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Electrical conductivity and thermopower of Cu–SiO$_2$ nanogranular films

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We have measured the thermopower S and electrical conductivity σ in a series of Cu$_x$(SiO$_2$)$_{1-x}$ nanogranular films between 2 and 300 K with Cu volume fraction x varying from 0.43 up to 1.0. At low temperatures, disorder-enhanced electron–electron interaction effects dictate the behavior of σ. A crossover of the temperature dependence from $\sigma \propto \sqrt{T}$ to $\sigma \propto T^{1/3}$ is observed as x is lowered and the metal–insulator transition is approached. S is small, shows linear temperature dependence, and is rather insensitive to the change of x. Effects of annealing are also discussed. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1493668]

Metal–insulator composites have demonstrated interesting physics when their constituent grain size is reduced to only a few nanometers. Recently, the giant Hall effect has been discovered in nonmagnetic Cu$_x$(SiO$_2$)$_{1-x}$ nanogranular systems.[1] Near 3 orders of magnitude enhancement in the Hall coefficient was observed when the Cu volume fraction x was reduced down to 0.51. This effect disappeared after annealing the samples that significantly enlarges the grain size. The giant Hall effect has been previously observed[2–6] also in magnetic (NiFe)–SiO$_2$ and Fe–SiO$_2$ nanogranular films. However, its discovery in the nonmagnetic Cu–SiO$_2$ films shows that quantum-interference effects associated with the small grain size could be responsible for the apparent decrease in the effective charge carrier concentration. In one study[7] of the electrical conductivity of Cu–SiO$_2$ composites with $0.17 \leqslant x \leqslant 0.33$, a variable range hopping conduction of the form $\sigma \propto \exp\{-(T_0/T)^{1/2}\}$ was observed and explained through the Coulomb interaction and the presence of a large random potential. Investigations of thermopower provide complimentary information to what one obtains through the study of electrical conductivity. However, there exist a limited number of experimental studies of thermopower in metal–insulator nanocomposites, especially at liquid-helium temperatures where the signal is small and measurement is very difficult. Hurvits *et al.*[8] measured the room-temperature thermopower of Al–Ge films and found it consistent with the theoretical predictions given by Bergman and Levy.[9] Jing and Yan[10] observed a small and temperature insensitive thermopower for magnetic (NiFe)–SiO$_2$ and Fe–SiO$_2$ composites near the percolation threshold between 70 and 300 K.

In this letter, we present detailed studies of electrical conductivity σ and thermopower S of the nonmagnetic Cu–SiO$_2$ nanogranular films from 2 up to 300 K and with Cu volume fraction x from 1.0 down to 0.434, which is just above the classical percolation threshold[1] $x_c \approx 0.43$. The effect of annealing is also discussed.

The films were prepared by co-sputtering the source materials onto glass substrates held at 50 °C. The base pressure of the sputtering chamber was below 2×10^{-7} Torr. The Cu volume fraction was determined from energy-dispersive x-ray spectroscopy analysis. All investigated films were about 1 μm thick. The annealing condition was 450 °C for 1 h. Resistivity was measured from 2 to 300 K using the standard four-probe ac technique with the aid of a 16 Hz excitation of a Linear Research bridge. Thermopower measurements were performed using a longitudinal steady-state technique. At low temperatures, thermopower signals were very small. Therefore, fine NbTi superconducting wires were used as our voltage leads from 2 to 8 K to avoid the contribution to the thermopower from the wires. Furthermore, we employed Ge thermometers, which have a resolution of 1 mK or better, to accurately determine the temperature gradient across the sample. From 8 to 300 K, we used copper–constantan thermocouples with the copper legs serving also as voltage leads. The thermopower was corrected for the contribution of the copper. A miniature strain gauge served as a heater in both cases.

The room-temperature value of electrical conductivity σ decreases by 4 orders of magnitude, from 3×10^4 down to about 4 S/cm, when the Cu volume fraction x is lowered from 0.804 down to 0.434. Figure 1 shows the temperature dependence of the normalized conductivities for four representative samples with $x = 0.434$, 0.510, 0.726, and 0.804.

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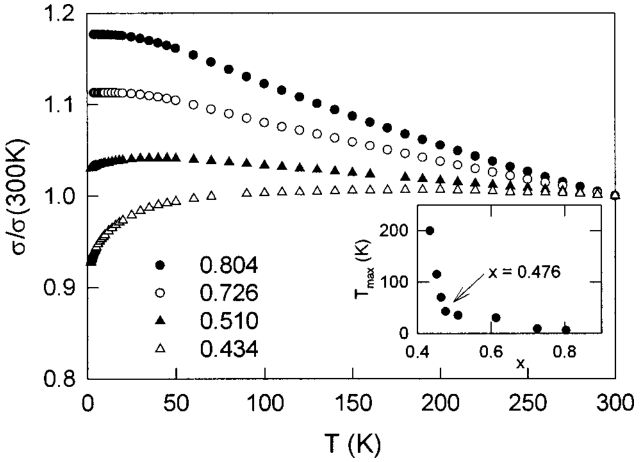

FIG. 1. Temperature dependence of normalized conductivity. The inset shows the temperatures T_{max}, where σ reaches a maximum for a given sample, plotted against x.

One general observation is that for a given sample, σ has a maximum value at a certain temperature T_{max}, which can be taken as a rough measure of the strength of disorder in the system.[11] T_{max} as a function of x is depicted in the inset of Fig. 1 where a rather abrupt change can be seen at the Cu volume fraction of about 0.47. Shown in Fig. 2 is the normalized electrical conductivity σ as a function of the square root of the temperature $\sqrt{T}$ from 2 to 10 K for $0.476 \leqslant x \leqslant 0.613$. A temperature dependence, $\sigma \propto \sqrt{T}$, is unambiguously demonstrated in the plot and can be well understood as the result of electron–electron interactions in a three-dimensional weakly disordered system.[12] However, as x is reduced below 0.47, the temperature dependence of σ deviates from $\sqrt{T}$ and it is found that $T^{1/3}$ is in fact a better description, as illustrated in the inset of Fig. 2. When the system is close to the metal–insulator transition, the diffusion coefficient D can no longer be treated as a constant and should be renormalized. One may take this into account by using the Einstein equation $\sigma = N(E_F)e^2D$, which leads to the $T^{1/3}$ dependence.[13] Here $N(E_F)$ is the electronic density of states at the Fermi level. The diffusion constant D enters the problem because the motions of carriers are diffusive in the presence of disorder, which results in multiple elastic scattering. Note that the change of temperature dependence coincides with the sudden rise seen on T_{max} versus x (see the inset of Fig. 1), indicating that stronger disorder indeed gives rise to the transition to the $T^{1/3}$ dependence.

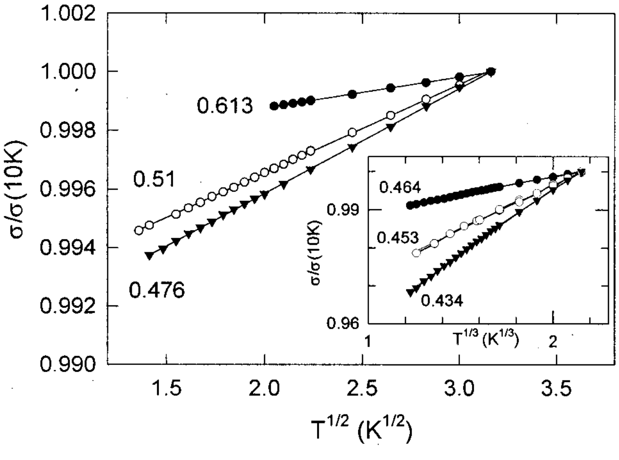

FIG. 2. Normalized conductivity as a function of $\sqrt{T}$ from 2 to 10 K for $x > 0.47$. The inset represents normalized conductivity as a function of $T^{1/3}$ for $x < 0.47$ over the same temperature range. All straight lines through the data points are guides for the eye.

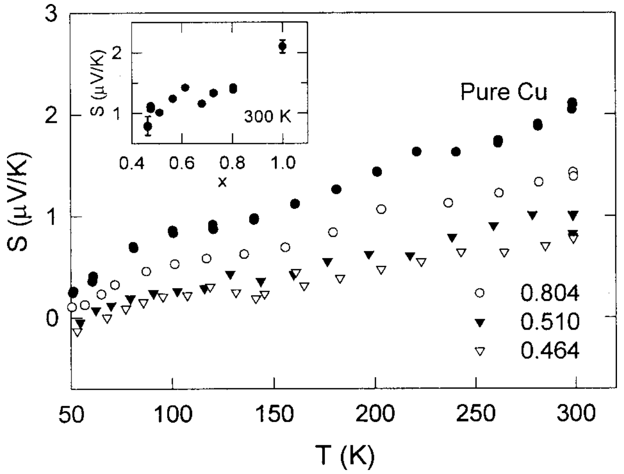

FIG. 3. Temperature dependence of thermopower S from 50 to 300 K. The thermopower of a pure Cu film is also plotted (filled circles) for comparison. The inset displays the room-temperature value of S as a function of x.

To study the effect of grain size, we annealed the sample with $x = 0.510$, which is at the quantum percolation threshold.[1] After annealing, the sample shows a ten times higher conductivity, still following the $\sqrt{T}$ dependence but with a much smaller slope, and T_{max} shifts from about 35 down to 20 K. These results are consistent with the transmission electron microscopy analysis which shows that the average grain size grows from 3 to about 10 nm upon annealing. The chance for a charge carrier to be scattered by grain boundaries is hence greatly reduced at a given temperature.

Figure 3 shows the thermopower S as a function of temperature for three representative samples with $x = 0.804$, 0.510, and 0.464 from 50 to 300 K. A pure Cu film is fabricated and measured in the same way, and the result is also plotted for comparison in Fig. 3. All samples have small thermopower values. S displays essentially linear temperature dependence and is rather insensitive to the amount of Cu in the system, in sharp contrast to the very rapid decrease of σ with decreasing x. The linear temperature dependence can be understood as the behavior of the diffusive thermopower of the Cu matrix, where charge transport takes place. The mean-free path of phonons is greatly limited by the small grain size. Therefore, the phonon drag effect, otherwise notable on pure Cu with a large crystalline size at around 50 K, does not seem to be present in these nanograin-size films. The inset of Fig. 3 plots the room-temperature values of S for samples with different copper content. The insensitivity of S to x is due to the fact that it is the thermopower of the Cu matrix that we are essentially measuring. Unlike σ, the behavior of S in metal–insulator composites has not been much explored. The slightly decreasing trend of S with respect to decreasing x might be due to the disorder-induced modification to the density of states around the Fermi energy. A slow variation of S across the percolation threshold is also in line with the prediction of Bergman and Levy.[9]

Shown in Fig. 4 is the thermopower as a function of

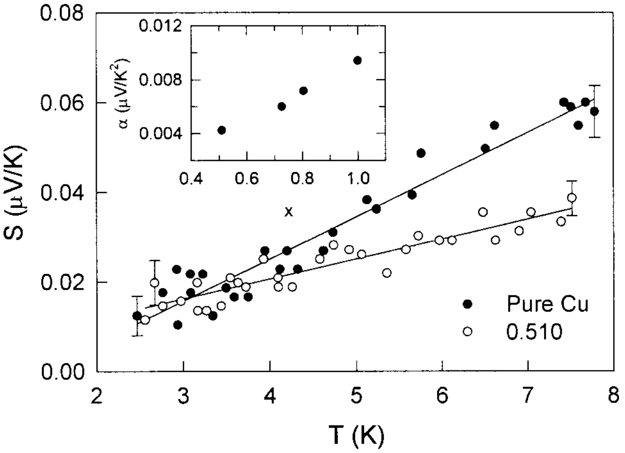

FIG. 4. Temperature dependence of thermopower S from 2 to 8 K. The straight lines are linear fits and error bars are included. The inset shows the slope α of the lines plotted against x.

temperature for a representative sample with $x = 0.510$ and for a pure Cu film from 2 to 8 K. Error bars are indicated in Fig. 4. One can see that S has very small values and varies linearly with temperature. It is again believed to be the behavior of the diffusive thermopower of the Cu matrix. The slope $\alpha = dS/dT$ is extracted and plotted against x, as shown in the inset of Fig. 4. It is clear that S becomes less sensitive to temperature as x is lowered, consistent with our observation at higher temperatures. Annealing introduces little change to the magnitude and temperature dependence of S, in sharp contrast to what it does to the electrical conductivity. Considering that S is shown to be rather insensitive to the strength of disorder in the system, this pronounced difference in the behavior of S and σ is perhaps not surprising.

In conclusion, the electrical conductivity σ and thermopower S are studied for $\mathrm{Cu}_x(\mathrm{SiO}_2)_{1-x}$ nanogranular films from 2 to 300 K with the Cu content between 0.43 and 1.0. At low temperatures, disorder-enhanced electron–electron interaction effect plays an important role in the charge transport. A crossover from $\sqrt{T}$ to $T^{1/3}$ dependence of σ is observed as the system approaches the metal–insulator transition. S is small and varies linearly with temperature at both low and high temperatures. Annealing has considerable influence on the behavior of σ.

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