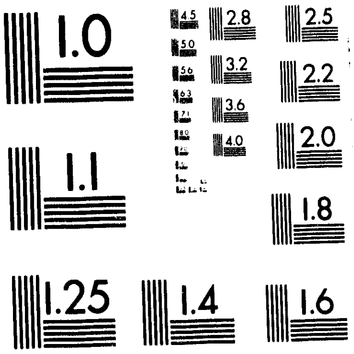
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COLLOID FORMATION IN COPPER - IMPLANTED FUSED SILICA AND SILICATE GLASSES

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Copper implantations (90 keV, 5x10^{16} ions/cm^2) were made into fused silica, borosilicate glasses and soda-lime glass. The copper distribution has been found to vary according to glass type. The optical absorption band characteristic of the implanted metal optical properties was observed only for copper-implanted fused silica. The absorption for all the other samples was either not observable or was negligibly small, however very small metallic particles are present also in the soda-lime glass. A subsequent nitrogen implantation (100 keV, 1.5x10^{17} ions/cm^2) completely eliminated the copper-colloid induced absorption in the copper-implanted fused silica, while it facilitated the formation of copper-colloids into the soda-lime glass.

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1. Introduction

Metal colloids are known to introduce optical non-linearities in glasses at wavelengths very near that of the classical electron plasma resonance. Such non-linearities lead to an intensity-dependent refractive-index and may allow the development of all-optical switching with fast speeds and low powers. Ion implantation is an especially attractive method for inducing colloid formation and confining the non-linearity to specific patterned regions [1,2 and references therein].

Together with silver and gold, copper is of particular interest for the formation of metal colloids in glasses. The major part of the published papers on copper colloid formation in implanted glasses is by researchers of Vanderbilt University and Oak Ridge Natl. Labs. (TN, USA) and Nagoya Institute of Technology (Japan) [references in 1,2]. Implants were mostly made in silica with 160 keV copper ions with fluences up to $6x10^{16}$ ions/cm^2. The presence of an optical absorption band centred at 2.2 eV was associated with the formation of copper colloids. Colloids were found only in silica glass; no colloids were detected for borosilicate or aluminosilicate glasses. The distribution of copper became bimodal in shape for fluences above $1x10^{16}$ ions/cm^2. Measurements of colloid size (by transmission electron microscopy (TEM)) showed that the colloids were crystalline and their diameter was almost linearly dependent on the copper concentration.

Here we report on the results of a study on the formation of copper colloids in silica and silicate glasses in as implanted conditions and after a further irradiation with nitrogen or argon ions.

2. Experimental

The glass types and their adopted acronyms were: fused silica (Corning 7940) - CFS, the borosilicate Pyrex - PYR, a potassium-borosilicate (0.2 K_2O, 0.8 B_2O_3, 3 SiO_2) - BSG and a soda-lime glass - SLG.

Samples were implanted with 90 keV, $5x10^{16}$ cm^{-2} copper ions. Half of each sample was subsequently implanted with 100 keV, 1.5×10^{17} cm^{-2} nitrogen ions. To test the effect of radiation damage, a SLG specimen was first implanted with 200 keV argon ions to the fluence of 2×10^{17} cm^{-2}. This glass, designated as ASLG, was then implanted with copper and nitrogen ions as specified above. Copper-implanted CFS and SLG were also subsequently implanted with 100 keV, 1×10^{17} cm^{-2} argon ions. Implantations were made at room temperature and low current densities. Ion profiles were calculated using the TRIM code [3]. Mean projected ranges and range stragglings in silica are ($R_p(\Delta R_p)$ in nm): copper: 70(23); nitrogen: 256(63); argon(200 keV): 214(56) and argon(100 keV): 111(36).

Depth profiles of the various glasses were made with 2.2 MeV He Rutherford backscattering spectrometry (RBS). Spectra were taken with an angle of 55° between the sample normal and the beam direction in order to enhance the profile depth scale.

The optical absorption was measured with a Perkin Elmer Lambda 9 UV-VIS-NIR dual-beam spectrophotometer.

Selected CFS and SLG samples were analysed also by X-ray photoelectron spectroscopy (XPS). Analyses were made in a VG Escalab Mk II spectrometer using non-monochromatised Al $K\alpha$ radiation (1486.6 eV). Analytical details were as described in previous work [4].

3. Results and discussion

3.1. Single copper implantation

The Cu-RBS spectra for CFS, PYR and SLG glasses are reported in Figure 1. The spectrum for BSG is very similar to that for PYR. The spectrum for ASLG (not reported) shows a deep penetration of copper (with a diffusion-like profile) well beyond that for the other glasses. This was also seen for silver implants [5] and is ascribed to radiation-enhanced diffusion.

The CFS glass exhibits the only strong bimodal character, with peaks centred at 61 and 95 nm. The first peak in the bimodal distribution is at a depth somewhat less than R_p, the second close to $R_p+\Delta R_p$. This was also observed by Hosono *et al.* for 160 keV copper-implanted silica [6]. In PYR (and BSG) copper is present at an appreciable concentration at the surface and, after a near surface region of lower concentration, peaks at about 87 nm. In SLG the copper profile is a broad (100-105 nm full width at half maximum) nearly symmetric peak centred at about 81 nm. The potassium in the PYR (and BSG) glass has been depleted by the implantation. The same occurred for sodium in SLG (and ASLG).

In Figure 2 the optical absorption spectrum of the CFS sample is reported together with that of the copper+nitrogen-implanted SLG specimen (which will be discussed later) and the absorption spectrum calculated on the basis of the Mie theory [7,8] for copper colloids in silica having radius of 15 nm. Calculated spectra for colloids of lower radius cannot be distinguished from this. Absorptions are not normalised and the spectra are vertically shifted for a more direct comparison. No copper-related absorption features have been detected for the copper-implanted silicate glasses, except for a very weak absorption in ASLG (only for a fluence higher than 6×10^{16} ions/cm^2).

The CFS specimen displays an optical absorption band peaked at about 560 nm, typical for absorption in metallic copper colloids, due to the copper surface plasma resonance absorption. This absorption band is consistent with predictions of the Mie theory for copper colloids in silica glass having radius less than 15 nm (see Figure 2). Hosono *et al.* [6] observed a nearly linear relation between particle diameter and concentration of copper at the peaks of the distributions. Using that relation, from the peak concentration values in CFS (Figure 1) we can infer that the copper-colloid diameters should be in the range 8-10 nm, in general accord with the results of calculations.

The binding energy (BE) values for the Cu-$2p_{3/2}$ XPS peak for Cu^0 (metallic copper), Cu^{+1} (Cu_2O) and Cu^{+2} (CuO) are 932.7, 932.4 and 933.8 eV, respectively [9]. From the analysis of this signal, copper in the metallic or in the +1 states cannot be safely distinguished. The identification of copper in the +2 charge state is easier and is made more evident by the presence of shake-up satellite lines. Cu^0 and Cu^{+1} can be distinguished from the kinetic energy (KE) values of the corresponding Cu-LVV Auger electrons, or, better, from the value of the parameter α = BE(Cu-$2p_{3/2}$) + KE(Cu-LVV). This parameter is equal to 1851.3 eV for metallic copper and to 1849.4 eV for copper in cuprous oxide [9].

Figure 3 shows the Cu-2p XPS signal for the CFS sample at the depth of about 65 nm. The Cu-$2p_{3/2}$ BE value is 932.7±0.2 eV. The part of the kinetic energy spectrum corresponding to the Cu-LVV Auger electrons is reported in Figure 4 (together with that for the double copper+nitrogen implantation, which will be discussed later). The shape of this signal is very similar to that characteristic for metallic copper and α = 1850.9±0.2 eV. The whole set of the experimental results firmly establishes the presence of metallic copper.

In the case of SLG, the Cu-2p XPS signal is slightly broader, but very similar to that of CFS. The Cu-$2p_{3/2}$ BE value is 932.6±0.2 eV. The shape of the Auger electron spectrum resembles that for the CFS sample and bulk copper. Now α = 1850.2±0.2 eV, a value which is intermediate between those for Cu^0 and Cu^{+1}. This fact can be explained with the presence in the SLG sample of very small copper particles, much smaller than those observed in CFS, so small that the measured values are averaged over the interactions between atoms inside the particles and those present at their surfaces, surrounded by oxygen atoms. Metal clusters smaller than about 1 nm cannot contribute to the surface plasmon resonance absorption since the mean free path of the conduction electrons is strongly limited by the cluster size. Because of this the characteristic absorption band is absent in the optical spectra for SLG and, probably, for the other silicate glasses.

We have not observed copper in the +2 state.

3.2. Double copper+nitrogen implantation

Figure 5 shows the Cu-RBS spectra for the copper+nitrogen-implanted CFS, PYR and SLG glasses.

As a result of the nitrogen irradiation, in CFS copper moves towards the surface, where it partially accumulates and is sputtered by the incoming ions. In PYR (and BSG) copper preferentially migrates inside the sample (with a diffusion-like profile). In SLG the shape of the profile does not change much, the copper amount is reduced as a result of sputtering and a partial migration inside the sample is observed (much less pronounced than that seen for PYR). In ASLG the copper concentration profile is not appreciably modified.

The characteristic copper-colloid induced absorption band disappears in the optical spectrum for the nitrogen-irradiated copper-implanted CFS sample, indicating a dissolution of the metal clusters. On the other hand the above-mentioned absorption band becomes detectable for the SLG specimen, as shown in Figure 2. This means that in SLG the size of the already present, very small, copper nuclei increases above the critical value to contribute to the surface plasmon resonance absorption. No copper-colloid related optical absorption is observed for PYR and BSG. The weak absorption measured for the copper-implanted ASLG is not influenced by the subsequent nitrogen irradiation, indicating that the already heavily damaged structure does not favour a further migration and aggregation of the implanted metal atoms.

The disappearance of the metallic character of copper in the doubly implanted (copper+nitrogen) CFS sample is evident from the XPS spectrum of this specimen. The Cu-$2p_{3/2}$ BE value is now 933.4±0.2 eV, a value higher than that for Cu^0 and Cu^{+1}, and lower than that for Cu^{+2}, but the presence of copper in the +2 charge state can be excluded due to the absence of the characteristic shake-up satellite lines. The shape of the Cu-LVV Auger electron signal, reported in Figure 4, resembles that of oxidised copper and $\alpha = 1847.3 \pm 0.2$ eV. This value is closer to that for Cu^{+1} (1849.4 eV) than to those for Cu^0 (1851.3 eV) and Cu^{+2} (1851.7 eV) [9]. Moreover, by comparing the peak intensities as a function of the sputtering time (not reported), there is clear evidence that part of the implanted nitrogen distribution follows the copper concentration profile. This is an indication of the chemical interaction between the two implanted species [2,4]. We observed also a single N-1s XPS peak centred at a BE value of 398.4±0.2 eV. This BE value is typical of nitride or oxynitride species [4,10].

3.3. Double copper+argon implantation

The argon irradiation of the copper-implanted CFS and SLG samples causes modifications of the copper concentration profiles similar to those observed after the nitrogen irradiation (movement toward the surface in CFS and a uniform decrease in concentration in SLG). The most significant difference has been detected in the optical absorption spectra: contrary to nitrogen, the argon irradiation does not modify the absorption behaviour of the copper-implanted samples. This further support the hypothesis of a chemical interaction between copper and nitrogen.

4. Conclusions

From the above reported results and considering also the results of out past study of silver implantation on the same substrates [5], the following main conclusions can be drawn :

i) from the point of view of the metal specie concentration profile, the selected substrates can be divided into three classes: silica, borosilicate and soda-lime glasses. The differences between them can be associated both to the different mechanical properties related to the glass structure, and to the different alkali content.

ii) The absence of a characteristic optical absorption band does not imply the absence of colloids in the implanted glass. As revealed by the XPS analysis of the copper-implanted soda-lime glass, such colloids can be present, but their size can be too small to contribute to the surface plasmon resonance absorption.

iii) A chemical interaction exists between copper and nitrogen in the implanted fused silica sample. Such an interaction causes the disappearance of metal colloids, with the formation of copper in the +1 charge state, probably copper oxynitrides.

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Figure captions

Figure 1: Partial RBS spectra for the copper-implanted fused silica (CFS), Pyrex (PYR) and soda-lime (SLG) glasses.

Figure 2: Optical absorption spectra for the copper+nitrogen-implanted soda-lime (SLG (Cu+N)) and the copper-implanted fused silica (CFS (Cu)) samples. The absorption spectrum calculated on the basis of the Mie theory for copper colloids in silica, having radius of 15 nm, is also shown.

Figure 3: XPS spectrum showing the Cu-2p signal for the copper-implanted fused silica sample.

Figure 4: Auger electrons kinetic energy spectra showing the Cu-LVV signal for the copper- and for the copper+nitrogen-implanted fused silica samples.

Figure 5: Partial RBS spectra for the copper+nitrogen-implanted fused silica (CFS), Pyrex (PYR) and soda-lime (SLG) glasses.

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