TITLE: Copper and Cobalt Nanoclusters Embedded in Hydrogenated Amorphous Carbon: An X-Ray Absorption Study

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Copper and cobalt nanoclusters embedded in hydrogenated amorphous carbon: an X-ray absorption study

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1. Introduction

Investigation of metallic clusters in insulating media, also called discontinuous or granular metals has recently attracted much interest. This interest was further stimulated by possible applications in single-electron devices. Recently, confinement of copper nanoclusters in hydrogenated amorphous carbon (α-C:H) was reported [1] The structure of α-C:H is a mixture of sp^2 and sp^3 bonded carbon species [2]. The presence of sp^3 bonding results is high hardness and optical transparency while incorporation of a metal ensures conductivity. Confinement of magnetic species in a dielectric matrix is of special interest for spin-electronic applications [3].

In this paper we report the results of X-ray absorption study (EXAFS and XANES) of the dependence of the structure of clusters on the concentration of the metal and on annealing.

2. Experimental

The α-C:H$\langle$Cu, Co$\rangle$ films were grown on fused quartz and/or crystalline silicon substrates by ion (magnetron) co-sputtering of graphite and copper targets in argon-hydrogen (80% Ar and 20% H_2) plasma. The substrate temperature, gas pressure in the growth cell and average magnetron power were 500 K, 10 mtorr, and 0.4–0.5 kW, respectively. The energy of Ar^+ ions was 350–450 eV. The metal concentration was varied from 0 to 30%. For more details on preparation see [1].

The measurements were performed at BL13B station at the Photon Factory 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. Details of the equipment are given in [4]. Cu K-edge EXAFS and XANES spectra of α-C:H$\langle$Cu$\rangle$ were measured at 300 K. As reference samples we have also measured the spectra for bulk metallic copper and for Cu_2O.

3. Results

The EXAFS oscillations, after subtraction of smooth backgrounds due to the atomic absorption from the fluorescence yield spectra, were multiplied by $k[k\chi(k)]$ and Fourier-transformed (Fig. 1) using the region extending from 4.5 to 15 Å^{-1}. A spectrum for bulk Cu is shown for comparison. One can see that for the as-made samples there is basically no peak corresponding to Cu–Cu interaction. Peaks at $R \sim 1$ Å are most likely due to poor background subtraction for a very dilute sample. A broad peak is observed in these samples at distances smaller than the Cu–Cu bond length. Curve-fitting analysis gives the

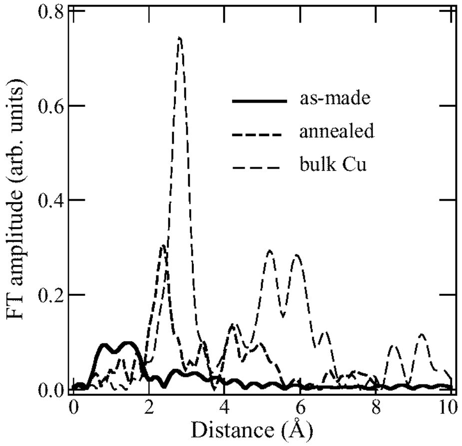

Fig. 1. Fourier transforms of EXAFS spectra for as-made and annealed samples with 12% Cu and that for bulk Cu.

average Cu–Cu coordination number of ~0.5 for those samples. Figure 2 shows XANES spectra for the measured samples and for the standards (bulk Cu and Cu_2O).

Upon annealing, a peak situated at ~2.1 Å which corresponds to the Cu–Cu first shell appears and grow. Further annealing results in appearing of peaks corresponding to higher shells. The XANES spectra are also modified and approach that for bulk copper.

Figure 3 shows XANES spectra for as-made cobalt-containing samples. The change in the spectra with the Co concentration is similar to that reported earlier for Cu. We have not found any magnetic-field effect in the as-made 25% Co sample. The conductivity, however, was found to drop by several orders of magnitude when ~40 V were applied to the sample which we believe was due to modification of the contact region.

4. Discussion

The observed coordination number of <1.0 in as-made samples can indicate either a complete absence of Cu–Cu correlations or probably also the formation of small portion of Cu dimers. The accuracy in determination of the coordination number does not allow us to unambiguously distinguish between single atoms and dimers.

It is not quite clear from the present study whether copper in this geometry mainly interacts with carbon or oxygen species of the surrounding matrix. The fact that the XANES spectra resemble that of Cu_2O and non-existence of Cu–C compounds support the latter possibility. The presence of Cu_2O has also been confirmed by IR spectroscopy.

Upon annealing, Cu–Cu correlations are clearly seen as a peak at 2.1 Å corresponding to the first-nearest and more distant shells are also seen. The obtained coordination number for a cluster in a sample annealed for 1 h is 4 ± 2 and the Debye–Waller (DW) factor is 0.08 Å (compared to 0.045 Å in bulk copper). The Cu–Cu bond length equals 2.54 Å which is 0.02 Å shorter than in the bulk metal. 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, anharmonicity of the atomic potential, and pure geometrical factor (atoms which are at the surface of the cluster only have copper neighbours on one side), the latter being probably the most important. With the obtained

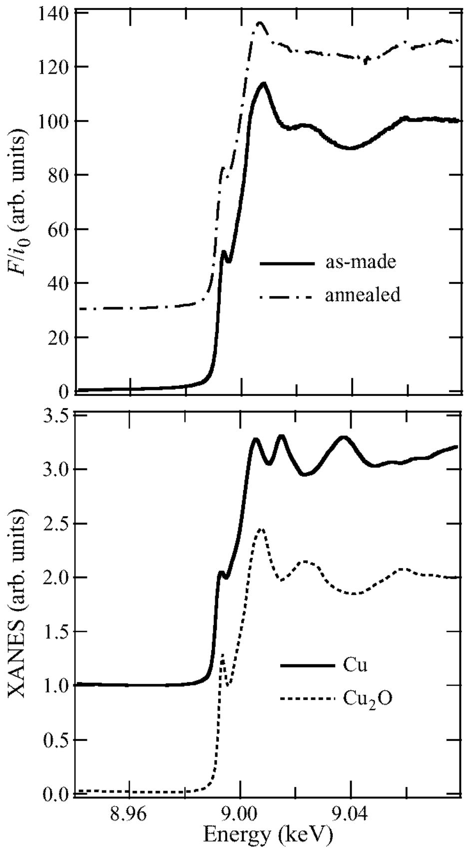

Fig. 2. XANES spectra for as-made and annealed samples (top) and references (bottom).

coordination number the cluster size can be estimated as being 5 to 20 Å assuming the spherical shape of the cluster [5, 6].

For cobalt, only as-made samples have been studied so far and the observed change in the spectra suggests increased Co–Co correlations in samples with higher Co concentrations. There is a systematic change in the spectrum indicating a change in the density of states. This change is similar to that for copper. Further studies or annealed samples are needed and are currently underway.

5. Conclusion

Application of EXAFS and XANES spectroscopies have revealed that in as-prepared samples containing up to 24% copper the metal atoms is randomly distributed throughout the film with possible formation of a small number of dimers. Upon annealing copper clusters are formed.

For cobalt, we observed also Co–Co correlations in as-made samples but it is not yet clear whether nanoclusters are formed upon annealing.

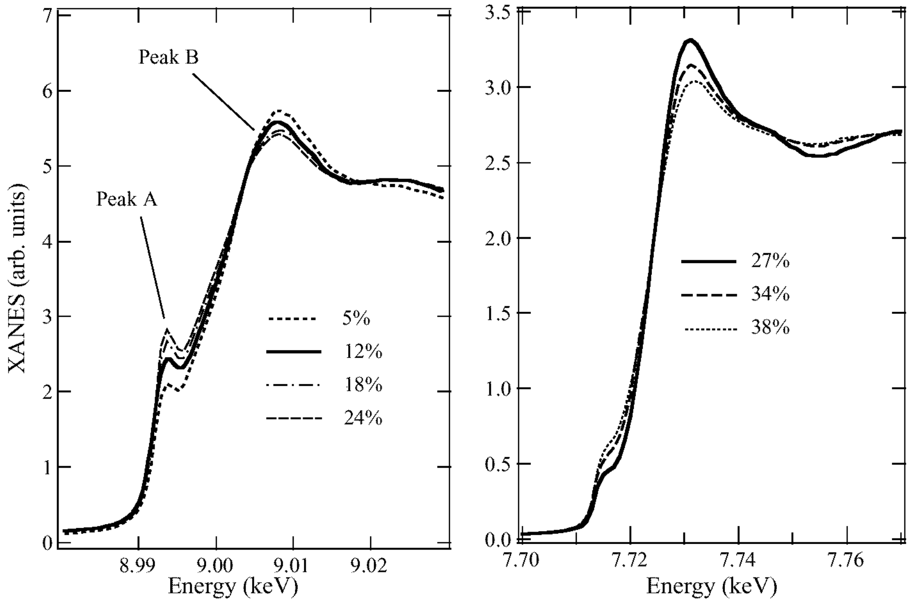

Fig. 3. Normalized XANES spectra for as-made samples containing copper (left) and cobalt (right) in different concentrations.

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