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Electrical conductivity of $Mo_6S_3I_6$ and $Mo_6S_{4.5}I_{4.5}$ nanowires

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Abstract

Electrical conductivity measurements on novel materials composed of bundles of $Mo_6S_3I_6$ and $Mo_6S_{4.5}I_{4.5}$ nanowires pressed in a sheet form, in the frequency range from 10 Hz to 1 MHz for temperatures between 4 K and 330 K, are reported. Temperature dependence of the quasistatic electrical conductivity show similar dependence at higher temperatures as expected for three-dimensional variable range hopping mechanism with decreasing electrical conductivity as temperature decreases. Below 50 K the electrical conductivity becomes completely temperature independent. It seems that at lower temperatures fluctuation-induced tunnelling mechanism dominates in these nanostructured materials.

Keywords: Nanowires; Electrical conductivity; Electron microscopy

1. Introduction

Nanostructured materials and devices are important for fundamental research and applications because they provide a link between molecular and solid state physics, and have potential to reach far higher device densities compared to traditional semiconductor technology. One kind of nanostructured materials is one-dimensional nanowires and nanotubes. Much effort has focused on carbon nanotubes, but up to now it has been proved difficult to synthesize them in a way that produces identical nanotubes in bulk. Recently, after systematic study of synthesis conditions in the ternary molybdenum–sulphur–iodine system we discovered a new class of one-dimensional materials, with the formula $Mo_6C_{9-x}H_x$ (C: chalcogen, H: halogen, $3<x<6$), which appears to surpass many of the shortcomings of carbon nanotubes. One of the members of this group is material with formula $Mo_6S_3I_6$, where $x=6$.[1] It was obtained by direct synthesis from the elements in a sealed, evacuated quartz ampoule. Material is composed of identical small-diameter nanowires, weakly bound in bundles by van der Waals forces in a hexagonal packing arrangement. The individual nanowires are best described as one-dimensional Mo–S–I cluster polymers, composed of Mo6 octahedral clusters, connected by bridging anions, which are above each face and corner.[2] This structure leads to tunable electronic, chemical and mechanical properties. The nanowires on the other hand, are joined together into bundles very weakly with van der Waals forces, explaining their exceptional dispersion characteristics[3,4] and remarkable tribological properties.[5] The straightforward one-step synthesis and simple isolation procedure clearly means that scaling up can be performed, suggesting a great technological advantage over existing materials. With further investigations of synthesis parameters we found a new member of that class with a formula $Mo_6S_{4.5}I_{4.5}$. Most of the work on the field of transport properties of this type of materials (Mo–S–I nanowires) is published elsewhere.[6]

The aim of this work is to study the temperature and frequency dependence of the dc electrical conductivity in the sheet formed bundles of $Mo_6S_3I_6$ and $Mo_6S_{4.5}I_{4.5}$ nanowires and to compare results of both materials. We present quasistatic measurements of the temperature dependent electrical conductivity obtained on Mo–S–I nanowires in a dc measuring field and measurements of conductivity at low frequencies between 10 Hz and 1 MHz. It was found that two-channel electrical conductivity mechanism could be responsible for a temperature crossover from variable range hopping dominated temperature dependence to the nearly independent tunnelling conductivity. Such crossover was observed also in some other nanowire systems.[7,8]

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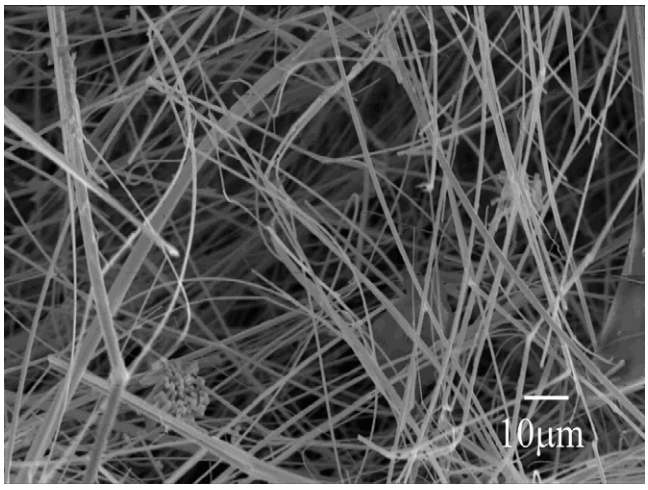

Fig. 1. Image of bundles of $Mo_6S_3I_6$ nanowires taken by SEM: the majority of the material has a fur-like appearance, with individual needles having a diameter of about 50–500 nm and a wide range of lengths up to 5 mm.

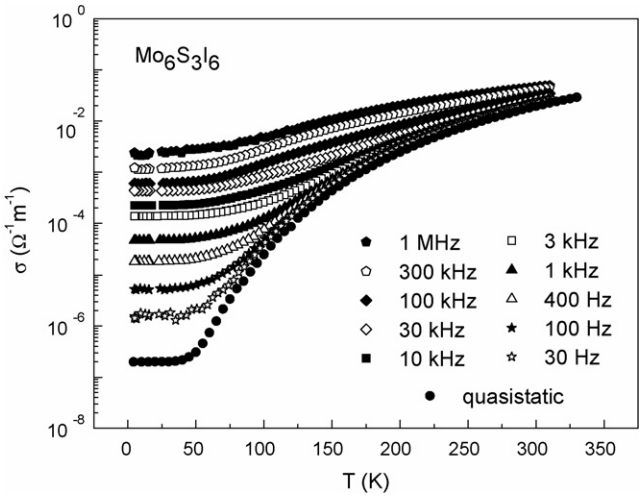

Fig. 2. Electrical conductivity for paper sheet form of $Mo_6S_3I_6$ bundles measured at several frequencies between 10 Hz and 1 MHz in temperature range 4–330 K.

2. Experimental results and discussion

Samples of Mo–S–I nanowires were prepared in a sheet form. The thickness of sheet was 40–50 μm and lateral dimension was about 9 mm × 6 mm for samples that were used in conductivity measurements. The orientation of bundles of nanowires within the sheet was approximately isotropic. Material is composed of identical small nanowires (approximately 1 nm in diameter) which are bound in larger bundles having a diameter of about 50–500 nm and a wide range of lengths up to 5 mm (Fig. 1).

Electrodes were pressed on both sides of the sample. Contacts were made by silver paste. No difference was observed if silver paste electrodes were replaced with gold or copper electrodes. Quasistatic electrical conductivity was performed by the Keithley 617 programmable electrometer on samples dried in vacuum. Frequency dependent measurements were measured between 10 Hz and 1 MHz by using a HP 4284A Precision LCR meter. The experimental variations of the electrical conductivity (σ) were measured in the temperature range from 4 K to 330 K following the standard four probe method, with the typical heating/cooling rate of 30 K/h.

It was found that the temperature dependence of the quasistatic conductivity can be well described by the three-dimensional variable range hopping law (3D VRH),[9] down to about 50 K temperatures. In strongly disordered systems, the temperature dependence of electrical conductivity is generally described with $\sigma_V = \sigma_0 \cdot \exp(-(T_0/T)^{\beta}$. For $\beta = 1/4$, the conduction mechanism is the 3D VRH. The existence of 3D interaction behaviour in conductivity of Mo–S–I nanowires does suggest a role for 3D disordered regions between their bundles and within bundles. Below 50 K conductivity could be well described with the fluctuation-induced tunnelling ansatz: $\sigma_T = \sigma_0 \cdot \exp(-T_1/(T_2 + T))$.

In Fig. 2, the conductivity is plotted as a function of the temperature for different frequencies. Temperature dependence of the electrical conductivity measured between 330 K and 4 K show similar dependence at higher temperatures, as expected for 3D VRH mechanism with rapidly decreasing electrical conductivity as temperature decreases, but it becomes completely temperature independent below 50 K, where dominates fluctuation-induced tunnelling conduction.

The two-channel mechanism involving VRH and fluctuation-induced tunnelling could be represented in the equivalent circuit in Fig. 3. At higher temperature above 50 K VRH channel is a main conductive path since its resistivity is much smaller than that of the tunnelling channel which remains nearly temperature independent. However, on cooling its resistivity increases much faster than the resistivity of the tunnelling channel and below 50 K it exceeds greatly the resistivity of the tunnelling channel, thus making the tunnelling channel the primary conductive path.

We repeated experiment with the same conditions also on bundles of $Mo_6S_{4.5}I_{4.5}$ nanowires. Very similar frequency and temperature dependence was observed in conductivity; however, small deviations observed in the temperature range denoted by arrow in Fig. 4 could be an indication for the existence of the

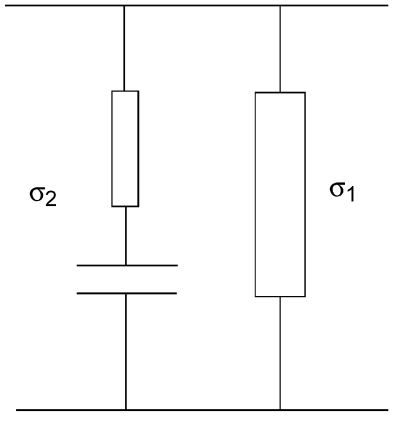

Fig. 3. Schematic model of two parallel conductivity channels. σ_1 represents variable range hopping mechanism and σ_2 indicates tunnelling. At higher temperatures ($T > T_{room}$) dominates first channel which is governed by the 3D VRH mechanism while the second channel governed by the tunnelling mechanism takes over at lower temperatures (below 50 K).

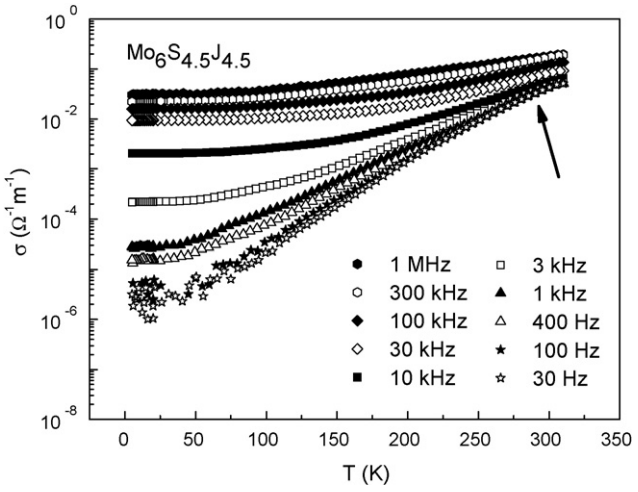

Fig. 4. Temperature dependence of the conductivity on $Mo_6S_{4.5}I_{4.5}$ nanowires sheet at several frequencies between 10 Hz and 1 MHz in temperature range 4–330 K. The arrow denotes changes in a slope indicating possibly a third conductivity mechanism.

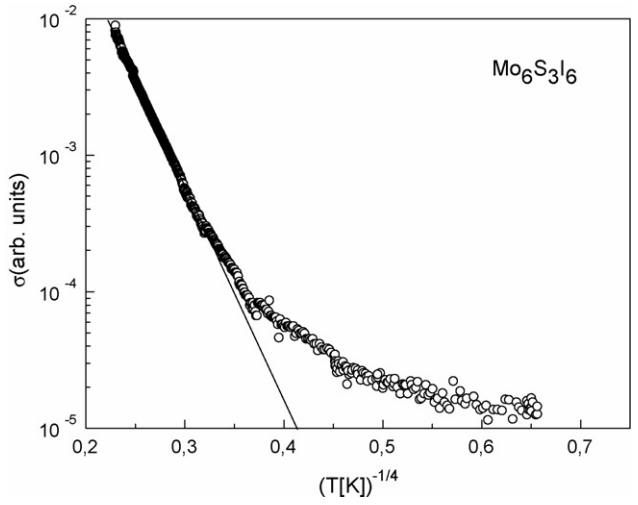

Fig. 5. Temperature dependence of the electrical conductivity for single bundle of $Mo_6S_3I_6$ nanowires fitted to 3D VRH ansatz down to about 50 K where crossover to a nearly saturated behaviour takes place.

third conducting mechanism in this particular nanowire system. It should be pointed out that the crossover to tunnelling mechanism takes place at same temperatures as in the case of $Mo_6S_3I_6$ nanowires.

In order to answer the question whether the tunnelling takes place between the bundles or is intrinsic property of nanowires within bundle we conducted measurements of the electrical conductivity on a single isolated bundle of $Mo_6S_3I_6$ nanowires.

Temperature dependence of the electrical conductivity was performed also on a single bundle of the $Mo_6S_3I_6$ nanowires. The data were fitted to 3D VRH down to about 50 K where crossover to a nearly saturated behaviour takes place (Fig. 5).

Experiments performed on a single bundle showed rather similar crossover temperature behaviour of the electrical conductivity suggesting that the tunnelling takes place either within the nanowire or between the nanowires within the bundle rather than between bundles of nanowires.

3. Conclusions

In this paper, transport properties of Mo–S–I nanowires, pressed in a sheet form were measured below 1 MHz in the temperature range between 4 K and 330 K can be described with the help of combination of two parallel channel model: hopping and tunnelling. The conductivity measurements extended down to the quasistatic experimental time scale agree qualitatively with theoretical results based on 3D hopping conduction mechanism. Strong increase of conductivity with temperature above 50 K is clear indication that 3D VRH mechanism is playing a key role in conduction at these temperatures.

Suggested two-channel mechanism with VRH and fluctuation-induced tunnelling described well the observed data on $Mo_6S_3I_6$ nanowires, however, small deviations observed in case of $Mo_6S_{4.5}I_{4.5}$ nanowires indicate that the third mechanism may play an important role in this nanowire system.

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