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The formation of copper nanoclusters in SiO_2: an X-ray absorption study

A. V. Kolobov†§, H. Oyanagi‡, S. A. Gurevich§, V. V. Horenko§ and K. Tanaka†
† Joint Research Center for Atom Technology,
National Institute for Advanced Interdisciplinary Research,
1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan
‡ Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305, Japan
§ Ioffe Physico-Technical Institute, 194021 St Petersburg, Russia

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. 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 [1]. 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) measurements and present information on the structure of copper clusters embedded into SiO_2. In particular, it was shown that copper atoms randomly distributed in SiO_2 in as-made samples with low copper concentration form nanoclusters with fcc structure upon increase of copper content and/or upon annealing.

2 Experimental

Cu-SiO_2 samples were prepared by RF-magnetron co-sputtering of copper and silica 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 [2] 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. Metallic bulk copper and CuO_2 have been used as standards in the data analysis.

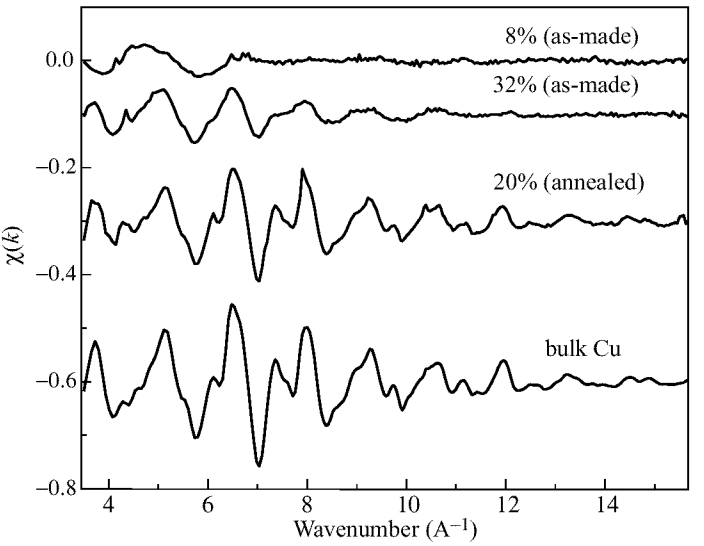

Fig 1. Raw EXAFS spectra of as-made samples with different Cu concentration measured at room temperature. Concentration of copper is marked in the figure. EXAFS spectra for annealed sample with intermediate Cu concentration as well as that for bulk copper are shown for comparison.

3 Results

Figure 1 shows raw Cu K-EXAFS oscillations measured at room temperature for 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 shown in the same figure for comparison.

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 ($\sim$ 1.2 Å which may be indicative of dimer formation. As the concentration of copper increases, the Cu-Cu peak clearly appears.

The least-squares curve-fitting, based on the single-scattering theory [3] and FEFF [4] 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

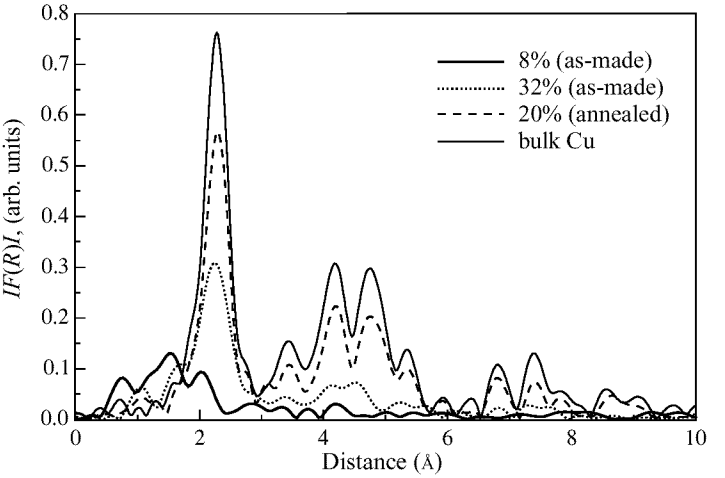

Fig 2. Fourier transforms of the spectra shown in figure 1.

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

Copper concentration, vol.%	Coordination number	Bondlength Å (±0.005)	DW factor Å
8	0.9±0.2	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
bulk Cu	12.0	2.26	0.044

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 more than 25 vol. % of copper, while the coordination number remains smaller.

4 Discussion

It is reasonable to assume that in an as-prepared samples with low copper concentration 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 which implies that a certain portion of Cu atoms (about 25%) does not form dense clusters.

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 [5] 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 in bulk copper. Upon annealing, the fcc structure is established as clearly evidenced by the Fourier transformed spectrum (Fig. 2).

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References

[1] Vishenski S,V., *Phys. Low-Dim. Struct.* **11/12**, 9 (1994).
[2] Oyanagi H., Haga K., and Kuwahara Y., *Rev. Sci. Instrum.* **67** 350 (1996).
[3] Stern E.A., *Phys. Rev.* **B10** 3027 (1974).
[4] Rehr J.J., Albers R.C., and Zabinsky S.I., *Phys. Rev. Lett.* **69** 3397 (1992).
[5] Gurevich S.A., et al. *Phys. Solid State*, **39** 1692 (1997).