Superficies y Vacío ***9****, 296-299, Diciembre 1999.* *© Sociedad Mexicana de Ciencia de Superficies y de Vacío*

Effect of thermal treatment on the optical properties of colloidal Cu nanoparticles prepared by ion-implantation in quartz glass

A. Bautista-Hernández, U. Pal
Instituto de Física, Universidad Autónoma de Puebla, Apdo. Postal J-48, Puebla, Pue. 72570, Mexico

L. Rodríguez-Fernández, J. C. Cheang-Wong
Instituto de Física, Universidad Nacional Autónoma de Mexico, 01000 Mexico D. F., Mexico

High energy (2 MeV) Cu ions were implanted in quartz glass with different doses in the range of $5x10^{15}$ to $1x10^{16}$ ions/cm^2 with a fixed current density of 1.5 μA. Rutherford back-scattering spectrometry (RBS) has been used to study the distribution of Cu in the matrix. Copper clusters containing two and three atoms and colloidal copper particles were formed within silica matrix. Optical absorption measurements and the Maxwell-Garnett (MG) theory with mean-free-path (MFP) correction have been used to study the formation and growth of the nanoparticles in the matrix and the effect of thermal annealing on them.

PACS: 78.70-g, 78.66Sq, 78.40Kc, 78.66-w, 81.05Ys.

1. Introduction

The process of implantation of metallic particles in silica glasses for the modification and preparation of materials has been advanced substantially in the last few years [1]. Ion-implantation is an attractive method for inducing colloid formation of metals and semiconductors in dielectrics for their possible applications in non-linear optical devices [2]. In the formation of nanometric particles, the technique has 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 the case of silica glass, the ion implantation is unique in that it allows the preparation of materials that are not obtainable by conventional glass melting techniques [3].

The formation of nanometric particles of Cu in silica by implantation without subsequent annealing has been demonstrated by several workers [4,5]. This suggests that Cu has a relatively high mobility in silica glass. However, the effects of annealing temperature on the formation and growth of Cu particles are not clear. In addition, there are few reports on the high-energy Cu implantation into silica glass with relatively lower doses [6,7].

In this work, high energy Cu ions are implanted in silica glass with relatively lower doses and treated thermally at different temperatures to study the effect of annealing on their optical properties. In addition, RBS is used to study the depth profile and the segregation of Cu in the matrix. The MG theory with MFP correction has been used to evaluate the size of the Cu particles in the samples.

2. Experiment

The samples were prepared by using a 3 MeV Tandem accelerator. Fused silica glasses (Quartz Scientific) of about 1 x 2 cm^2 were used as substrates. The substrates were implanted with 2.0 MeV Cu^+ ions with nominal doses of $5x10^{15}$, $9x10^{15}$ and $1x10^{16}$ ions/cm^2 for the samples *a*, *b* and *c* respectively. The current density was kept fixed at 1.5 μA for the all samples.

Rutherford backscattering spectrometry, using 4 MeV He^+ has been employed to study the depth profiles of Cu in the substrate after implantation. For the analysis of depth profiles, the program RUMP (Rutherford universal manipulation program) [8], in combination with results of RBS measurements have been used. The samples were annealed at 400, 600, 800 and 1050°C in air for 1 hour, using a tubular furnace. The optical absorption measurements were done at room temperature in the interval of 190 to 700 nm using a Shimadzu (UV 3100S) spectrophotometer using an un-implanted substrate as reference.

3. Results and discussion

Figure 1 shows the depth profile of Cu in silica glass for

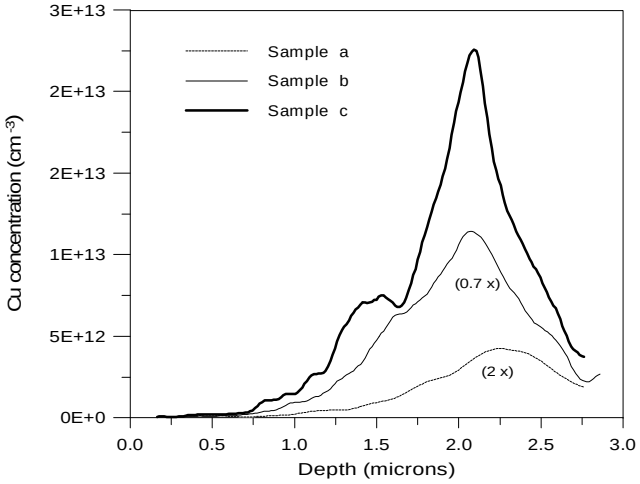

Figure 1. Depth profiles of Cu in silica glass for different implantation doses without annealing treatment.

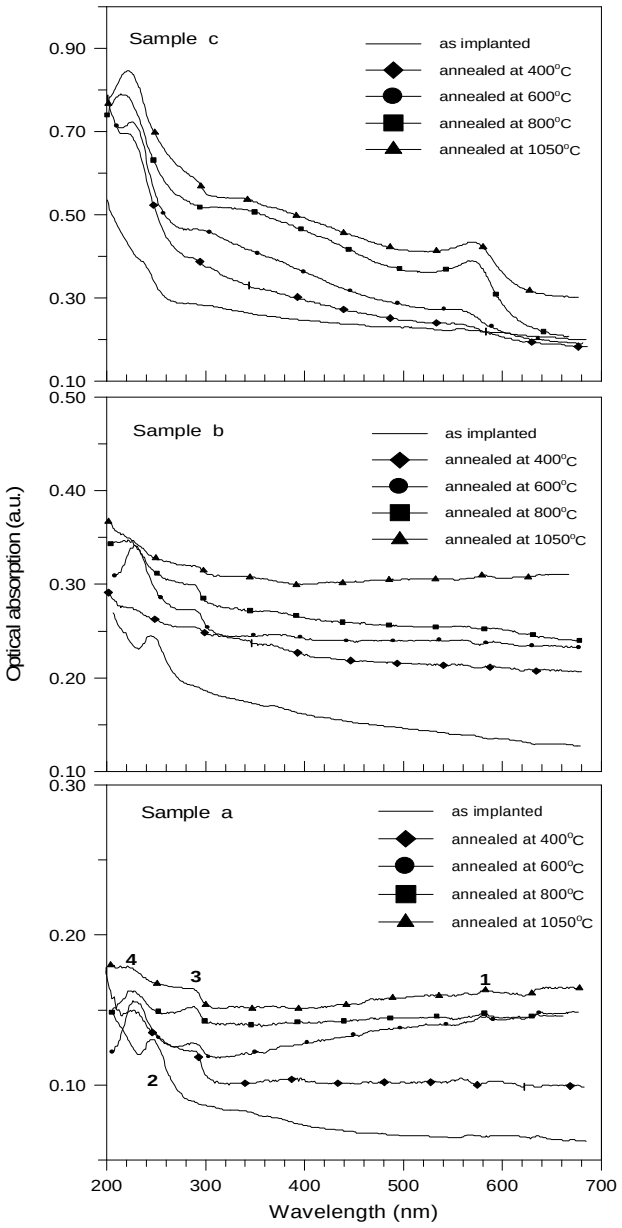

Figure 2. Optical absorption spectra for the samples prepared with different implantation doses, after and before annealing treatments.

different doses of implantation, without annealing treatment.

Three important observations can be made from the RBS spectra: i) with the increase of implantation dose, the principal distribution of Cu becomes sharper and more intense, ii) the position of the main distribution peak shifts towers lower depths with the increase on implantation dose, and iii) on increasing the implantation dose, there appeared another peak at lower depth revealing a clear bimodal distribution for the samples prepared with higher implantation dose. A possible explanation of the observed behaviors might be that: During implantation, the first batch of Cu ions traveled to a maximum depth, depending on their initial energy. The Cu ions of the following batches encountered with the Cu atoms already incorporated in the matrix and collided with them. As a result, they traveled a lesser distance than the preceding batches of ions. So, in the 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 on the substrate. With the increase of implantation dose, as the effect of Cu-Cu interaction is high, the probability of loosing energy of the latter coming Cu ions is also high. Therefore, a fraction of incoming Cu ions loose 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 RBS spectra. The same argument can be used to explain the occurrence of the additional peak at lower depths in the depth profiles of the samples prepared with higher implantation doses.

Figure 2 shows the optical absorption spectra of the samples *a, b* and *c* before and after thermal annealing treatments. The as-grown samples did not reveal clearly the absorption peak near about 560 nm (band 1), characteristic of colloidal Cu particles of nanometric size [4,5], which might be due to smallness of the Cu particles in the samples as has been observed by Cheshnovsky et al [9] and Mazzoldi et al. [4]. However, the background absorption for all the three samples increased with the increase of annealing temperature. The band 1 is relatively prominent in sample c and its intensity increased with the increase of annealing temperature. The position of the band shifted towards higher wavelength due to the formation of bigger Cu particles with the increase of annealing temperature.

For all the as-grown samples we can observe the formation of a band close to 245 nm (band 2). The band is generally assigned to the defect, called B_2-centre created due to the formation of oxygen vacancy in silica matrix by ion-implantation [10]. The oxygen vacancy has trapped two electrons, i.e. a Si-V-Si configuration (V = vacancy). The concentration of this B_2-center could be greatly reduced by a subsequent "ion-annealing" [11,12]. However, we could observe a similar reduction of B_2-center concentration in our samples by thermal annealing. On annealing the samples thermally at or above 400°C, the band disappeared and other two bands near about 285 nm (band 3) and 225 nm (band 4) formed. The positions of these two bands varied in between 285-290 and 221-227 nm respectively. Based on the experimental observations of Moskovits and Hulse, and the molecular-orbital calculations of Anderson [13], we assign these two bands to the Cu_2 and Cu_3 clusters respectively. In fact, the growth of particles in the matrix depend on the amount of materials present in the sample [14] and the formation of aggregates of small size, such as clusters is possible when the implantation dose is low. Both the bands generally shifted towards higher energy on thermal annealing, which possibly due to the change of Cu-Cu bond length in the clusters.

The evolution of band 1, which is prominent after thermal annealing of sample c, has been analyzed in

details with the MG theory using the MFP correction for the dielectric function of the nanoparticles in the following section to study the growth of Cu particles.

The mean-free-path (MFP) correction

The MFP model has been used widely for the calculation of optical properties of several materials consist of colloidal nanoparticles immersed in solutions [15,16]. We used this model to analyze the formation and growth of Cu particles in silica glass on thermal annealing. The MFP correction to the dielectric constants includes the collisions between the conduction electrons and the particle surface. This effect becomes prominent when the particle size is comparable or less than the MFP of the electrons.

In the MFP correction, an effective relaxation time, τ_B is introduced as

$$\tau_E^{-1} = \tau_B^{-1} + \tau_S^{-1}$$

where τ_B is the bulk relaxation time, $\tau_S^{-1}=V_F/R$ is the relaxation time for surface scattering, where R is the particle radius and V_F is the Fermi velocity. This effective relaxation time is introduced in the expression of dielectric constant to accommodate the increase in the imaginary part of dielectric constant with decreasing particle size. The expression of MG absorption coefficient for composite medium can be written as

$$a = \frac{9 f k_0 e_m e_2}{[e_1 + 2e_m]^2 + e_2^2}$$

where f is the volume fraction of copper in the composite, ε_m is the dielectric constant of the surrounding medium, $k_0=\varepsilon_m^{1/2}\omega/c$ (ω is the wave number and c is the light speed) and ε_1 and ε_2 are the real and imaginary parts of the dielectric constant of metal particles. Substituting the modified expression of dielectric constant in the expression MG absorption coefficient, we calculated the absorption coefficient of Cu particles. For the calculation of the position of the absorption band related to the size of particles, we have taken the dielectric constant value of bulk Cu obtained experimentally by Ehrenrich et al.[17].For the Drude part, we considered $\check{z}\omega$ = 10.80 eV and $\tau_B = 2x10^{-14}$ s, as suggested by Ruppin [16].

In figure 3, the absorption coefficient of the Cu particles after thermal treatments at different temperatures are fitted with the calculated absorption coefficient using MG theory with MFP correction. The fittings are more or less good except for the unannealed sample and for the 400-500 nm spectral range. In table 1, the absorption peak positions and the calculated radii of the samples are given. The radius proposed for the formed particles show an increase in particle size with the increase of annealing temperature. In addition, the as implanted samples contain Cu particles of size smaller than 1 nm. The nonappearance of a clear absorption peak (band 1) in the unannealed samples certainly can be associated to the smallness of the particles as suggested by Cheshnovsky [9].

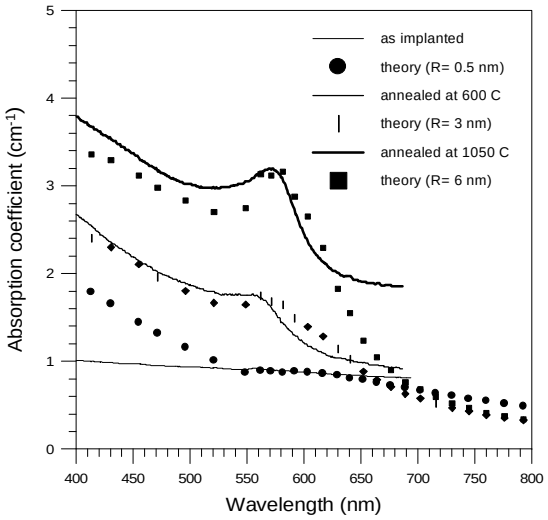

Figure 3. Absorption coefficients of sample c on annealing at different temperatures and their theoretical fits.

Table 1. Absorption peak positions of the band 1 and calculated radii of Cu particles for the sample c.

Annealing temp. (°C)	Abs. peak position (nm) Exp.	theory	Radius (nm)
As implanted	556	558.1	0.5
400	560	561.2	2.0
600	562	563.2	3.0
800	570	569.8	5.0
1050	571	570.2	6.0

4. Conclusions

Cu ions are implanted in silica glasses with different implantation doses and annealed at differents temperatures to study the effect of annealing on the formation and growth of Cu nanoparticles. RBS spectra revealed that the distribution of the Cu in silica depends on the implantation dose. With the increase of implantation dose, Cu segregate towards substrate surface. For the samples prepared with low implantation dose, with or without thermal annealing, the size of the Cu particles remain below 1nm and the clusters of Cu_2 and Cu_3 are formed. In the samples prepared with higher implantation dose, Cu nanoparticles are formed, the size of which increases with the increase of annealing temperature.

Acknowledgements

The work is partially supported by CONACyT, Mexico (Project No. 28380E).

References

[1] R. H. Magruder, III, R. A. Zhur and R. A. Weeks, *Nucl. Instr. and Meth. In Phys. Res.* **B 59/60** (1991) 1308.

[2] R. H. Haglund, Jr., L. Yang, R. H. Magruder, III, C. W. White, R. A. Zuhr, Lina Yang, R. Dorsinville and R. R. Alfano, *Nucl. Instr. And Meth. in Phys. Res.* **B91** (1994) 493.
[3] R. H. Magruder, III, R. A. Weeks, R. A. Zuhr and G. Whichard, *J. Non-Crys. Sol.* **129** (1991) 46.
[4] P. Mazzoldi, F. Caccavale, P. Chakraborty, L. Tramontin, A. Boscolo-Boscoletto, F. Trivillin, G. Battaglin and G. W. Arnold, *Nucl. Instr. and Meth. in Phys. Res.* **B 91** (1994) 505.
[5] R. H. Magruder, III, R. F. Haglund, Jr., L. Yang, J. E. Wittig, R. A. Zuhr, *J. Appl. Phys.* **76** (1994) 708.
[6] S. Nakao, Y. Miyagawa, K. Saitoh, M. Ikeyama, H. Niwa, S. Tanemura, S. Miyagawa and M. Tazawa, *Jpn. J. Appl. Phys.* **36** (1997) 7681.
[7] A. Bautista-Hernández, U. Pal, L. Rodríguez-Fernández and J. C. Cheang-Wong, communicated.
[8] L. R. Doolittle, *Nucl. Instr. and Meth. in Phys. Res.* **B 15** (1986) 227.
[9] O. Cheshnosvsky, K. J. Taylor, J. Conceicao and R. E. Smalley, *Phys. Rev. Lett.* **64** (1990) 1785.
[10] G. W. Arnold and P. Mazzoldi, Chapter 5, in *Ion Beam Modification of Insulators*, edited by P. Mazzoldi and G. W. Arnold (Elsevier, Amsterdam, 1987).
[11] G.W. Arnold, *IEEE Trans. Nucl. Sci*. **NS-20** (1973) 220.
[12] A. Manara, M. Antonini, P. Camagni, and P.N. Gibson, *Nucl. Instr. And Meth.* **B1** (1984) 475.
[13] M. Moskovits and J. E. Hulse, *J. Chem. Phys.* **67** (1977) 4271.
[14] U. Kreibig and M. Vollmer, in *Optical Properties of Metal Clusters* (Springer-Verlang, Berlin, 1995).
[15] D. M. Trotter, Jr., J. W. H. Schreurs, and P. A. Tick, *J. Appl. Phys.* **53** (1982) 4657.
[16] R. Ruppin, *J. Appl. Phys.* **59** (1986) 1355.
[17] H. Ehrenreich and H. R. Philipp, *Phys. Rev.* **128** (1961) 1622.