The Formation of Copper Nanoclusters in SiO_2 Studied by X-ray Absorption Spectroscopy

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Abstract

Results on Cu K-edge x-ray absorption study of copper dispersed in SiO_2 are reported. Randomly distributed in as-made samples at low concentration, copper atoms tends to form clusters at larger concentrations. The cluster size reaches a size of 20 to 50 Å after which the cluster growth stops. Only the first-neighbour peak is observed in as-made samples indicating either a very strong disorder in clusters or their low-dimensionality. Annealing results in the formation of copper clusters of the same size with fcc structure.

1. Introduction

Composite materials containing metallic particles of nanometer sizes embedded in insulating media have attracted wide interest because of their unique properties distinct from both metal and insulator. Optical properties of such materials have been studied for a long time theoretically [1,2] and experimentally [3,4] and were reviewed in [5]. Electrical properties of composite metal-insulator materials have also been extensively studied [6,7]. A new activity in this field was invoked by the suggestion that single-electron transport phenomena can be observed in metal-insulator composites at elevated temperatures [8]. For many such applications the detailed knowledge of structure parameters are of primary importance.

In this paper we report the results of Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near Edge Structure (XANES) and present structural information on the structure of copper clusters embedded into SiO_2. Some of results have already been reported elsewhere [9]. In particular, it was shown that copper atoms randomly distributed in SiO_2 in as-made samples form nanoclusters with fcc structure upon annealing. In this paper we report the results of a study of copper structure in as-made samples with different concentration of copper.

2. Experimental

Experimental Cu-SiO_2 samples were prepared by RF-magnetron copper and silica co-sputtering in Ar gas atmosphere to obtain 0.1 µm thick films. By choosing the sputtering rates at each magnetron source the concentration of copper in silica was varied in a wide range from 8 to 40 volume %. The obtained films were annealed in hydrogen atmosphere, the temperature ranging from 700°C to 950°C, from 10 to 30 minutes.

The measurements were performed at BL13B station at the Photon Factory [10] using a 27-pole wiggler in a fluorescence mode. An array of 19-element high-purity Ge solid-state detectors was used to detect the fluorescence. EXAFS spectra with good signal-to-noise ratio were obtained for very diluted thin films with a thousand Ångstrom thickness. Samples were mounted on an aluminum holder in an evacuated cryostat equipped with windows (KAPTON) for incident and fluorescent X-ray beams. A closed-cycle He refrigerator with a cooling power of ~9 W at 20 K was used. Cu K-edge EXAFS and XANES spectra were measured in the temperature range from 30 K to 300 K. Metallic bulk copper and CuO_2 have been used as standards in the data analysis. The spectra for the standards have been measured in a transmission mode under otherwise similar conditions.

3. Results

Figure 1 shows raw Cu K-EXAFS oscillations measured at room temperature for the as-prepared samples with copper concentration of

8 and 32 % as a function of photoelectron wavenumber *k* after subtracting the smooth background due to the atomic absorption. The background function given as a combination of the third and forth order polynomials, with tabulated coefficients (Victoreen Function) which smoothly interpolate EXAFS oscillations using a cubic spline method, was normalized to the edge jump and subtracted from the fluorescence spectrum. One can see that in the spectrum for the low concentration the signal intensity is lower and oscillations damp at lower *k*-values, which is characteristic of interaction with a light element. The spectrum for the sample with larger copper concentration clearly resembles that of bulk copper.

The EXAFS oscillations multiplied by k [$k\chi(k)$] were Fourier-transformed (Fig. 2) into the real space using the region extending from 4.5 to 15 Å^{-1}. It is seen that the sample with the lowest concentration does not have a peak at distances corresponding to Cu-Cu bond length. There is a small feature in that spectrum located at a somewhat smaller distances (~1.2 Å) which may be indicative of dimer formation.

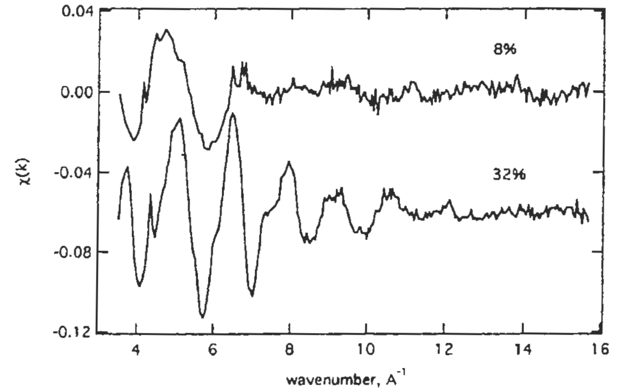

Fig. 1 Raw EXAFS spectra of as-made samples with different Cu concentration measured at room temperature. Concentration of copper is marked in the figure.

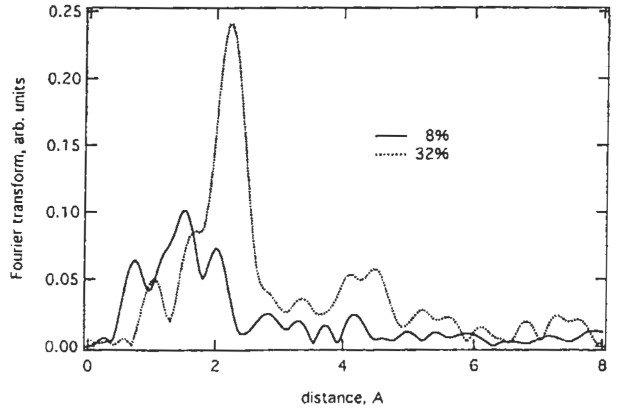

Fig. 2 Fourier transforms of the spectra shown in figure 1.

As the concentration of copper increases, the Cu-Cu peak clearly appears. Its intensity increases with the increase in copper concentration and the peak position slightly shifts to longer distances. Peaks corresponding to the second and third shells are hardly seen in either of as-made samples.

The least-squares curve-fitting, based on the single-scattering theory [11] and FEFF [12] amplitudes, gives values of the average coordination numbers, bond lengths and disorder parameters (Debye-Waller factor) summarized in Table 1. One can see from the table that a small feature in the sample containing 8% Cu can, indeed, be attributed to dimers whose bond length is between that of a free dimer and a Cu-Cu bond length in bulk copper. As the concentration of copper increases, both the coordination number and bond length also increase. The Cu-Cu bond length in a cluster becomes equal to that in bulk metal at concentration of about 25 vol. % of copper, while the coordination number remains smaller. Further increase in the copper concentration does not lead to an increase in the coordination number but the DW-factor decreases. The resulting cluster size is the same as that obtained by annealing the samples with lower Cu concentration [9].

Table 1 Coordination numbers, bond length and MSRD for Cu-Cu interaction in as-made samples with different Cu concentrations.

Copper concentration, vol.%	Coordination	Bondlength Å	DW factor Å
8	0.9 ± 0.15	2.45	0.042
16	2.7 ± 0.5	2.54	0.073
20	5.6 ± 0.8	2.54	0.092
25	8.1 ± 1.0	2.55	0.096
32	8.0 ± 1.0	2.56	0.080

XANES spectra of as-made samples containing different amount of copper show a systematic change in relative intensity of peaks indicating a change in the density of states. At higher copper concentration the first peak splits into two indicating the formation of metal-like cluster (Fig. 3). A more detailed analysis of XANES spectra is currently underway. Comparison of XANES spectra of an as-made sample with those for bulk copper and Cu$_2$0 discussed previously [9] have demonstrated that Cu-O interaction is negligible.

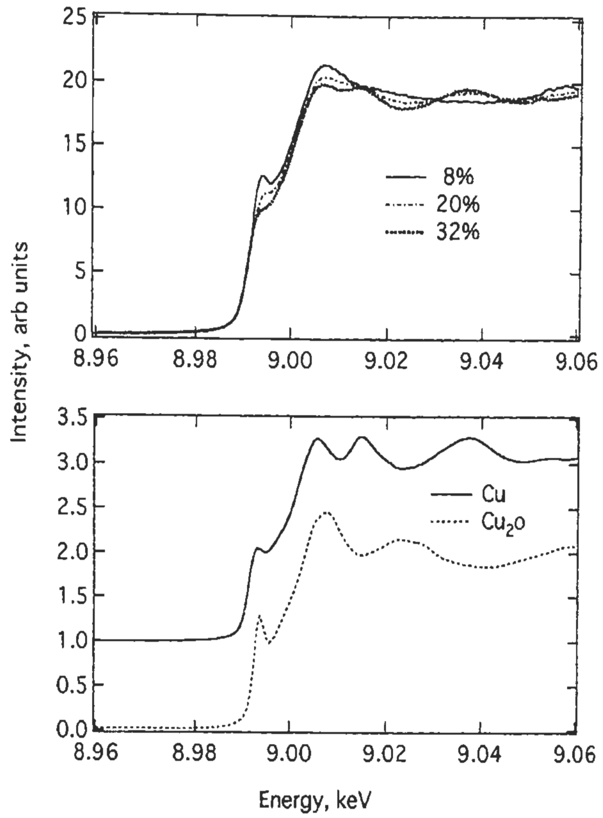

Fig. 3 XANES spectra of as-made samples with three different copper concentrations. XANES spectra of standards (bulk Cu and Cu_2O) are shown at the bottom of the figure for comparison.

4. Discussion

It is reasonable to assume that in an as-prepared sample copper is randomly distributed throughout the SiO_2 matrix. In this case one should expect a very weak Cu-Cu correlation which agrees well with the obtained data for the as-prepared sample with the lowest concentration of copper. As the concentration of copper increases, Cu-Cu correlation becomes stronger and small Cu-clusters are formed which become larger in size as the copper concentration is further increased. Interestingly, after the coordination number reaches 8 no further increase in the coordination number is observed.

There are various reasons which may account for a coordination number in clusters being smaller than that in the bulk. They include cluster size dependence of photoelectron mean free path [13], unharmonicity of the atomic potential [14] and pure geometrical factor (atoms which are at the surface of the cluster only have copper neighbours on one side) [15, 16], the latter being probably the most important. With the obtained coordination number the cluster size can be estimated as being 20 to 50 Å [9, 15] assuming the spherical shape of the cluster. The fact that the cluster size does not increase above a certain limit neither with the increase in the copper concentration nor with the annealing time [9] may be explained by an interplay between bulk and surface energies.

Another interesting feature is the absence of higher shells in the Fourier transforms of the spectra for as-made samples. Given the size of the cluster of 50 Å such peaks should have been observed. Their absence may be considered as an indication of strong disorder which agrees with the obtained values of mean-square relative displacement (MSRD) in as-made films being larger than that in annealed sample or in bulk copper. Although the formation of amorphous copper is not so straightforward strong interaction of cluster with the matrix could, perhaps, cause large structural distortions. Another likely possibility to explain the absence of higher shells could be low dimensionality of clusters.

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