

## Electrical conduction in nanocomposites of copper in silicate glasses

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1996 J. Phys.: Condens. Matter 8 5717

(<http://iopscience.iop.org/0953-8984/8/31/005>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.206

The article was downloaded on 13/05/2010 at 18:28

Please note that [terms and conditions apply](#).

# Electrical conduction in nanocomposites of copper in silicate glasses

A K Maity, D Nath and D Chakravorty†

Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India

Received 4 May 1995, in final form 8 February 1996

**Abstract.** Nanocomposites of metallic copper in a silica-based glass have been prepared by the hot compaction of ion-exchanged and reduced glass powders. The diameter of copper particles ranges from 5.7 to 9.2 nm. The specimens exhibit a semiconducting behaviour in the temperature range 80–333 K with an unusually low activation energy of the order of 3.0 meV. This result appears to be consistent with a quantum size effect.

## 1. Introduction

Nanocrystalline materials have attracted considerable attention in recent years because of their novel physical properties (Chakravorty and Giri 1992). Several physical and chemical methods have been developed to synthesize these materials. An ion exchange and reduction technique has been used recently to prepare composites of nanosized metal particles in a glass–ceramic (Roy and Chakravorty 1990). Such nanocomposites are found to be suitable for investigating the electrical properties of metal in its nanocrystalline state (Roy and Chakravorty 1993a, b) because of a percolation configuration achieved over a thickness of the order of few tens of microns at the surface of the glass–ceramic system. We have now prepared nanocomposites in the bulk form by hot compaction of powders consisting of copper and silicate glass. The electrical resistivities of the samples exhibit an interesting temperature variation. The details are presented in this paper.

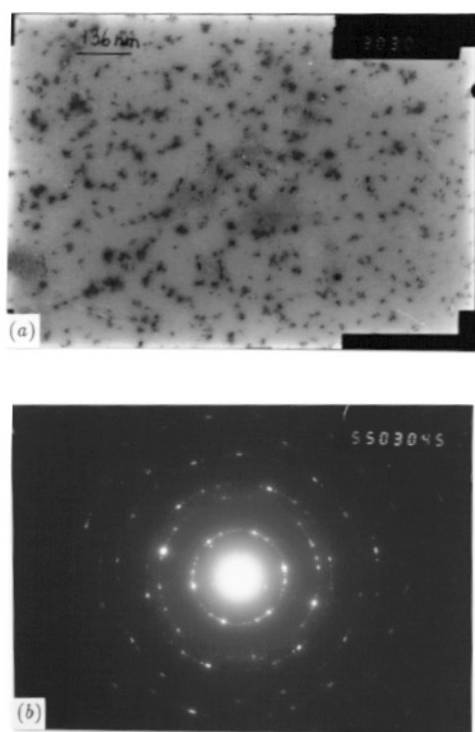
## 2. Experimental details

The composition of the glass used in this study was 10 mol% Na<sub>2</sub>O, 20 mol% B<sub>2</sub>O<sub>3</sub>, 15 mol% Bi<sub>2</sub>O<sub>3</sub> and 55 mol% SiO<sub>2</sub>. The glass was prepared by melting a mixture of the weighted amounts of reagent-grade chemicals, namely Na<sub>2</sub>CO<sub>3</sub>, H<sub>3</sub>BO<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> in an alumina crucible at a temperature of 1530 K. Molten glass was poured onto an aluminium mould and cast. The glass was then ground in a mortar and pestle, and glass powder with an average particle size of about 10 μm was obtained. The glass particles were then subjected to a Na<sup>+</sup> ⇌ Cu<sup>+</sup> exchange reaction by immersing them in a molten bath of CuCl at 773 K for 10 h. Nitrogen gas was passed over the molten bath to prevent volatilization of the molten electrolyte. After the ion exchange run the glass powder was washed with ammonia to remove any excess CuCl sticking to the surface of the glass particles. The latter were finally washed in distilled water. The ion-exchanged glass powder was then

† Also affiliated to Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560 064, India.

reduced in a stream of hydrogen at a temperature of 623 K for durations varying from 20 min to 1½ h. The reduced glass powders were packed in a graphite mould 1 cm in diameter. The mould was mounted onto a DSP 25 ATS sintering press supplied by Dr Fritsch Sondermaschinen, Germany. After the mould chamber had been evacuated to a pressure of about  $7.0 \times 10^{-3}$  Torr the powders were compacted at a temperature of 673 K for 5 min by applying a final pressure of 2.4 MPa. The electrical resistivities of the samples were measured by a four-probe method using silver paint (supplied by Acheson Colloiden BV Holland) electrodes on the specimen surface. The measurements were carried out over the temperature range 80–380 K.

For microstructural studies the reduced and ion-exchanged glass powder was further ground in a mortar and pestle and then dispersed in acetone using an ultrasonic vibrator. A drop of this mixture was poured on a 200 mesh carbon-coated copper grid and dried at room temperature. The latter was mounted in a JEM 200 CX transmission electron microscope. The presence of metallic copper was confirmed from the electron diffraction rings. The metal particle size distribution was analysed by a standard technique (Roy and Chakravorty 1990).



**Figure 1.** (a) Transmission electron micrograph for sample 1. (b) Electron diffraction ring for (a).

### 3. Results and discussion

Figure 1(a) is the transmission electron micrograph for the sample which had undergone a reduction treatment at 623 K for 20 min. The selected-area electron diffraction pattern for

**Table 1.** Comparison of interplanar spacings  $d_{hkl}$  obtained for sample reduced at 623 K for 20 min with standard ASTM data.

$d_{hkl}$ (nm)	
Observed	ASTM
0.2142	0.2088
0.1778	0.1808
0.1215	0.1278
0.1115	0.1090
0.1033	0.1043
0.0798	0.0808

figure 1(a) is shown in figure 1(b). The calculated interplanar spacings are given in table 1 and compared with standard ASTM data for metallic copper. The particle size histogram is shown in figure 2. The data are fitted by a log-normal distribution function, i.e.

$$\Delta n = \frac{1}{\sqrt{2\pi} \ln \sigma} \exp \left\{ -\frac{1}{2} \left[ \ln \left( \frac{x}{\bar{x}} \right) / \ln \sigma \right]^2 \right\} \Delta(\ln x) \quad (1)$$

where  $\Delta n$  is the fractional number of particles per logarithmic diameter interval  $\Delta(\ln x)$ ,  $\bar{x}$  the median diameter and  $\sigma$  the geometric standard deviation. Table 2 summarizes the values obtained for different samples after the above fitting. It is observed that copper particles having diameters in the range 5.7–9.2 nm can be synthesized by changing the duration of reduction treatment from 20 min to 1½ h. Evidently the particles grow by the diffusion of copper atoms to the nucleation sites.

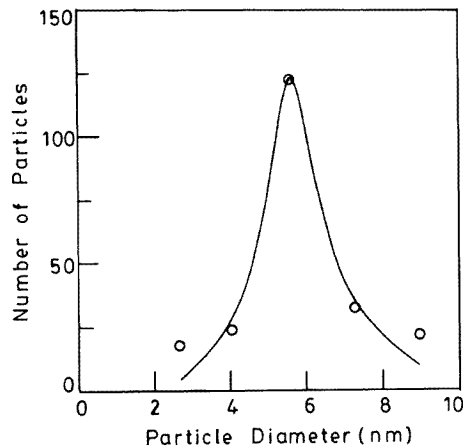
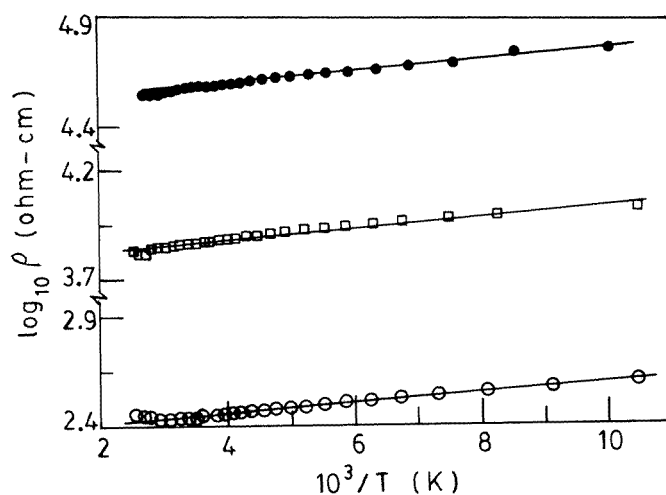
**Figure 2.** Particle size histogram for sample 1.

Figure 3 shows the variation in electrical resistivity as a function of inverse temperature for the three samples. It is seen that in the temperature range 80–333 K the samples exhibit a semiconducting behaviour. At temperatures higher than 333 K a metallic characteristic is evident. The activation energies estimated from the slopes of the resistivity variation are  $5.0 \times 10^{-3}$  eV,  $3.1 \times 10^{-3}$  eV and  $3.3 \times 10^{-3}$  eV for samples 1, 2 and 3, respectively. A resistivity range of about two orders of magnitude has also been observed in the present



**Figure 3.** Electrical resistivity as a function of inverse temperature for different samples: ●, sample 1,  $\bar{x} = 5.7$  nm; □, sample 2,  $\bar{x} = 7.7$  nm; ○, sample 3,  $\bar{x} = 9.2$  nm.

sample system. The possible physical mechanism responsible for such a low activation energy is discussed below.

It is necessary to keep in view some of the microstructural features of our system before we consider the model for the transport mechanism. The percolative chains of copper metal particles are believed to be concentrated at the surface of the glass particles which were subjected to ion exchange and reduction treatments. This should be evident from some of the results reported earlier. It was shown that to obtain a large number of small metal particles (in other words to increase the nucleation efficiency) it was necessary to grind the glass surface first before the ion exchange treatment (Chakravorty 1974). Such an operation introduced defects on the surface which helped to reduce the interfacial energy per unit area between the growing metal particle and the glass medium. This principle was also exploited in preparing electrically conducting glass-ceramic surfaces where the interface between the glass and the crystalline phases acted as the defect sites (Roy and Chakravorty 1990).

We carried out electrical resistivity measurements on samples prepared by the hot compaction of virgin glass powders. Typical values of resistivities at room temperature were about  $10^{10}$   $\Omega$  cm. From the resistivity variation as a function of temperature the activation energy was estimated to be about 0.9 eV. This arises from the ionic migration in this glass system (Anderson and Stuart 1954). Also the resistivity and activation energy of the above specimen were in agreement with those found for a bulk glass sample of the same chemical composition. We can therefore rule out the possibility that the grain boundaries between the glass particles play any role in the conductance properties of the nanocomposites described here.

Abeles *et al* (1975) and Abeles (1976) carried out extensive research to characterize the electrical behaviour of the cermet films prepared by the RF sputtering technique. The variation in electrical resistivity with temperature was explained on the basis of both tunnelling and classical percolation contributions to electrical conduction depending on the metal volume fraction. On the basis of the electron tunnelling mechanism (Tick and Fehlner

1972) the activation energy  $E$  is given by

$$E = \frac{1.44}{\varepsilon} \left( \frac{1}{r} - \frac{1}{r+s} \right) \text{ eV} \quad (2)$$

where  $\varepsilon$  is the dielectric constant of the intervening medium between the metal grains, and  $r$  and  $s$  are the metal particle radius and the inter-particle separation, respectively, in nanometres. Assuming that  $\varepsilon \simeq 4$  which may be taken as the dielectric constant of silica glass and substituting 2.87 nm for  $r$  we calculate from equation (2) a value of  $s$  equal to 0.07 nm in order to predict an activation energy of 3 meV. However, for such small tunnelling junctions the tunnelling events are suppressed because of a large charging energy associated with single-electron tunnelling (Schon and Zaikin 1990). A tunnel capacitance  $C \simeq 10^{-18}$  F is estimated for the present case and the charging energy  $e^2/2C$  is found to have a value of about 0.07 eV. This is an order of magnitude higher than the activation energy observed in these samples.

If we consider particles near the large end of the size distribution, e.g. 10 nm for sample 1, a separation of about 0.22 nm between the metal islands would predict an activation energy of about 3 meV. The Coulomb charging energy in such a situation would have a value of about 15 meV. However, as the probability of occurrence of such particles is about 0.04 (as computed from the histogram shown in figure 2) it is evident that the tunnelling conduction would be dominated by the particles having sizes given by the median diameter ( $\bar{x}$ ) values. The microstructural features delineated as above indicate that the conduction arises from the presence of a number of percolative metal chains formed at the boundaries of the glass grains. Because of a series configuration of the postulated tunnelling junctions described as above the majority of the latter would contribute an activation energy much larger than that observed experimentally.

**Table 2.** Reduction schedules and copper particle diameters in different samples.

Sample	Reduction treatment in hydrogen	Median particle diameter $\bar{x}$ (nm)	Geometric standard deviation $\sigma$
1	623 K for 20 min	5.7	1.2
2	623 K for 1 h	7.7	1.4
3	623 K for 1½ h	9.2	1.3

**Table 3.** Summary of parameters  $\omega_s$ ,  $\phi$ ,  $C$ ,  $\rho_0$  and  $P$  in equation (4) for different samples.

Sample	$\omega_s$	$\phi$ (eV)	$C$	$\rho_0$ ( $\Omega$ cm)	$P$ ( $\Omega$ cm)
1	0.08	0.0076	97	172	2180
2	0.10	0.0064	30	50	1140
3	0.20	0.0045	1.18	15	920

In view of the above we consider the possibility that the low activation energy arises from a quantum size effect. We can assume that there are a few percolative chains formed by the copper nanoparticles present at the surfaces of the glass grains which are hot compacted to produce the bulk solid. Each of these chains will consist of copper nanoparticles having

a distribution of particle sizes identical with that observed in the histogram of the sample concerned. The energy levels in the smaller particles will be discrete and the energy level separation is expressed as (Kubo 1962, Wood and Ashcroft 1982)

$$\phi \sim E_{F/N} \quad (3)$$

where  $E_F$  is the Fermi energy of copper and  $N$  the total number of atoms in the particle. According to this model the resistance  $R$  of the sample can be written as

$$R = \sum_r n_r R_r / N_p \quad (4)$$

where  $n_r$  is the number of elements in the chain having a resistance  $R_r$  and  $N$  the total number of chains present. To a first approximation, equation (4) can be written as follows:

$$R = \frac{t}{AN_p} \left[ \omega_m \rho_0 (1 + \alpha T) + \omega_s P \exp\left(\frac{\phi}{kT}\right) \right] \quad (5)$$

where  $t$  is the length of the percolative chain,  $A$  is the effective area of contact between the metal particles,  $\omega_s$  is the fraction of particles having small diameters which contribute to the activation energy  $\phi$ ,  $\omega_m = 1 - \omega_s$ ,  $\rho_0$  is the equivalent of the resistivity at absolute zero used to describe bulk metal resistivity, and  $\alpha$  is the temperature coefficient of resistivity for bulk copper. In the second term in the above equation,  $\exp(-\phi/kT)$  is proportional to the concentration of electrons at a temperature  $T$  and  $P$  is the proportionality constant. We have assumed the mobility to be constant in the temperature range under consideration. From equation (5) the expression for resistivity  $\rho$  is written as

$$\rho = C \left[ \omega_m \rho_0 (1 + \alpha T) + \omega_s P \exp\left(\frac{\phi}{kT}\right) \right] \quad (6)$$

where

$$C = \frac{1}{N_p} \frac{A_{total}}{A} \quad (7)$$

$A_{total}$  being the cross-sectional area of the specimen. It may be mentioned here that, as the Debye temperature of bulk copper is 315 K, the electrical resistivity could be expected to show a transition between a linear temperature dependence and a  $T^5$  variation. However, in our investigations carried out earlier on nanoparticles of copper grown within a suitably chosen glass-ceramic (Roy and Chakravorty 1993a, b) a linear variation in resistivity with temperature was observed. Also, using Ziman's equation the Debye temperature value estimated from the experimental data was found to be substantially lower than that for bulk sample. Taking  $\omega_s$ ,  $\phi$ ,  $C$ ,  $\rho_0$  and  $P$  as independent parameters the experimental resistivity-temperature curves are least squares fitted to equation (6). The solid lines in figure 3 are the theoretical curves obtained by this procedure. Table 3 summarizes the parameters extracted in the case of different samples. Substituting the value of  $E_F = 7.05$  eV for copper and the activation energies as determined by the least-squares fitting, we calculate the diameters of copper particles contributing to semiconducting behaviour at low temperatures for different samples. These are found to be 3.9 nm, 4.0 nm and 4.4 nm for samples 1, 2 and 3, respectively. It should be evident that  $\omega_s = n_i / \sum_i n_i$  where  $n_i$  represents the number of particles having the above-mentioned diameter for a particular sample. From the histograms of different samples we obtain  $\omega_s$ -values of 0.09, 0.12 and 0.18 for samples 1, 2 and 3, respectively. These are in satisfactory agreement with the  $\omega_s$ -values given in table 3. As the reduction treatment is increased, the average metal particle diameter increases and so does the total number  $N_p$  of the metallic percolation chains. From equation (7)

the value of  $C$  should therefore decrease as a function of metal particle diameter. This is borne out by the  $C$ -values listed in table 3. The temperature-independent term  $\rho_0$  arises owing to the presence of either point or line defects within the metal particles (Fujita *et al* 1976). As the particle size is increased, such defect centres would decrease because the thermodynamic system tends to become less metastable. The value of  $\rho_0$  should therefore decrease, as is evident from table 3. Such a trend was also observed in our earlier study on nanoparticles of copper synthesized within a glass-ceramic (Roy and Chakravorty 1993b). The proportionality constant  $P$  can be looked upon as representing the reciprocal of the density-of-states function  $g(E)$  near the Fermi level. The latter can be written as (Kittel 1961)

$$g(E) = \frac{4\pi V}{h^3} (2m)^{3/2} E^{1/2} \quad (8)$$

where  $V$  is the volume of the metal particle,  $h$  the Planck constant,  $m$  the electron mass and  $E$  the energy level. From equation (8), therefore, the value of  $P$  should decrease as  $V$  is increased. The extracted values of  $P$  for different samples as listed in table 3 do exhibit such a trend. The ratio of the cubes of particle diameters for samples 3 and 1, respectively, is found to be 4.2. The ratio of  $P$ -values for samples 1 and 3 as estimated from the curve-fitting procedure discussed above is 2.4. The agreement is reasonable considering the assumptions made in our analysis.

In conclusion, bulk specimens prepared by the hot pressing of reduced ion-exchanged powders containing metallic copper in a silica-based glass exhibit a semiconducting behaviour in the temperature range 80–333 K. The activation energy is unusually low, being of the order of 3.0 meV. It is not possible to explain this behaviour on the basis of an electron tunnelling mechanism. A quantum size effect appears to be consistent with the results reported.

### Acknowledgments

The work has been supported by the Department of Science and Technology, Government of India.

### References

- Abeles B 1976 *Applied Solid State Science* ed R Wolfe (New York: Academic) p 1  
 Abeles B, Sheng P, Coutts M D and Arie Y 1975 *Adv. Phys.* **24** 407  
 Anderson L and Stuart D A 1954 *J. Am. Ceram. Soc.* **37** 573  
 Chakravorty D 1974 *J. Non-Cryst. Solids* **15** 191  
 Chakravorty D and Giri A K 1992 *Chemistry of Advanced Materials* ed C N R Rao (Oxford: Blackwell Scientific) p 217  
 Fujita T, Oshima K and Kuroishi T 1976 *J. Phys. Soc. Japan* **40** 90  
 Kittel C 1961 *Introduction to Solid State Physics* (New York: Wiley) p 250  
 Kubo R 1962 *J. Phys. Soc. Japan* **17** 975  
 Roy B and Chakravorty D 1990 *J. Phys.: Condens. Matter* **2** 9323  
 ——— 1993a *Solid State Commun.* **87** 71  
 ——— 1993b *J. Appl. Phys.* **74** 4190  
 Schon G and Zaikin A D 1990 *Phys. Rep.* **198** 237  
 Tick P A and Fehlner F P 1972 *J. Appl. Phys.* **43** 362  
 Wood D M and Ashcroft N W 1982 *Phys. Rev. B* **25** 6255