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Probing electrical transport in nanowires: current maps of individual V_2O_5 nanofibres with scanning force microscopy

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Abstract
In this work we present two scanning force microscopy (SFM) techniques applied to the electrical characterization of V_2O_5 nanofibres with one end connected to a metallic electrode: first a non-contact imaging technique combined with the acquisition of current versus voltage curves in a selected spot, and second jumping mode SFM that allows simultaneous acquisition of topograhic images and current maps with nanometric resolution.

Both the conductivity ($\sim$20 S cm^{-1}) and the contact resistance ($\sim$62 MΩ) of the fibres are determined. A non-linear behaviour of the conductivity is observed for large applied electrical fields ($E > 10^5$ V cm^{-1}) as found previously for V_2O_5 films.

1. Introduction

The continuous reduction of electronic device sizes has opened new possibilities in integrated circuit fabrication that should become available in the near future [1]. This development is reflected in the rapidly increasing interest in conductors of molecular dimensions, like silicon nanowires [2], molecular layers [3], carbon nanotubes [4] and DNA [5]. Molecular wires are, due to their electronic properties [6], interesting for both fundamental research and technological applications. Nowadays, carbon nanotubes seem to be the option of choice for the scientific community; however, their different chiralities with different electrical behaviours are at the present time out of control due to unknown factors in the synthesis process. Therefore nanowires with a better definition of their structure and electrical properties are required; this is the case of the V_2O_5 nanofibres.

From a theoretical point of view, electrical conduction through molecular wires has been studied in detail following different approaches [7]. Experimentally, however, the situation is less favourable, since it is quite difficult to characterize in detail the properties of such small systems. Scanning force microscopy (SFM) is well suited to determine the electrical properties of different samples [8] on the nanometre scale, and has been used to determine the conduction properties of molecular wires [9]. In this communication, we present two complementary techniques based on SFM, which allow us to determine the conductivity of individual V_2O_5 nanofibres deposited on silicon oxide as a function of their length. The first technique uses non-contact SFM images to locate the fibre of interest. Then the conducting tip of the SFM is brought into mechanical and electrical contact with one spot of the wire to be studied, and current versus voltage curves are acquired [10]. The second technique is based on the jumping mode (JM) [11], an imaging mode where the tip is cyclically brought in and out of contact with the sample surface at each image point. This method can be used to obtain current maps of the surface.

2. Experimental procedure

V_2O_5 nanowires [12] are ribbon-like structures with typical dimensions of 1.5 nm height, 10 nm width and up to several

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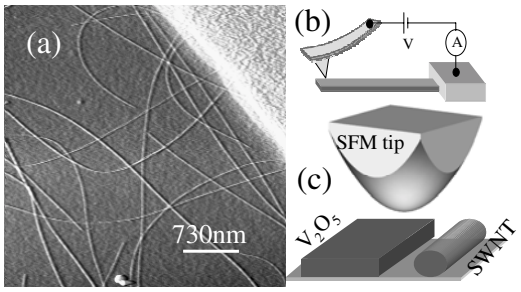

Figure 1. Experimental set-up: (a) region of SiO_2 with a gold electrode and a random population of V_2O_5 nanofibres connected to the electrode. (b) Experimental procedure. (c) Comparison of V_2O_5 nanofibres with other cylindrical molecules.

micrometres length. The V_2O_5 fibres were obtained by the acidification of ammonium metavanadate in aqueous solution (0.2 g 100 ml^{-1}) using an acidic ion exchanger (Dowex 50WX18, 2 g 100 ml^{-1}) [13]. After ageing of the colloidal suspension for one week, the fibres were deposited on surface-functionalized Si/SiO_2 substrates. Surface modification was performed by immersing the substrates into a 1 mM aqueous solution of 3-aminopropyl-triethoxysilane for 2 min at room temperature. Previous four-probe electrical studies of V_2O_5 nanowires [14] reported a conductivity of $\sim$0.5 S cm^{-1}.

After deposition of the nanowires on a SiO_2 substrate, a 4 μm diameter tungsten wire placed on the sample is used as a mask during the evaporation of gold. The final result is a sample with two gold electrodes separated by a gap free of gold with a random distribution of V_2O_5 nanowires. Some of the fibres are partially covered with gold and can thus be probed with the metallic SFM tip along its uncovered length (figure 1). In order to register electrical current, cantilevers with 80 kHz resonance frequency and force constant 0.75 N m^{-1} consecutively covered with titanium and gold are used. In this set-up, the macroscopic Au electrode is used as the first electrode, the SFM tips as the second mobile electrode and the fibres are the sample to be studied.

3. Results and discussion

3.1. DSFM and I/V characteristics

In the first method described in this work, dynamic force microscopy (DFM) [15] is used to image the samples. For appropriate feedback parameters this is a non-contact technique, which is important to avoid damage of the metallized tip and the sample. In fact, we used the contact mode in the first experiments, but found that forces induced by the scanning lead to degradation of tip and sample. After acquisition of an image using DFM, adequate locations along the fibres are selected to perform local conductivity measurements. For this, we have implemented a special routine in the used software [16], which allows us to perform force versus distance curves (F/Z), and apply a voltage ramp to the tip at the maximum loading force. In this way, current versus voltage (I/V) curves are obtained at a well defined loading force of the tip–sample contact [17]. In a typical experiment, a single V_2O_5 fibre is selected, and the resistance versus length is obtained by acquiring I/V curves at different locations along the fibre. Figure 2 shows the result of a corresponding experiment on an individual fibre (figure 2(a)),

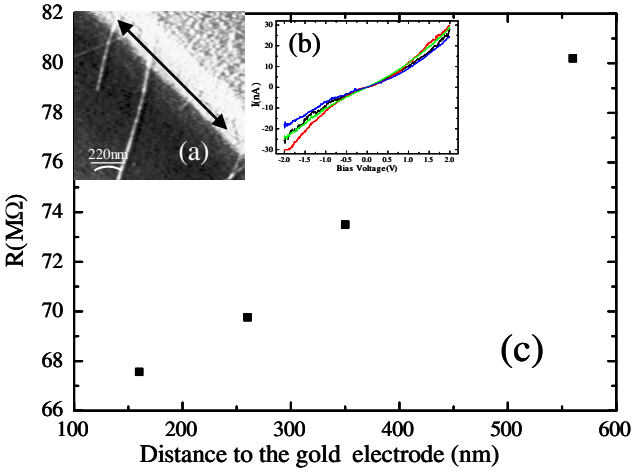

Figure 2. (a) DFM topographic image of the fibre selected for the experiment; the gold electrode is clearly shown in the top right corner; the black arrow indicates the boundary between the gold electrode and the SiO_2 substrate. (b) I/V series performed along the longest fibre of (a). (c) Evolution of the resistance along the fibre, calculated from the data of (b) around 1.5 V. A conductivity of $\sigma = 20.5$ S cm^{-1} and a contact resistance of $R_c = 62$ MΩ are deduced from these data.

(This figure is in colour only in the electronic version)

which allows us to determine both the fibre conductivity as well as the fibre–electrode resistance. Typical values obtained for the conductivity are $\sim$20.5 S cm^{-1}, and $\sim$62 MΩ for the fibre–electrode resistance. Notably, similar experiments on metallic single-walled carbon nanotubes revealed contact resistances and resistivities much smaller than in the V_2O_5 fibre case [18].

A disadvantage of the previously described technique is that only a few spots can be probed along the fibre with a reasonable effort. Therefore this technique cannot be used to acquire reproducible current maps while imaging.

3.2. Electrical characterization by JM: current maps

In order to probe more points on a fibre, we used JM [11] which provides reproducible electrical contacts between tip and a nanometre-sized sample, as shown in previous work [17]. In addition, it has been shown that JM, although being a contact technique, minimizes shear forces and thus damage delicate samples [19]. In general terms, JM performs an F/Z at every point of the image. A bias voltage is applied to the conducting tip while it is in contact with the surface and the current flowing through the tip is monitored. Since the substrate is insulating, it is only when the tip establishes contact with a fibre connected to the gold electrode that the electrical circuit is closed and a current passes through the tip (figure 1(b)). A current map is composed by registering simultaneously the topographic data and the electrical current at every point of the image. As an important advantage of measuring the current in JM, resistance versus length curves can be obtained with high spatial resolution.

We have carefully checked that JM does not modify V_2O_5 fibres. This is not the case for all types of molecular wire, like single-walled carbon nanotubes or DNA [19]. The main reason for this difference is attributed to the shape and size of

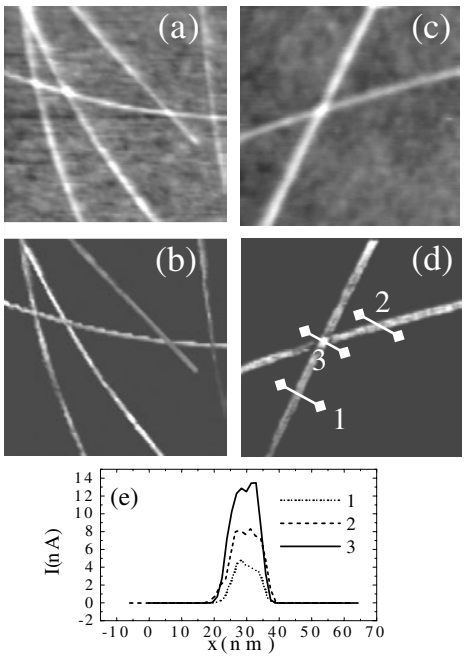

Figure 3. (a) JM topographic image of several fibres. (b) Current map simultaneously acquired with the topography, in the crossing point marked by the white arrow the fibre on top can be clearly identified, in this case the force exerted by the tip does not improve the electrical contact between fibres. (c) Topographic image of a crossing point of two V_2O_5 nanofibres connected to a gold electrode, (far away in the up-right corner). (d) Simultaneously obtained current map, with a bias voltage of -2 V applied to the tip, the electrical contact between the fibres is produced by the SFM tip. (e) Profiles taken along the white lines on (d), the current obtained in the crosspoint is the sum of the current through the two fibres.

the objects (see figure 1(c)). A V_2O_5 fibre can be considered a flat ribbon on the substrate, with a molecule/surface contact area typically seven times larger than in the case of single-walled carbon nanotubes. Therefore the interaction between the V_2O_5 fibre and the substrate is strong enough to withstand the force exerted by the tip in JM. In contrast, carbon nanotubes and DNA molecules are thinner and roughly of cylindrical shape, resulting in a much lower interaction with the substrate as compared to the V_2O_5 fibres.

In figure 3, two topographic (a), (c) and current map (b), (d) images of V_2O_5 fibres on the SiO_2 surface are shown, respectively. The gold electrode is outside the images, about 1 μm away (in the direction of the top right corner). We note that attempts to image the gold surface of the electrode with a metal covered tip result in irreversible damage of the tip coating due to metal–metal adhesion. Therefore current imaging is limited to regions corresponding to the insulating substrate. In these regions, current is clearly detectable along the fibres[5]. The current profiles along the directions indicated in figure 3(d) (see figure 3(e)) reveal different currents for different fibres. From the images we conclude that the current injected into each fibre depends mainly on the quality of the fibre–gold electrode contact and the intrinsic fibre resistance. The fibre/tip resistance is constant in the experiment.

An important finding is that the fibres normally do not make good electrical contact with each other. In fact, at the

[5] Because of the high concentration of fibres and their length, all the fibres of the image are electrically connected to the gold electrode.

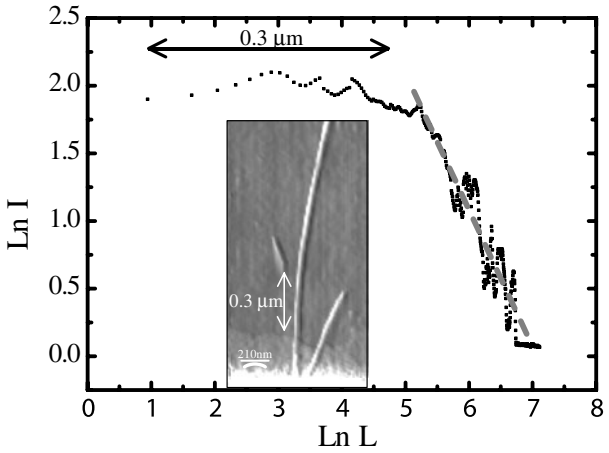

Figure 4. In the inset, the topographic image of a V_2O_5 nanofibre connected to a gold electrode is shown. The chart represents the log–log plot of the current versus length for the longest fibre of the inset. A linear behaviour with slope -1.01 is found for $L > 300$ nm ($E < 1.3 \times 10^{-5}$ V cm^{-1}); for lower values of L the dependence is weaker due to a higher conductivity than that expected for an ohmic conductor.

crossing points of figure 3(b) the electrical current can clearly be attributed to the current through one of the two fibres. If the fibres were electrically connected, one would expect that the current along either of the two fibres tends to the same value towards the crossing point. As can be deduced from the data in figure 3(b), this is not the case for the present sample. We note that, although this is the general case, different situations were also found, as depicted in figure 3(d). Here, at the crossing point the current measured is the sum of the individual current passing through the fibres in the proximity of the crossing spot (figure 3(e)). We explain this behaviour by the formation of a temporarily improved electrical contact due to the force that is exerted on the crossing point when tip–sample contact is established. Consequently, only at this image point is the measured current the sum of the individual currents flowing through the fibres. Interestingly, this effect does not depend on the applied force, but could depend on the intrinsic structure or geometry of the crossing between fibres.

Figure 4 shows a logarithmic plot of the current versus distance taken in JM along the longer fibre shown in the inset. Two regions of different slopes can be clearly distinguished. The straight line shown in figure 4 has been fitted using least mean squares. The corresponding slope, -1.01, is in good agreement with the expected behaviour for an ohmic conductor of length L, where the current presents a dependence of $\propto 1/L$. For shorter distances from the gold electrode ($L < 300$ nm) the conductivity is higher, and the current depends much more weakly on the distance, suggesting a non-ohmic transport regime. The conductivity of vanadium pentoxide thin films is reported to increase with electric field within the high field regime [20]. The linear behaviour observed for $L > 300$ nm is in good agreement with the threshold given in [21], considering that the voltage applied to the sample is 2 V (corresponding to a field of 2 V/300 nm $\approx 1.3 \times 10^{-5}$ V cm^{-1}). These results are in good agreement with the findings of Kim *et al* [21] and can be explained with a small polaron hopping model for conduction in the fibres.

In summary, we have demonstrated that SFM techniques are suitable to electrically characterize individual V_2O_5 nanofibres. Two complementary techniques based on SFM have been described: non-contact imaging combined with the acquisition of I/V curves on the molecular wire, and JM measuring the current during the contact period. These techniques have been applied to the characterization of individual V_2O_5 fibres. Their conductivity was determined to be $\sim$20 S cm^{-1}, and the contact resistance to the electrodes was obtained to be $\sim$62 MΩ. It is demonstrated that the electrical connectivity of the fibres crossing is very poor, although it sometimes can be improved by the SFM tip. The resistance versus length dependence has been measured with nanometre resolution, finding a non-linear behaviour due to the effect of the high electrical field in regions close to the electrode ($L < 300$ nm), suggesting a non-ohmic transport regime.

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