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Effect of thermal annealing on the optical properties of high-energy Cu-implanted silica glass

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Abstract

Silica glasses implanted with 2 MeV Cu⁺ ions at various doses from 9.95×10^{16} to 2.2×10^{17} ions/cm² were thermally annealed in air in between 600°C and 1050°C. Rutherford backscattering measurements were used to determine the concentration of implanted ions and their distributions in the samples. The Cu distribution in the samples depended on the implantation dose. Optical absorption spectra, measured in between 200 and 800 nm at room temperature, revealed a peak at about 560 nm, attributed to colloidal Cu particles, for all the samples even before heat treatment, which indicates the formation of particles even at lower doses, when high energy implantation is used. Using the equation derived from the framework of free-electron theory, the average radii of the Cu particles were determined from the experimental surface plasmon absorption peaks. The average radius of Cu particles decreased slightly on annealing at 600°C, suggesting the formation of additional small Cu precipitates at this temperature. However, the average radius of Cu particles increased as the annealing temperature increased from 800°C to 1050°C. The anomalies between the calculated average radius of the particles and the absorption peak positions at higher annealing temperatures were explained. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The use of ion implantation for the modification and preparation of materials has advanced substantially in the past few years [1–3]. Formation of metal nanoparticles such as Cu, Ag and Au in glass has attracted much attention recently because of its potential applications to non-linear

optical devices [4–10]. In the formation of nanoparticles in glasses, ion implantation is a useful technique with several advantages, such as high precision in controlling beam position, controllability in depth profile and concentration, purity and the ability to overcome low solubility restrictions. In addition, high energy ion implantation is appropriate for control of depth profile. In most of the studies, the energy of implantation was of the order of keV and there are only a few reports [11,12] on the use of MeV Cu implantation. One immediate consequence of using MeV ions is that the depth of implantation is larger.

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It has been shown [13] that the optical properties of this type of materials are strongly dependent on the size of the particles. The implantation dose dependence of the radius of the formed particles has been studied [14]. For other metals like Au and Ag, the growth of clusters on subsequent annealing has been also reported [10,15]. However, in the case of Cu, relatively large Cu particles can be obtained without subsequent annealing [5,6,16]. This suggests a relatively high mobility of Cu ions in silica glass. Increase of the size of the Cu particles on thermal annealing has been speculated. However, the effects of annealing temperature on the formation and growth of Cu particles are not clear and there are only few reports concerning high-energy Cu implantation into silica glass.

In the present work, high energy Cu ions are implanted in silica glasses and treated thermally at different temperatures to study the effect of thermal annealing on their optical properties. The effects of thermal annealing on the formation and growth of Cu nanoparticles are examined.

2. Experimental

Fused silica glasses of about 1 cm×2 cm were implanted with 2 MeV Cu⁺ ions using the 3 MeV Pelletron accelerator of the Instituto de Física, Universidad Nacional Autónoma de México. While the beam current was fixed $\sim 1.5 \mu\text{A}$ (current density of the order of $20 \mu\text{A}/\text{cm}^2$), the nominal implantation doses were 9.95×10^{16} , 1.25×10^{17} and 2.20×10^{17} ions/cm² for samples (a)–(c), respectively. For implantation, the silica glasses were mounted on a stainless steel target-holder by means of metallic clips. Though in our experimental set-up we cannot control the temperature of the samples, only the ion beam heated them. However, our implantations were performed at a relatively low current density, preventing the samples from reaching temperatures higher than 300°C [17,18]. The samples were annealed at 600°C, 800°C and 1050°C in air for 1 h, using a tubular furnace. Optical absorption measurements were performed in the interval of 200–800 nm at room temperature with a double-beam UV-visible spectrophotometer using an unimplanted sample

in the reference beam. The wavelength resolution of the spectrometer was ± 1 nm. Rutherford backscattering spectrometry (RBS) with a 4 MeV He⁺ beam has been employed to study the concentration and depth profile of Cu in each sample after implantation. The depth resolution of our RBS system was about 80 nm. The experimental RBS spectra were simulated by means of the Rutherford universal manipulation program (RUMP) code [19] to determine the amount and depth profile of the Cu in the samples.

3. Results

Fig. 1 shows the RBS spectra of the as-implanted samples. The spectra were normalized with the substrate plateau, and then simulated with the RUMP program. The total ion dose calculated from the backscattering measurements was typically 90% of the nominal dose, indicating a minimum sample charging during implantation. While no substrate-edge shift was observed, only the peak corresponding to the Cu-backscattered ions changes with the implantation dose. Indeed, as the implanted dose increases, it seems that the Cu ions reach shorter depths into the silica glass. These features can be observed in detail in the Cu concentration depth profiles extracted from the

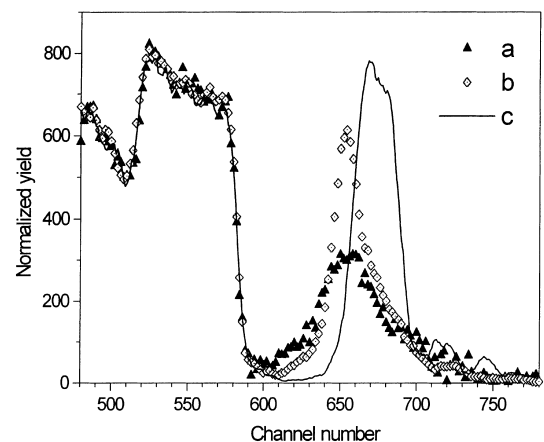


Fig. 1. 4 MeV He⁺ RBS spectra of the as-implanted samples with nominal doses of (a) 9.95×10^{16} , (b) 1.25×10^{17} and (c) 2.20×10^{17} ions/cm².

RUMP simulations and plotted in Fig. 2 in terms of atoms/cm³. TRIM-95 simulations of Cu distribution in silica glass for the different doses have also been included in the figure. The experimental projected range, height and full width at half maximum (FWHM) of the main peak are in good agreement with the TRIM simulated ($R_p \approx 1.4 \mu\text{m}$) results, especially for the sample (a), implanted at the lowest dose. For the sample (a), we can observe a bimodal distribution of Cu, i.e. an additional small hump at a depth of about $0.8 \mu\text{m}$ appeared towards the sample surface. As the implantation dose increases the TRIM simulated distributions deviate more from the measured Cu distribution.

Figs. 3(a)–(d) show the absorption spectra of the as-implanted and thermally treated (at 600°C , 800°C and 1050°C) samples. From the spectra, we can observe an absorption peak around 560 nm , characteristic of colloidal Cu particles of nanometer size [20,21]. This peak appears even for the as-implanted samples and for those implanted with the lowest dose, indicating the formation of Cu nanoparticles even before the thermal treatments. It is to be noted that, in case of samples prepared with a dose very close to the lowest dose we used ($9.95 \times 10^{16} \text{ ions/cm}^2$), other works [11] have not reported the appearance of the absorption peak.

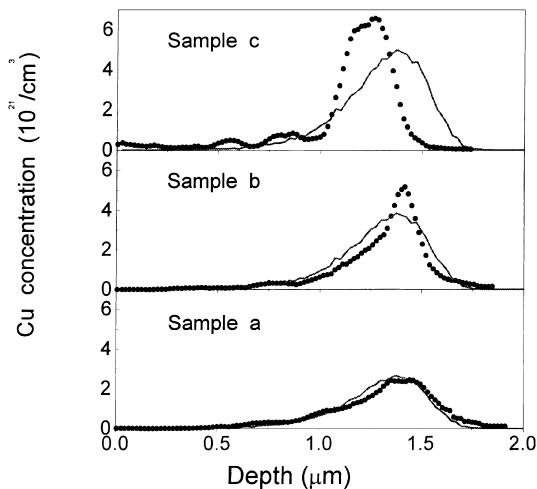


Fig. 2. The depth profiles of Cu concentration in as-implanted samples with nominal doses of (a) 9.95×10^{16} , (b) 1.25×10^{17} and (c) $2.20 \times 10^{17} \text{ ions/cm}^2$. The continuous lines show the TRIM simulated results.

The position, shape and intensity of the absorption peak depended on the implantation dose. Intensity of the absorption peak increased with the increase of implantation dose. On increasing the implantation dose, the absorption peak became sharper and displaced towards higher wavelengths, indicating an increase of particle size [7,10]. The background absorption of the spectra increased monotonically with the implantation dose due to the increase of the volume fraction of Cu in the samples.

There was no significant change in the absorption spectra of samples (a) and (b) upon annealing at 600°C . However, for the sample (c), implanted with the highest dose, a significant change in intensity and shape of the absorption peak is observed. These changes were significant when samples (a) and (b) were annealed at 800°C , but were less significant for the sample (c). The intensity of the absorption peaks grows with the increase of annealing temperature up to 1050°C , being the peaks more sharper and shifting gradually towards higher wavelengths.

4. Discussion

Three important observations can be made from the depth concentration profiles (Fig. 2) of the samples: (i) with the increase of implantation dose, the main distribution of Cu passes from the bimodal to a Gaussian form with a subsequent decrease of shoulder peak height; (ii) the main distribution peak shifts towards lower depths with the increase of implantation dose; and (iii) other small peaks appear outside the main distribution, at much lower depths when the implantation dose is high.

Though the observations (i) and (ii) have also been reported by Nakao et al. [11], they did not offer any explanation to those features. Appearance of an extra peak in the RBS spectra on annealing the samples at or above 800°C has also been observed by them, and was assigned to the segregation of Cu towards the sample surface. However, the Cu depth profiles in our samples did not change noticeably on annealing up to 1050°C . On the other hand, as the beam current density in

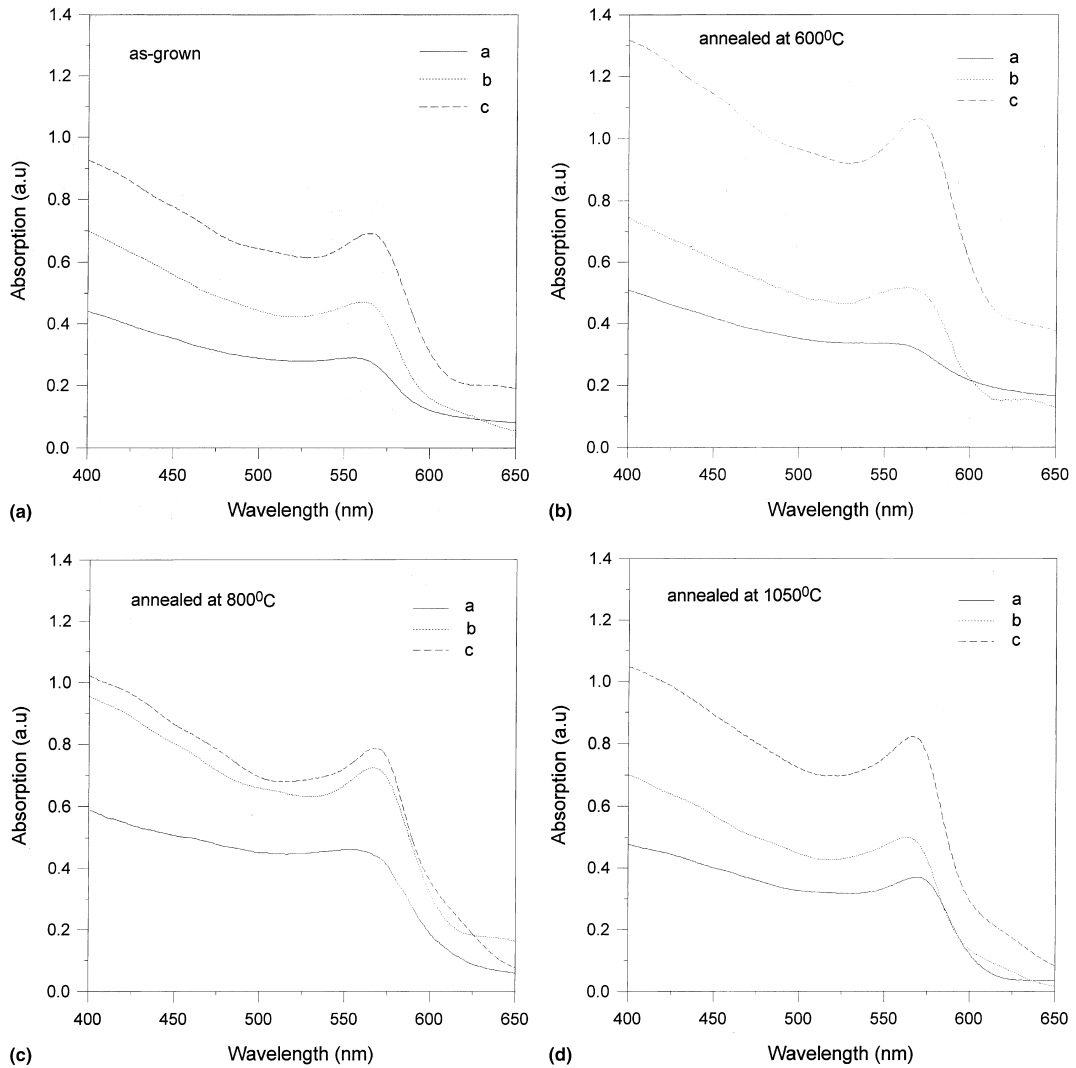


Fig. 3. (a) Optical absorption spectra of the as-implanted samples; (b) Optical absorption spectra of the samples after annealing at 600°C; (c) Optical absorption spectra of the samples after annealing at 800°C; (d) Optical absorption spectra of the samples after annealing at 1050°C.

our experiments was kept at about $20 \mu\text{A}/\text{cm}^2$, we consider that the sample temperature during implantation remained below 300°C [17,18]. Therefore, though the effect of thermal segregation of Cu towards the sample surface on the modification of depth profiles can not be discarded, there might be another phenomenon acting simultaneously. We assume, that an interaction between the incoming Cu ions with the already incorporated Cu in the samples plays a role on the shape of the

depth profile and distribution of Cu in the samples.

During implantation, the first batch of Cu ions reaches to a maximum depth, depending on their initial energy and stopping power of the matrix material. As the second batch of ions encounters the Cu atoms already incorporated into the matrix, and interacts with them, they travel a shorter distance and hence their projected range is less than for the first batch of Cu ions. So, in case of

the samples prepared with lower doses, as the probability of Cu–Cu interaction is less, the distribution maxima of Cu in the samples lie at higher depths from the surface of the substrate. With the increase of implantation dose, as the effect of Cu–Cu interaction increases, the probability of losing energy of the latter coming ions is also high. Therefore, a fraction of the incoming Cu ions lose their energy substantially even before reaching to the region of the main distribution; which explain the change in the form and position of the main distribution peak in the Cu depth profile. The same argument can explain the occurrence of additional peaks at lower depths for the samples prepared with very high dose of implantation. The experimental mean projected range is shorter than the TRIM-calculated value by about 10% for the sample implanted with the highest dose.

In the optical absorption spectra, the peak situated at around 560 nm was attributed to the surface plasmon resonance absorption of Cu nanoparticles [5–7,10]. The average radius of Cu nanoparticles can be determined by means of the equation [9,12,22] $r = V_F / \Delta\omega_{1/2}$, where V_F is the Fermi velocity of Cu (1.57×10^8 cm/s) and $\Delta\omega_{1/2}$ is the FWHM of the plasmon resonance absorption band. The FWHM is determined by assuming the absorption peak as 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 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. Figs. 4(a) and (b) show the peak positions and the calculated average radius of Cu particles, respectively, as the function of annealing temperature. We can notice from Fig. 4(b) that the average radius of the Cu particles decreased on annealing the samples at 600°C. The result is consistent with the results reported by other workers [11,23]. The decrease of average radius at this temperature is possibly due to the formation of additional small Cu precipitates in the matrix. Cheshnovsky et al. [23] reported that the surface plasmon resonance absorption does not develop clearly until the Cu particle diameter reaches approximately 0.7 nm. They concluded that the size of Cu precipitates may be less than 0.7 nm when the annealing temperature is increased

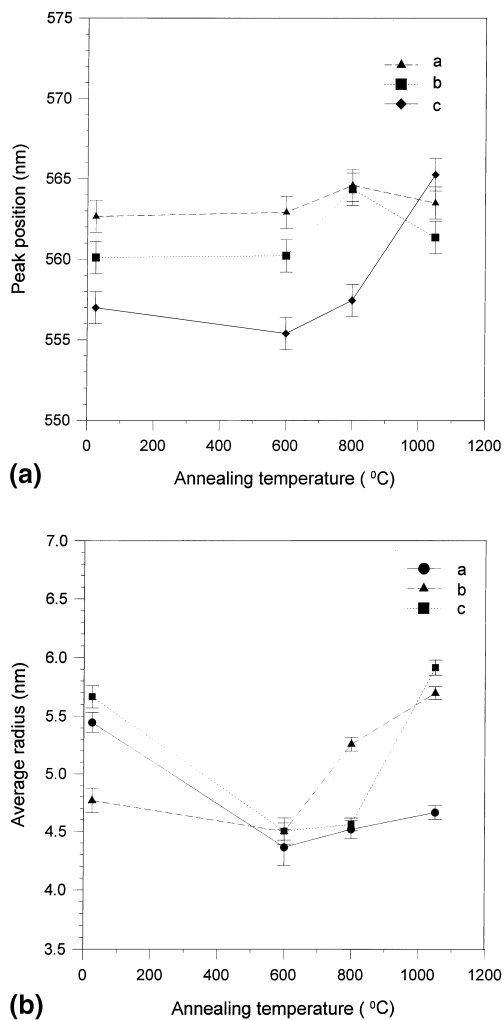


Fig. 4. (a) Absorption peak positions as a function of annealing temperature for the samples implanted with different doses; (b) Average radii of Cu particles as a function of annealing temperature obtained from the fitting of the absorption peaks, assuming a Gaussian distribution.

up to 700°C. With the increase of annealing temperature from 600°C to 1050°C, the radius (r) of the Cu nanoparticles increased. However, the calculated r value for the samples (b) and (c) increased more sharply than sample (a). On the other hand, the peak position for the samples (b) and (c) (see Fig. 4(a)) shifted slowly towards higher wavelengths on annealing up to 800°C and then towards lower wavelengths after annealing at 1050°C. Whereas, the shift of the peak position for

the sample (a) is faster and regular. This behaviour of peak shift on thermal annealing for the sample (a) is consistent with the reports [7–9], that the peak position of the surface plasmon resonance absorption shifts towards long wavelength with the increase of the size of metal particles. A different behaviour is observed for the samples (b) and (c), implanted with higher doses. A possible explanation of such inconsistency might be as follows: high-dose of implantation creates numerous Cu nanoparticles which leads to an increase in the density of Cu particles in the matrix. At high temperatures, the growth of Cu particles also occurs. But, as the Cu concentration in these samples is very high, with the growth of particle size on annealing at high temperatures, the possibility of retaining their spherical shape is less. Therefore, the particles might have taken an arbitrary shape with shorter effective radius, causing a shift of peak position towards a lower wavelength. As, in the calculation of radius from the absorption peaks, we assumed a spherical shape of the particles, our calculated values of radius for the samples increased with the increase of annealing temperature. However, a more clear understanding of this anomaly requires further study.

5. Conclusions

High energy Cu ions have been implanted in fused silica glasses with different doses and annealed between 600°C and 1050°C to study the effect of thermal treatment on the formation and growth of Cu nanoparticles. Cu nanoparticles are formed in fused silica even at moderate implantation doses when high energy Cu ions are implanted. Though the projected range of the Cu ions primarily depends on the implantation energy, their distribution depends, to some extent, on the total implantation dose. The average radius of the Cu particles decreases slightly upon annealing at 600°C due to the formation of additional small Cu precipitates. On annealing in between 800°C and 1050°C, there was no reduction of the absorption peak intensity or the background absorption (due to loss of Cu by segregation towards surface or ejection), which suggests the formation

of stable Cu particles in silica using a moderate or a high dose of implantation. Though the size of the Cu particles increases with the increase of annealing temperature beyond 600°C, the shape of the particles may have been distorted from the spherical to arbitrary form, resulting in the reduction of their effective radius.

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