The Formation of Copper Clusters Embedded in Hydrogenated Amorphous Carbon: an X-ray Absorption Study

A.V. Kolobov[1,2,*], H. Oyanagi[2], S.G. Yastrebov[3],
V.I. Ivanov-Omskii[3], and K. Tanaka[1]

1 Joint Research Center for Atom Technology - National Institute for Advanced Interdisciplinary Research, 1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan
2 Electrotechnical laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305, Japan
3 A.F. Ioffe Physico-Technical Institute, 26 Polytechnicheskaya St, 194021 St Petersburg, Russia
** on leave from A.F. Ioffe Physico-Technical Institute, St Petersburg, Russia*

(Received: 13 February 1998; accepted: 27 February 1998)

Abstract:

Structure of copper dispersed in hyrdrogenated amorphous carbon in concentrations up to 24 at.% has been studied by x-ray absorption spectroscopy. It is demonstrated that is as-made samples copper is randomly distributed with a possible formation of dimers. Upon annealing, nanoclusters of copper are formed which possess fcc structure with the bond length equal to and the average coordination number less than the corresponding values in bulk copper. The size of clusters is estimated to be 5 to 20 Å

Introduction

Investigation of metallic clusters in insulating media, also called discontinuous or granular metals, is of interest for reasons of their unusual properties different from both metals and insulators [1]. This interest was recently stimulated by possible applications in single-electron devices. Recently, confinement of copper nanoclusters in hydrogenated amorphous carbon (a-C:H) was reported [2,3] The structure of a-C:H is a mixture of sp^2 and sp^3 bonded carbon species [4]. The presence of sp^3 bonding results is high hardness and optical transparancy while incorporation of copper ensures conductivity.

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

Experimental

The a-C:H<Cu> 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 500K, 10 mTorr, and 0.4 - 0.5 kW, respectively. The energy of Ar^+ ions was 350- 450/eV. The copper concentration was varied from 0 to 24% which was controlled by changing the relative areas of graphite and copper targets. The measured (average) composition was within ±1% of the calculated value. Film thicknesses were in a range of a few thousand Ångstroms.

The measurements were performed at BL13B station of the Photon Factory [5] 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 Ångstroms thickness within one hour. The sample was 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 ~9W at 20K was used.

Cu K-edge EXAFS and XANES spectra of a-C:H<Cu> were measured at 300K. As reference samples we have also measured the

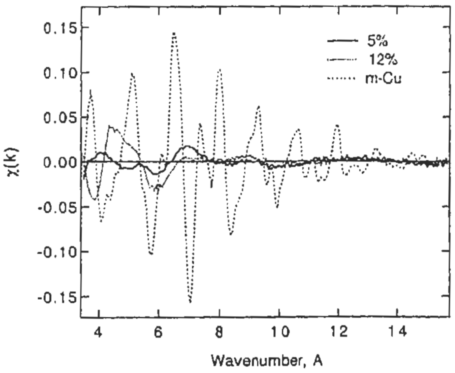

Fig.1 Raw EXAFS oscillations of a-C:H<Cu> with 5 and 12 at. % copper. The corresponding spectrum for bulk copper is shown for comparison.

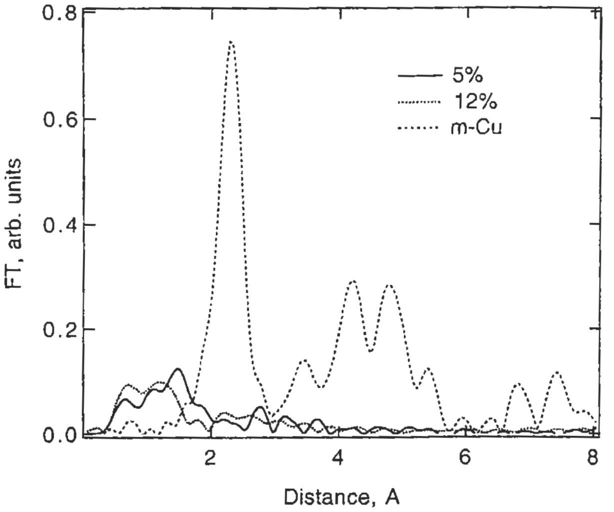

Fig.2 Fourier transforms of spectra shown in Fig. 1.

spectra for bulk metallic copper and for Cu$_2$O.

3. Results

Figure 1 shows raw EXAFS spectra for a-C:H<Cu> films with 5 and 12 % copper as a function of photoelectron wavenumber k after subtraction of smooth backgrounds due to the atomic absorption, from the fluorescence yield spectra. The spectrum for bulk copper is also shown for comparison. The background function given as a combination of the third and forth order polynomials, with tabulated coefficients [6] (Victoreen Function) which smoothly interpolate EXAFS oscillations using a cubic spline method, was normalized to the edge jump and subtracted from the fluorescence spectrum.

The EXAFS oscillations multiplied by k $[k\lambda(k)]$ were Fourier-transformed (Fig. 2) using the region extending from 4.5 to 15 A-1. One can see that for the samples with 5 at.% and 12 at% Cu there is no peak corresponding to Cu-Cu interaction. Peaks at R~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 using a single-scattering theory [7] and FEFF amplitudes [8] gives the average Cu-Cu coordination number of ~0.5 for those samples.

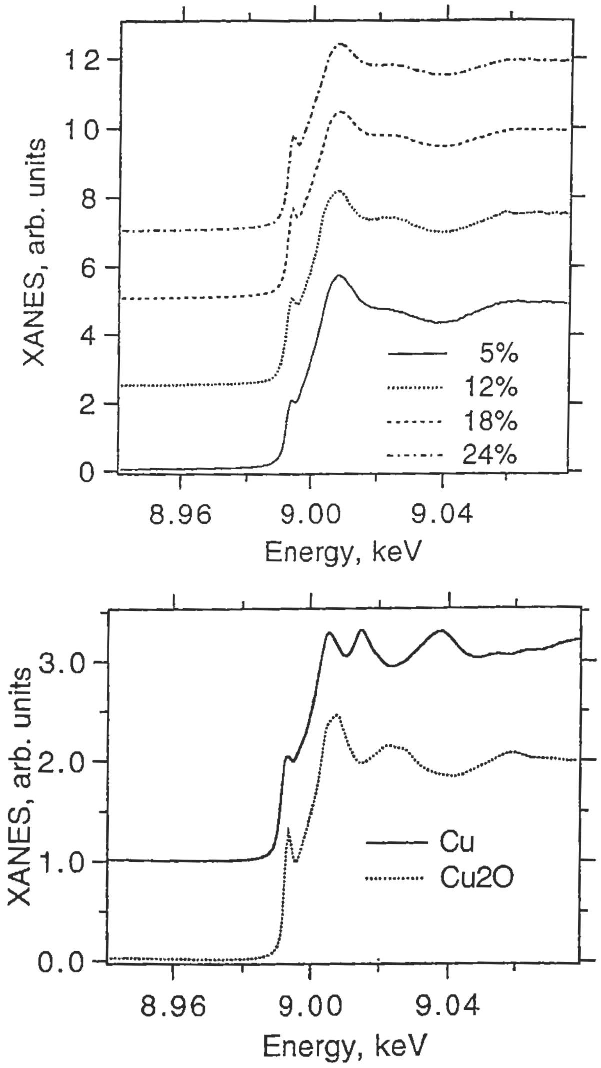

Fig.3 XANES spectra of a-C:H<Cu> samples with various copper concentrations (top) and those of references (bottom).

Figure 3 shows XANES spectra for the measured samples and for the standards (bulk Cu and Cu$_2$O). It should be noted that the samples were measured in the fluorescence mode while the references were measured in the transmission mode. This difference results in various scales of the y-axis (while the energy axis is obviously the same for the two cases). One can see that the spectra for the measured samples resemble strongly the spectrum for Cu$_2$O indicating that copper in the samples exists in the form of copper oxide.

Below we present the data related to the modificaion of the cluster structure by annealing. Raw EXAFS spectra and corresponding Fourier transforms for the sample with 12% copper are shown in Figs 4 and 5, respectively. One can see that while in the as-prepared sample the EXAFS oscillations are weak and the envelope has a maximum at low k, upon annealing the amplitude of oscillations increases and the maximum of oscillations shifts to higher k representing Cu-Cu

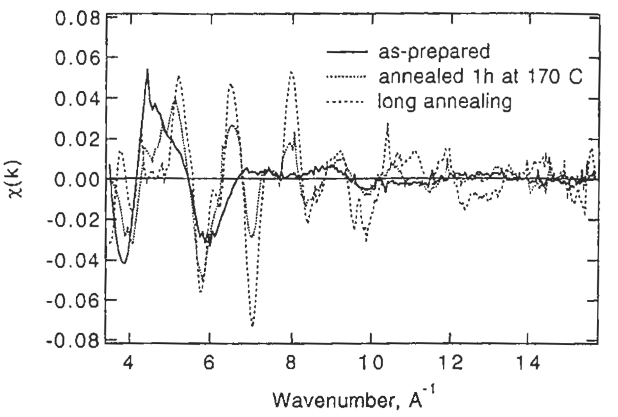

Fig.4 Raw EXAFS oscillations of an a-C:H<Cu> sample with 12 at. % copper, as-prepared, annealed for 1 h, and annealed overnight.

interaction. In the Fourier transformed, spectra annealing manifests itself in appearance and growth of a peak situated at ~2.1 Å which corresponds to the Cu-Cu first shell. Further annealing relults in appearing of peaks corresponding to higher shells.

Discussion

As suggested earlier from the optical studies [2,3], copper in a-C:H<Cu> can form two different kinds of inclusions. First, copper can be randomly distributed within the graphite-like constituent of a-C:H<Cu> matrix. In such a case the average Cu-Cu interaction is negligible and one should expect a very low average coordination number for this interaction as observed experimentally. The observed coordination number of < 1.0 can indicate either a complete absence of Cu-Cu correlations or probably also the formation of a small portion of Cu 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 although the former one cannot be completely excluded. It is interesting that stabilisation of Cu dimers by oxygen was observed recently [9] for Cu grown electrochemically on GaAs surfaces.

On annealing, Cu-Cu correlations are clearly seen as a peak at 2.1 Å corresponding to the first-nearest neighbor. On further annealing, more distant shells are clearly seen in positions coresponding to those in bulk copper which

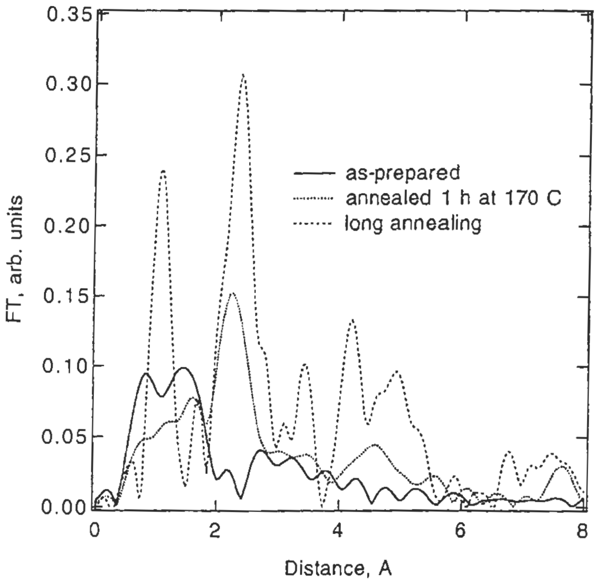

Fig.5 Fourier transforms of spectra shown in Fig. 4

means that the clusters have fcc structure. The obtained coordination number for a cluster in a sample annealed for 1 h is 4±2 and the Debye-Waller (DW) factor is 0.08Å (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, the pure geometrical factor (atoms which are at the surface of the cluster only have copper neighbours on one side), being probably the most important. With the obtained coordination number the cluster size can be estimated as being 5 to 20 Å [10, 11] assuming the spherical shape of the cluster. An increased disorder most likely results from lattice mismatch and strain in the cluster.

Further annealing results in the formation of larger clusters (CN= 6±3) accompanied by more ordering (DW factor 0.06 Å). The bond length becomes equal to that in bulk copper.

Conclusion

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

Acknowledgement

This work, partly supported by NEDO, was performed in the Joint Research Center for Atom Technology (JRCAT) under the joint research agreement between the National Institute for Advanced Interdisciplinary Research (NAIR) and the Angstrom Technology Partnership (ATP). It was also supported in part by Russian Foundation for Basic Research (Gr. N97-02-18110-a and Gr.N97-03-32273-a).

References

1. S.V. Vishinski, Phys. Low-Dim. Structures, **11/12**, 9 (1994)
2. V.I. Ivanov-Omskii, M.I. Abaev, and S.G. Yastrebov, Tech. Phys. Lett., **20**, 917 (1994)
3. V.I. Ivanov-Omskii, A.V. Tolmachev, and S.G. Yastrebov, Phil. Mag., **B73**, 715 (1995)
4. J. Robertson, Adv. Phys., **35**, 317 (1986)
5. Oyanagi, H., Shyoda, R., Kuwahara, Y., and Haga, K., J. Synchrotron Radiation 2, **99** (1995)
6. International Tables for X-ray Crystalligraphy, vol. III, Kynoch Press, 1962
7. Stern, E.A., Phys. Rev. , B**10**, 3027 (1974)
8. Rehr, J.J., Albers, R.C., and Zabinsky, S.I., Phys. Rev. Lett. **69**, 3397 (1992)
9. T. Kondo, K. Tamura, M. Koinuma, H. Oyanagi, and K. Uosaki, Chem Lett., **761** (1997)
10. M. Borowski, J. Phys. iV France, Colloque C2, suppl to J. de Physique, C2-**259** (1997)
11. A.V. Kolobov, H. Oyanagi, S.G. Yastrebov, V.I. Ivanov-Omskii, and K. Tanaka, in NATO ASI Series, 3. High Technology - Vol. **38**, Diamond Based Composites and Related Materials , ed.M.A.Prelas et al., Kluwer Academic Publishers,1997, p.191.