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Structural Investigation of Small Cu Clusters Obtained by Ion-Implantation in Amorphous Silica

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Abstract In this paper we present an EXAFS study on Cu clusters obtained by ion-implantation in amorphous silica substrates. As-implanted and 700°C annealed samples were analyzed both at liquid nitrogen temperature and room temperature in order to determine the structural parameters. Evidence of a lattice contraction beyond the anharmonic correction were found in the tiniest particles, as well as a clear contribution of static disorder to the total Debye-Waller factor. No change of the Debye temperature due to overpressure was found in agreement with the calculations.

1. INTRODUCTION

Metal doped glasses are widely used in optics for the construction of waveguides. Recently [1] a great attention has been given to metallic clusters embedded in insulating glasses because of the enhanced third order dielectrical susceptibility. This phenomenon observed in glasses doped with Au, Ag, Cu [1 and references therein], is strongly dependent on the details of the metal band structure. Metallic clusters have been studied with different techniques and have been found to exhibit slightly different structural parameters with respect to the corresponding metal bulk. In particular a reduction of the coordination number [2], and a contraction of the lattice parameter [3] are found together with a variation of the Debye-Waller factor: in some cases a higher one [4] due to the enhanced surface to bulk ratio, in other cases a smaller one [5,6] due to an overpressure on the nanoparticles. Critical analyses on the lattice contraction seen in EXAFS [7] have been published showing the need to perform low temperature experiments in order to get reliable data. Molecular Dynamics (MD) calculations [8] have also shown that a transition from fcc structure to icosahedral structure is expected for small diameters ($D < 50 \text{ \AA}$). The main effect on EXAFS spectra of the icosahedral structure was shown to be [9] an enhancement of the static part of the Debye-Waller factor and lower values of the coordination number in the various shells. The aim of the present experiment is thus to determine the local structure of Cu metallic clusters embedded in amorphous silica, obtained by ion-implantation and annealing.

2. EXPERIMENTAL

2.1 Sample preparation: Substrates of pure amorphous silica (Heraeus Herasil, 1mm thick) were implanted at room temperature with 160 KeV Cu^+ ions, implant currents were kept below $2 \mu\text{A}/\text{cm}^2$. Implants were performed at C.E.A Grenoble; simulations made with the TRIM code [10] have shown a projected range of 120 nm and a range straggling of 38 nm. Samples named 1 and 2 were implanted at $5 \cdot 10^{16} \text{ at}/\text{cm}^2$, while samples 3, and 4 at $1 \cdot 10^{16} \text{ at}/\text{cm}^2$; subsequently, samples 1 and 3 were annealed in air at 700°C for 30', the others left as-implanted. Samples were characterized by optical absorption looking at the position and width of the surface plasmon absorption line and the particle diameters were determined in the framework of the classical line broadening theory [11] with the known values of Cu dielectric constant.

2.2 EXAFS measurements: EXAFS measurements at the Cu K-edge were performed at E.S.R.F. on the GILDA beamline in fluorescence mode [12]. The monochromator was equipped with two (311) Si crystals and was used in dynamical focusing mode. Energy resolution was around 0.5 eV; harmonics rejection was achieved by two Pd coated mirrors with a cutoff energy of 23 KeV. The incoming flux was measured by an ionization chamber filled with N_2 . The fluorescence signal was detected by a large area PIN Si photodiode used in current mode. Measurements were performed both at 77K (LNT) and at 300K (RT).

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3 DATA ANALYSIS

EXAFS analysis was performed using the software package "EXAFS pour le MAC" [13]. Backscattering amplitude and phase were taken from bulk metallic Cu at LNT. Structural data were determined by a nonlinear multiparameter fit using a single-scattering model with gaussian distribution; errors were defined with a confidence level of 95%. The results of the analysis on the first shell of metallic Cu of the EXAFS spectra are shown in Table I, LNT data were obtained fitting N, R, $\Delta\sigma_{\text{exp}}$ and ΔE_0 , while RT data were obtained by only fitting the $\Delta\sigma_{\text{exp}}$ parameter. Fourier transforms of the spectra are shown in fig 1, left (see caption for details).

Table I: Results of the EXAFS Analysis: $\Delta\sigma_{\text{exp}}$ values are relative to the model compound. Parameters without error bars were kept fixed during the fit. N and R values for the model compound were taken from diffraction data, σ_{exp} was arbitrarily set at 0.0001 Å.

Sample	LNT Data			RT Data		
	N	R (Å)	$\Delta\sigma_{\text{exp}}$ (Å)	N	R (Å)	$\Delta\sigma_{\text{exp}}$ (Å)
1	10 ± 1	2.55 ± 0.01	0.001 ± 0.005	10	2.55	0.071 ± 0.005
2	7.0 ± 1	2.55 ± 0.01	0.0001 ± 0.005	7.0	2.55	0.067 ± 0.005
3	6.2 ± 1	2.54 ± 0.01	0.035 ± 0.01	6.2	2.54	0.076 ± 0.01
4	1.4 ± 0.3	2.52 ± 0.02	0.035 ± 0.01			
Model Comp.	12	2.556	0.0001	12	2.556	0.065 ± 0.003

3.1 Nearest Neighbours Reduction: In all the specimens a reduction of the expected coordination number was found, that can be explained with the small diameter of the particles. In the case of sample 4 the strong reduction may be attributed to the oxidation of a fraction of the Cu atoms. Also the coordination numbers of 2nd and 3rd coordination shells were found, using as reference the backscattering parameters of the relative shells of the Model Compound at LNT. The values found were compared with the expected values for clusters of diameter D using the approximated formula: $N_n(D) = N_n^{\text{Bulk}} \left(1 - \frac{3 R_n}{2D}\right)$ [14] where R_n is the n-th shell radius, D is the cluster diameter, N_n is the n-th shell coordination number. The result are shown in tab II

Table II: Comparison of the Coordination numbers of the first 3 shells with the values of formula with a best fit D value.

Sample #, D	N_1 EXAFS	N_1 (D)	N_2 EXAFS	N_2 (D)	N_3 EXAFS	N_3 (D)
1, D= 25 (Å)	10 ± 1	10	4.6 ± 0.8	4.6	17 ± 2	17
2, D= 13 (Å)	7.0 ± 1	8.5	3.3 ± 1	3.5	13 ± 2	12

First shell analysis on sample 3 using the N_1 (D) exact formula for fcc clusters [14], led to a 6 Å mean diameter value.

3.2 First Bond Length Contraction The samples containing smaller clusters show a reduction of the first shell radius, in agreement with previous studies on Cu clusters [2]. The contraction is very small in sample 3 while it is 0.04 Å in sample 4. χ^2 contour plots at 95% confidence level of the R and ΔE_0 parameters show well distinct regions between sample 1 and sample 4. In order to determine the order of magnitude of anharmonic effects we have taken data on the higher moments $\langle x^n \rangle$ of the radial distribution function $g(r)$ of a 256 Cu atom clusters found by MD [7] and applied the phase correction formula [15]. With $\langle x^2 \rangle = 0.00347 \text{ Å}^2$ and $\langle x^3 \rangle = 0.000118 \text{ Å}^3$ at 100K, it was found that the correction to R is only 3 ‰, at a mean value of $k = 7.5 \text{ Å}^{-1}$, below the values observed in the present analysis. Knowing the bulk compressibility of Cu [16] ($K_b = 7.3 \cdot 10^{-3} \text{ GPa}$), we have determined the pressure acting on the particles. This pressure, resulting from the embedding matrix pressure and the surface tension of the particle, is around 2.6 GPa for sample 3 and 5.8 GPa for sample 4. These pressures fall in the same range found in previous studies on rare-gas clusters embedded in crystalline Si [6 and references therein].

3.3 Debye-Waller Factors The Debye-Waller factors (DWF) σ^2 (Fig1, Right) in the case of larger clusters (samples 1,2) are very similar to those found for metallic Cu and are in agreement with previous determinations [17]. The absolute values of σ^2 were determined by the formula [18] $\sigma^2 = \frac{h}{2\pi M k T_E} \frac{1}{\coth\left(\frac{T_E}{2T}\right)} + \sigma_s^2 + \Delta\sigma_{\text{exp}}^2$ where h is the Planck constant, M the atom

mass, k the Boltzmann constant, T the temperature and T_E the Einstein temperature (estimated as $T_E = \frac{3}{4} T_D$ for fcc crystals),

σ_s^2 the static part of the disorder (set to zero in the model compound and in large clusters). For smaller clusters data show an increase in the DWF that can be ascribed to a static contribution of around 0.0013 Å^2 in sample 3. This is qualitatively the behaviour of the transition from fcc to a relaxed icosahedral structure [8,9]; however MD calculations made on Au clusters [9] predict an enhancement of the static disorder of around 0.008 Å^2 well above our findings. Apart the static component the dynamic part of the disorder is well described by the bulk Debye Temperature $T_D = 330 \text{ K}$ [16]. Using the known values of the Gruneisen parameter for Cu [16] we have estimated the increase of T_D due to the overpressure to be 8% higher than in the uncompressed case, too small to be revealed by the present data.

4. CONCLUSIONS

We have determined the structural parameters of small Cu nanoparticles embedded in amorphous silica obtained by ion implantation and subsequent annealing. Mean diameters range between 6 and 25 Å, the smaller occurring in as-implanted specimens at lower implantation doses. The smaller particles ($D < 1\text{ nm}$) exhibit a contraction up to 1.5% of the first shell distance and static contribution to the Debye-Waller factor. The particle size and lattice contraction agree with data taken from the broadening and shift of the surface plasmon absorption line in the optical range.

Fig 1: Left: comparison between Fourier transforms (k^3 , $k=3-17\text{ Å}^{-1}$) of EXAFS spectra at Liquid Nitrogen Temperature. Right: Debye-Waller factors of Cu clusters. The fit to the sample 3 data was made via the Rehr Formula [25] with $T_e = 274\text{ K}$ and a static contribution of 0.0013 Å^2 .

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