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Transport properties of $Mo_6S_3I_6$ nanowire networks

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We present measurements of resistivity on $Mo_6S_3I_6$ nanowire networks under different conditions. The room-temperature values of conductivity of as-grown nanowire networks are on the order of $\sigma_{300K}=0.04$ S/m and show linear current-voltage characteristics, indicating that—in agreement with band structure calculations—there is a finite density of states at the Fermi level. The conductivity of pristine samples is thermally activated, closely following three-dimensional variable range hopping (VRH) behavior of the form $\sigma=\sigma_0 \exp-(T_0/T)^{\beta}$, where $\beta=1/4$. Removal of interstitial iodine from the network by annealing in a vacuum gives rise to a cross over to one-dimensional VRH with $\beta=1/2$ and a concurrent *increase* in room-temperature conductivity. The introduction of water vapor leads to a decrease in conductivity and reveals that the resistivity of the network is sensitive to interstitial water molecules. © *2006 American Institute of Physics*.
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New quasi-one-dimensional materials such of different types, have important applications in electronics. Metallic nanowires or nanotubes, due to their high aspect ratios, are of great interest as additives to organic polymers enabling the manufacture of transparent conducting composites for example. They might also be very useful for nanoscale horizontal interconnections and vias in device circuits and for the construction of various sensors. Recently, electronic devices have been proposed based on carbon nanotube (CNT) networks, which do not rely on positioning and orientation of individual nanotubes.[1] CNTs exist in both semiconducting and metallic form, but presently they cannot be easily separated to a high degree of purity and are not very soluble. Introducing surfactants increases their solubility, but significantly degrades internanotube contact, resulting in inferior electrical conductivity characteristics of the composite.[2] As a promising alternative, $Mo_6S_{9-x}I_x$ nanowires have recently been found to be easily synthesizable in bulk quantities, and thus could potentially replace carbon nanotubes in numerous applications overcoming their abovementioned shortcomings.[3] Moreover, they were found to exhibit very good dispersion characteristics in a variety of solvents, including water.[4] $Mo_6S_{9-x}I_x$ with $x=6$ is predicted to be semimetallic on the basis of local density approximation band structure calculations.[5] Recent measurements of $Mo_6S_{9-x}I_x$/polymethyl-methacrylate composites have given remarkably low percolation thresholds and relatively high conductivities at low loadings, suggesting very competitive use in a variety of applications.[6] A remarkable feature of the material are the very weak interwire forces, which suggests that transport properties should be highly one-dimensional.[5–7] In this letter, we concentrate on macroscopic transport measurements of $Mo_6S_3I_6$ nanowire bundle networks, reporting on the temperature dependence of the resistivity, the influence of removal of interstitial iodine by high-temperature annealing and the effect of humidity on the resistivity of the networks.

$Mo_6S_3I_6$ was synthesized directly from the elements in a quartz tube as described previously.[3] The material is dispersed in water using a ultrasonic bath, filtered through a quantitative membrane filter and dried. Annealing was performed at 500, 700, or 900 °C for 12 h in a sealed quartz ampoule evacuated to 10^{-7} bar. Upon annealing at 700 °C and above a deposit on the inside of the quartz tube was observed. The deposit was dissolved in the ethanol and analyzed with ultraviolet-visible spectrometer. The obtained spectrum showed two characteristic iodine peaks at 292 nm and at 360 nm, which confirmed that iodine was released from the samples upon annealing. The scanning electron microscope (SEM) image of the material after annealing is shown in Fig. 1(a). X-ray diffraction (XRD) was also performed to check if the structure had changed, or if the additional impurity phases, particularly $Mo_6S_6I_2$, which is metallic, might be present [Fig. 1(d)]. Since neither a change of the structure nor presence of impurity phases were observed, we believe that released iodine was coming from interstitial sites in between nanowires or bundles. The material was then pressed into pellets which results in a network of interconnected nanowire bundles with typically 75±5% of theoretical density. Four contacts were made using silver paste (SPI No. 4999) and measurements were made with a Keithley 238 current source and Keithley 2000 voltmeter in an Oxford instruments cryostat.

The current-voltage (*I-V*) characteristics of as-grown and annealed samples are shown in Fig. 1(c). σ_{300K} varies by less than 20% in different pellets, indicating that a high degree of reproducibility is achieved in sample preparation. σ_{300K} is found to change upon annealing, from approximately $\sigma_{300K}=0.04$ S/m in unannealed to $\sigma_{300K}=0.2$ S/m upon annealing at 900 °C. In all cases, the *I-V* characteristic was found to be linear over a large range of electric field *E*.

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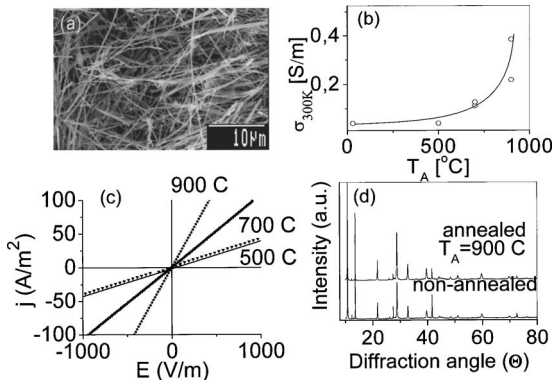

FIG. 1. (a) Scanning electron micrograph (SEM) of the $Mo_6S_3I_6$. (b) The room temperature conductivity σ_{300} as a function of annealing temperature T_A. (c) Current-voltage characteristic of bulk $Mo_6S_3I_6$ for pristine (line) and annealed samples at 500, 700, and 900 °C. No discernible difference is observed after annealing. (d) An XRD diffraction pattern of the measured sample shows no trace of impurities and no detectable change of structure, only a slight change in peak intensities after annealing.

The dependence of σ_{300K} on T_A is shown in Fig. 1(b).

In Fig. 2, we show the temperature dependence of the resistivity of the as-grown and annealed material. We clearly observe thermally activated conductivity behavior from 50 K to room temperature. (Below 50 K, the resistance becomes too high to measure reliably). Figure 2(b) shows that the behavior very closely follows an exponential law of the form $\sigma=\sigma_0 \exp\text{-}(T_0/T)^{\beta}$, where $\beta=1/4$ is characteristic of three-dimensional Mott variable range hopping (VRH) (Ref. 9) for the pristine sample, and remarkably, $\beta=1/2$ for the annealed samples [Fig. 2(d)]. The latter exponent is characteristic of one-dimensional VRH. Repeated measurements on different samples reveal identical temperature behavior, consistently showing a cross over from $\beta=1/4$ to $\beta=1/2$ upon annealing at 700 °C and above.

Since the pellets contain some empty space, it might be expected that water vapor, or other gases may permeate into the network voids, which may cause a change in the inter-wire and interbundle contact resistivity. As an example, to test the pressed pellet sensitivity to water molecules, we have performed measurements of the resistivity under saturated water vapor conditions. The sample was placed in a chamber

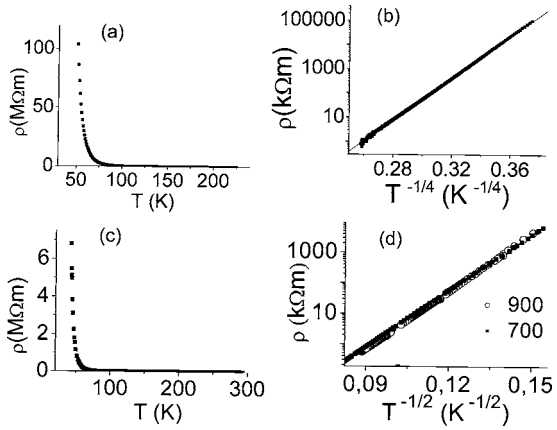

FIG. 2. Resistivity as a function of temperature of bulk $Mo_6S_3I_6$: (a) For pristine samples, and (c) for annealed samples (T_A=700 °C and 900 °C). (b), (d) By using proper scaling, we show that VRH-like behavior is obeyed over a wide range of temperatures for both, but with different exponents: $\beta=1/4$ for pristine samples, and $\beta=1/2$ for annealed samples.

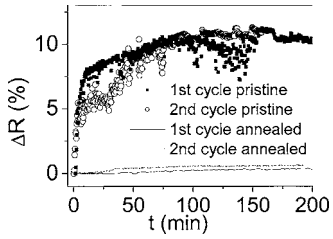

FIG. 3. The resistance change as a function of time in pressed pellets of $Mo_6S_3I_6$ for pristine samples (open circles) and after one wetting/drying cycle (filled squares). The annealed samples have a dramatically reduced humidity dependence (solid and dashed line).

connected to a saturated water vapor bath at 30 °C, and the resistivity was monitored as a function of time. The results, shown in Fig. 3, show that the pristine (unannealed) samples display a rapid change of resistance when exposed to moisture within the first minute, after which time the resistance saturates at a value which is approximately 10% higher than in a dry atmosphere. One might expect that the presence of water inside the sample should have a shorting effect, which would result in a decrease in the resistivity. Instead, the resistivity *increases*, suggesting that water has an effect in reducing the interbundle conductivity, similar to the effect of iodine. Remarkably, the effect of moisture under identical conditions on the annealed sample is much smaller, being less than 1% indicating that interstitial material (removed upon annealing) has an important role in determining the overall network resistance and suggests that pre-existing iodine in pristine samples increases the sensitivity to water. To see if the moisture effect is reversible, we have subsequently dried the exposed sample in an oven at 50 °C for 10 h. The resistivity change upon exposure was then remeasured. From the results, shown in Fig. 3, it appears that the change of moisture-induced resistivity $\Delta R/R$ is very similar before and after cycling, although a small increase in absolute value is observed after the first cycle which is attributed to inevitable irreversible changes of interbundle contacts resulting from temperature/moisture cycling.

When trying to understand the origin of the observed behavior, both interwire and interbundle transport need to be considered. Band structure calculations on $Mo_6S_3I_6$ suggest that the material is best described as a highly anisotropic semimetal.[5] Narrow bands cross the Fermi energy E_F for wave vectors along the nanowire (i.e., crystal *c*) axes, while no band crossings exist perpendicular to the nanowire axis (along *a* or *b*). This implies that coherent electron transport is not possible perpendicular to the nanowire axis. Along the *c* axis (i.e., along the nanowire), coherent transport may also be strongly subject to localization due to the highly one-dimensional character of these materials. Thus, the electron transport properties of extended networks are expected to be dominated by interbundle and interwire hopping. The observation of VRH temperature dependence with a three-dimensional exponent $\beta=1/4$ is thus not surprising, and similar behavior has also been observed previously in CNT networks.[8] It is somewhat surprising that the exponent changes upon high-temperature annealing to $\beta=1/2$. Which could, according to theory,[9] be attributed to a change of dimensionality from three to one dimensions. The change of dimensionality could be understood in terms of the removal of atoms at contact points in between nanowires, which play a role of conducting (tunnelling) bridges between nanowires.

However, the fact that at the same time σ_0 *increases* is not straightforward to understand and must be caused by another mechanism. Impurities, such as $Mo_6S_6I_2$ crystals, can in principle give rise to increased conductivity, but XRD spectra do not show the presence of additional impurity phases after high-temperature annealing. The fact that the change in resistivity upon annealing (Fig. 1) is linear with annealing temperature, excludes the possibility of a structural phase transition, which is confirmed by the XRD data (Fig. 1).

Removal of interstitial iodine atoms has two additional effects: (a) It reduces the number of scattering centers, thus increasing the mean-free path ℓ_m, and (b) effectively causes doping with electrons. Assuming that iodine is bound in pristine samples by a partial charge transfer, then I removal in the form of I_2 results in a net charge transfer of electrons to the nanowires, increasing the carrier density, and consequently the conductivity. The greater sensitivity to humidity for the pristine samples implies that iodine acts as a sensitizer for humidity detection.

To conclude, it is clear from this work that the overall transport properties of $Mo_6S_3I_6$ networks are governed by interwire and interbundle hopping, and as a result the conductivity of networks appears to strongly dependent on the presence of interstitial atoms or molecules, such as iodine or water. This suggests that a variety of MoSI-based network molecular sensors could be developed, which would, due to the very different chemical nature of the $Mo_6S_{9-x}I_x$ nanowires offer complementary detection capabilities to CNT networks.

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