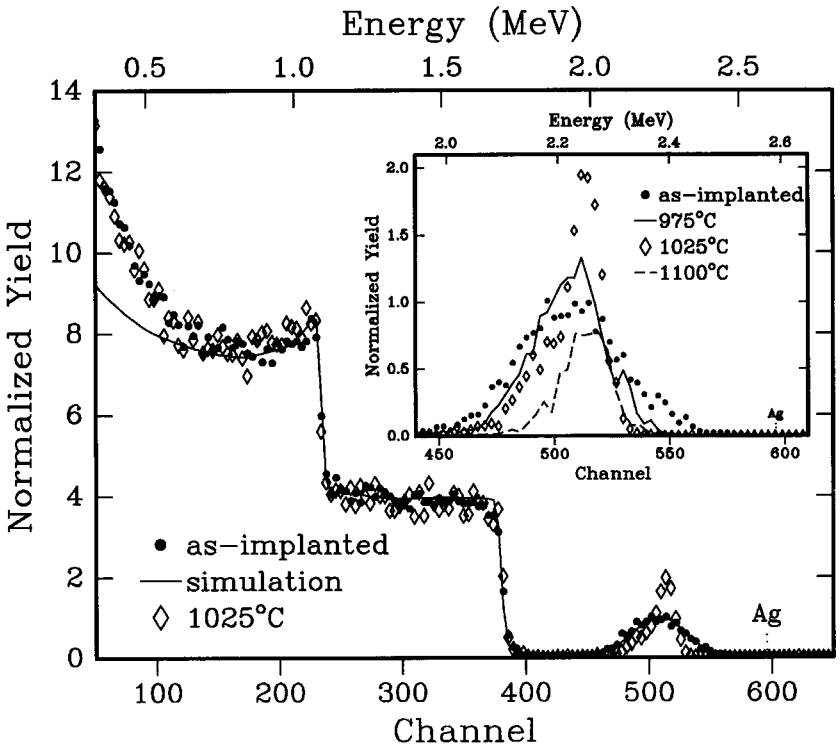

Figure 4. 3 MeV $^4He^+$ RBS spectra of the 2.4×10^{16} Ag/cm^2 as-implanted sample, its RUMP simulation and after annealing at 1025 °C in a reducing environment. The inset shows in detail the Ag spectra corresponding to three different annealing temperatures (975, 1025 and 1100 °C). The energy of He^+ ions backscattered by Ag surface atoms is also indicated.

$\sim (5800 \pm 15) \times 10^{15}$ atoms/cm^2. This value actually corresponds to the projected range determined by the TRIM-95 code [13] for 2 MeV Ag ions implanted in silica (for a density $\rho = 2.3$ g cm^{-3}), i.e., 840 nm. For comparison, the Ag ion range distribution calculated by TRIM is also included in the inset, indicating that the experimental depth profile is slightly broader than the TRIM simulation. The Gaussian distribution of the as-implanted sample still holds for the samples annealed at 300 and 600 °C. However, for temperatures higher than 900 °C the Ag depth profiles cannot be simulated only by a Gaussian distribution. Figure 6 shows the effect of annealing in a reducing atmosphere at various temperatures on the Ag depth profiles for the 2.4×10^{16} Ag/cm^2 implanted sample. All the Ag depth profiles have a skewed Gaussian shape with a peak centred in the range 740–765 nm ($\sim 5.2 \times 10^{18}$ atoms/cm^2), and shoulders at both sides of the peak. The samples annealed at 1025, 1050 and 1075 °C present just one shoulder at the deeper side of the peak, resulting in a kind of bimodal distribution as reported by other authors [6].

Moreover, in all cases the Ag depth profiles become sharper and non-Gaussian, but they can be fairly simulated as the sum of two or three Gaussian curves as shown in figure 7. These results show that the Ag material moves preferentially towards the centre of the distribution, i.e., the Ag atoms migrate neither to the surface of the sample nor deeper into the bulk as reported by other authors (in the case of keV Ag implantation) [6, 7]. Almost 85% of the implanted Ag was lost after the 1100 °C annealing (for 60 min), presumably by lateral migration through the sample and by evaporation from the borders of the sample. This behaviour was confirmed by

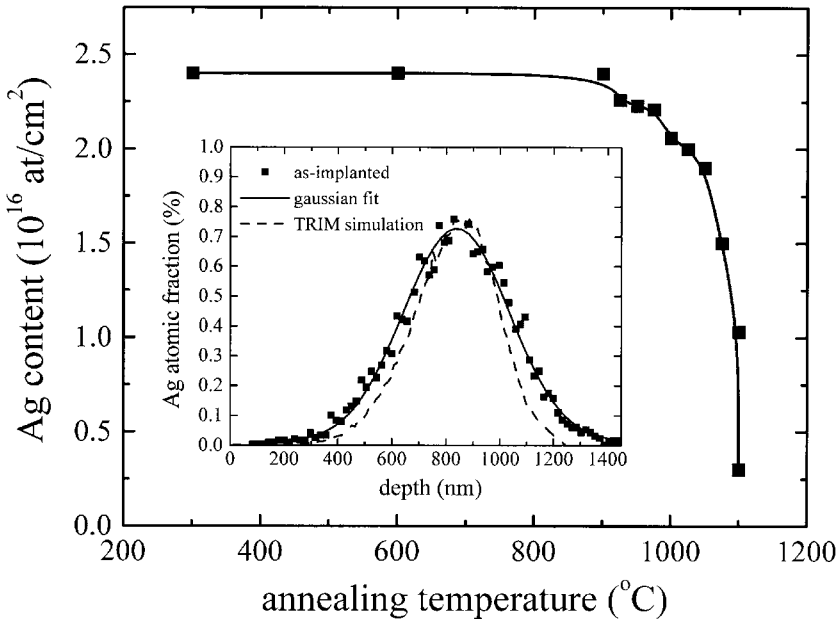

Figure 5. Ag content determined by RBS as a function of the annealing temperature for the sample implanted with a fluence of 2.4×10^{16} Ag/cm^2. The inset shows the Ag concentration depth profile of the 2.4×10^{16} Ag/cm^2 as-implanted sample, its simulated curve using a Gaussian distribution and the Ag ion range distribution calculated by TRIM.

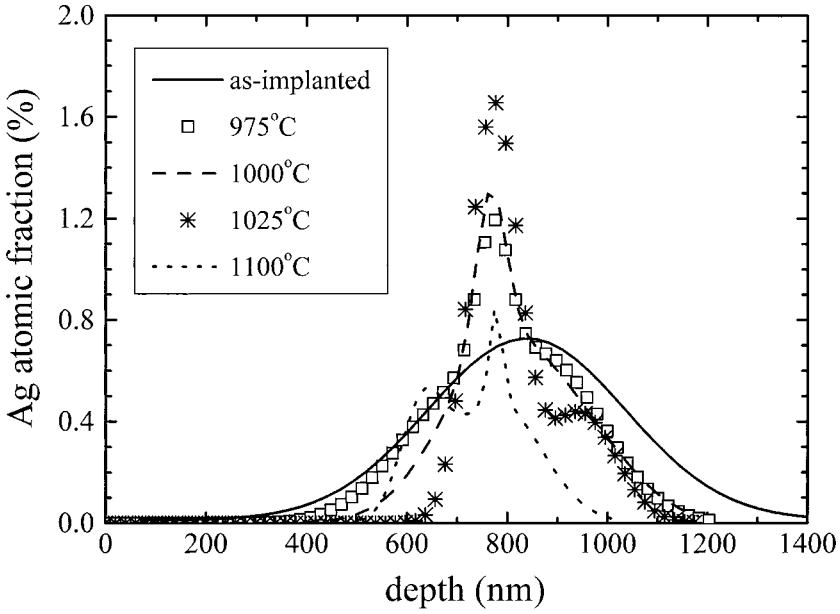

Figure 6. Ag concentration depth profiles for the sample implanted with a fluence of 2.4×10^{16} Ag/cm^2 and annealed in a reducing atmosphere ($70\%N_2 + 30\%H_2$) at various temperatures.

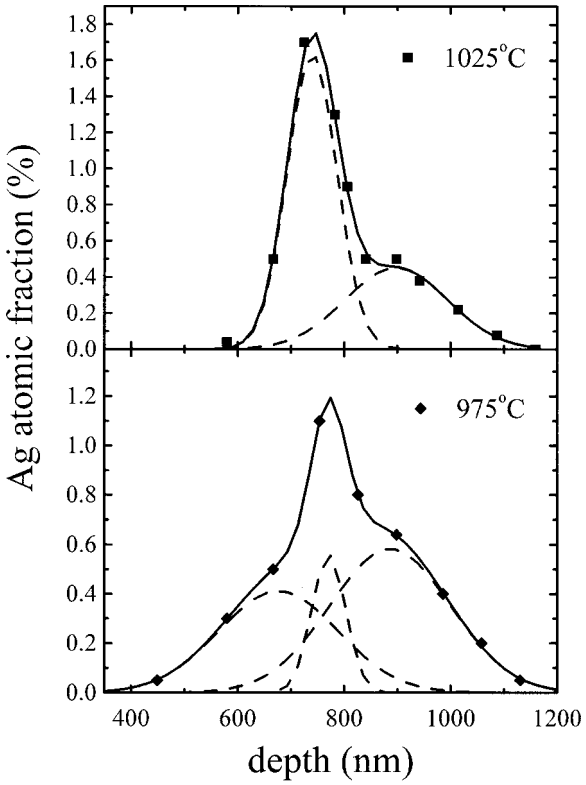

Figure 7. Ag concentration depth profiles for the sample implanted with a fluence of 2.4 × 10^{16} Ag/cm^2 and annealed at 975 °C and 1025 °C in a reducing atmosphere. The simulation (——) corresponds to the sum of two or three Gaussian curves (----).

measuring the Ag concentration at various points away from the sample centre after annealing at 1075 and 1100 °C for 30 min (figure 8). Indeed, for the sample annealed at 1075 °C, the Ag content decreases from 1.5 × 10^{16} Ag/cm^2 in the centre to 1.1 × 10^{16} Ag/cm^2 near the border of the sample (∼4 mm away from the centre). In the case of 1100 °C annealing, the Ag concentration varies from 1 × 10^{16} Ag/cm^2 in the centre to ∼8 × 10^{15} Ag/cm^2 in the sample border. Similar experiments are being conducted concerning a detailed study of samples annealed in an oxidizing atmosphere.

3.3. Size of the Ag nanoclusters

It is well accepted that the position, width and shape of the surface plasmon resonance is determined by the metal dielectric function, as well as by the size, shape and concentration of the particles, and the surrounding dielectric [3]. Also, the resonant contribution to the absorption in metal nanocluster composite glasses diminishes with the cluster radius, so that the size effects are difficult to distinguish in absorption spectra for nanoparticles with less than approximately 1 nm diameter [3]. For this reason, it is important to determine the average radius of our Ag nanoparticles as a function of the annealing temperature, and correlate these results with those determined by RBS, which indicate that the Ag concentration diminishes and the Ag depth profiles become sharper as the temperature increases for thermal annealing in a reducing atmosphere.

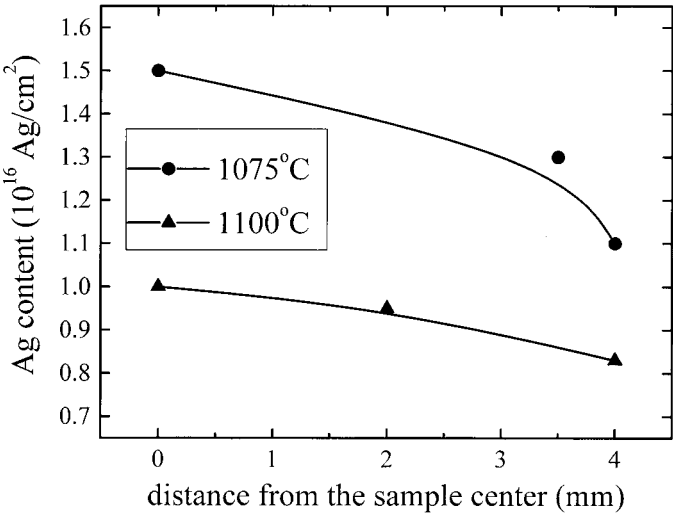

Figure 8. Ag content determined by RBS as a function of the distance from the sample centre for the sample implanted with a fluence of 2.4×10^{16} Ag/cm^2 and annealed at 1075 and 1100 °C in a reducing atmosphere for 30 min. The solid lines are just a guide for the eye.

The average radius of Ag nanoparticles can be determined by means of the equation $r = V_F/\Delta\omega_{1/2}$, where V_F is the Fermi velocity for Ag (1.39×10^8 cm s^{-1}) and $\Delta\omega_{1/2}$ is the FWHM of the plasmon resonance absorption band [14]. The FWHM is determined by assuming the absorption peak has a Gaussian distribution and fitting the flank of the absorption band on the long wavelength side. The value of $\Delta\omega_{1/2}$ is determined by using $\Delta\omega_{1/2} = 2\pi c(1/\lambda_1 - 1/\lambda_2)$, where λ_1 and λ_2 are the wavelengths at FWHM. Figure 9 shows the calculated average radius of existing Ag clusters as a function of the annealing temperature for the sample implanted with 2.4×10^{16} Ag/cm^2 and annealed in a reducing environment. We can notice that the average radius of the Ag particles is about 3.6 ± 0.2 nm at 900–925 °C (corresponding to the maximum intensity of the surface plasmon resonance), and then it decreases to $\sim 3 \pm 0.2$ nm upon annealing at 950 °C. For higher temperatures, however, the average radius of the remaining Ag clusters increases almost linearly with the annealing temperature. Thus, a linear fit is included in figure 9 corresponding to the data in the temperature range 950–1100 °C. The calculated slope indicates that the average radius of the Ag clusters grows continuously up to ~3.9 nm at a rate of 0.006 nm °C^{-1}. Nevertheless, it is important to take into consideration that our results show that both the surface plasmon resonance (figure 2) as well as the Ag content (figure 5) decrease continuously with the annealing temperature (>925 °C), even if the average radius of the remaining clusters increases. We consider that this cluster regrowth is mainly due to the coalescence of atomically dispersed Ag atoms during the slow cooling of the sample after high-temperature annealing.

According to our results, it is clear that not all the implanted Ag is aggregated into nanoclusters large enough to contribute to optical absorption after the thermal treatments (the minimum radius for Ag nanoclusters is predicted to be 1–2 nm [6]). Moreover, the decrease of both the surface plasmon resonance intensity as well as the cluster average radius from 3.6 nm at 900–925 °C to ~3 nm upon annealing at 950 °C confirms that some breakup of the previously formed particles occurs. This was explained by the particle-size dependence of the melting temperature, allowing the melting of small Ag nanoclusters at a temperature below that of the bulk material [10]. Thus, the amount of Ag in the matrix may be atomically

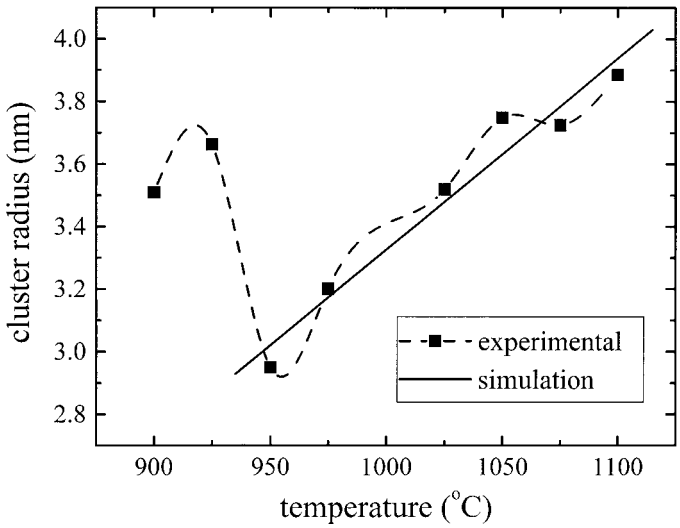

Figure 9. Calculated average radius of Ag clusters as a function of the annealing temperature for the sample implanted with a fluence of 2.4×10^{16} Ag/cm^2 and annealed in a reducing environment. The dashed line is just a guide for the eye and the solid line corresponds to a linear fit of the data in the temperature range of 950–1100 °C.

dispersed or in the form of additional small Ag precipitates to the detriment of the former large clusters. The continuous elevation of the annealing temperature enhances this mechanism and also the Ag mobility, allowing the migration of Ag atoms away from their initial implanted location, presumably by lateral migration through the sample, and finally the evaporation by the borders of the sample, as discussed above.

For the samples annealed at temperatures in the range 950–1100 °C, we consider that the observed cluster growth (figure 9) can take place by an aggregation mechanism similar to Ostwald ripening mainly during the cooling of the sample, and by this process, small precipitates will shrink, while larger precipitates will grow, leading to a coarsening of the precipitate microstructure [15, 16]. If during the high-temperature annealing there is a collection of clusters of varied sizes produced by the melting of larger particles, then during the cooling of the sample new large clusters will grow or 'ripen' at the expense of the smaller ones and of isolated Ag atoms. Most of the atomically dispersed Ag atoms will leave the sample, decreasing the total amount of Ag in the sample (figure 5).

On the other hand, the narrowing of the Ag concentration depth profile near the ion projected range (figure 5) presumably occurs due to the precipitate growth by an aggregation mechanism similar to Ostwald ripening during the cooling part of the thermal annealing at elevated temperatures. Moreover, diffusion of individual atoms into the matrix will proceed from the smaller to the larger cluster until the former disappears entirely. However, according to our results, this aggregation mechanism seems to be overcome by the lateral migration of Ag atoms through the silica and their evaporation by the borders of the sample. Therefore, the intensity of the surface plasmon resonance must be the result of the superposition of various (partially competing) thermally assisted processes, such as the melting of small Ag nanoclusters at a temperature below that of the bulk material, the cluster growth by an aggregation mechanism similar to Ostwald ripening and the migration of Ag atoms away from the sample due to their high mobility in silica. Also, during the cooling part of the annealing new nucleation and regrowth of particles occur, leading to a competition between regrowth

and cooling speeds. In our experiments, we turned off the furnace and left the sample to cool down to room temperature. It is clear that a rapid cooling from high temperature may help us to freeze the samples in the thermodynamic conditions appropriate to this high temperature and retain the actual Ag particle size and Ag depth profile.

Further studies are in progress in order to determine the optical absorption of the glass matrix containing the metal clusters using the Mie theory [17], because the position, width and shape of the surface plasmon resonance depend on the metal dielectric function, as well as on the size, shape and concentration of the particles, and on the surrounding dielectric. The details of these studies as a function of the annealing temperature in reducing and oxidizing atmospheres will be presented in a forthcoming paper.

4. Concluding remarks

High-energy Ag ions were implanted in fused silica glasses with different doses and annealed between 300 and 1100 °C to study the effect of thermal treatments on the formation and growth of Ag nanoparticles. Our results show that annealing in a reducing atmosphere (70%N_2 + 30%H_2) enhances the formation of larger Ag clusters in comparison with annealing in air (oxidizing atmosphere). This process allows us to create narrow size distributed Ag nanoclusters, whose spatial distribution depends strongly on thermal annealing, as the Ag depth profiles become narrower and sharper with increasing temperature. For a heat treatment beyond a critical temperature (>950 °C), the surface plasmon resonance starts to disappear as Ag atoms dissolve from the clusters, and our RBS results show that Ag atoms migrate laterally through the sample and the Ag material is lost at the borders of the sample. This is a clear trend in which silver nanoparticles are dissolved during high-temperature annealing because their melting temperature is drastically decreased in comparison with the bulk melting point. Simultaneously, the average radius of the remaining Ag clusters increases with the annealing temperature. We describe this behaviour as a result of two competing thermally assisted processes, such as cluster growth by an aggregation mechanism similar to Ostwald ripening during the cooling part of the anneal and the migration of the Ag atoms away from the sample due to their high mobility in silica. A better understanding of this behaviour requires further investigations. A series of experiments are being conducted concerning a detailed study as a function of the temperature of samples annealed in the oxidizing atmosphere.

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