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Resistance–temperature dependence in carbon nanotube fibres

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ABSTRACT

The electrical transport of a carbon nanotube assembly is determined by its morphology and composition. These vary with the assembly production processes and post-process treatments applied. Here, we present the study of the electrical – structural dependence of wire like assemblies of carbon nanotubes i.e. carbon nanotube fibres produced via floating catalyst chemical vapour deposition processes. We propose that the analysis of resistance – temperature characteristics of the fibres provides vast amount of information for the assessment of the quality of the fibres and thus the efficacy of fibre production and post-production processes. To aid qualitative and quantitative analysis of the experimental results we propose a new universal model which allows the fitting of experimental data in the full range of temperatures and a straightforward comparison of the recorded characteristics.

1. Introduction

Carbon nanotube (CNT) assemblies have a potential to become a conductive material of the future for electrical and electronic devices [1,2]. Of particular interest are CNT fibres i.e. wire-like macroscopic assemblies of axially aligned CNTs, for the application as the next generation of electrical wires [1]. It has been recently shown theoretically that a fibre made of defectless single-walled armchair nanotubes of one chirality, with precise length of contacts between them, should conduct as one nanotube i.e. transport electrons ballistically (without scattering) [3]. Such fibre would considerably outperform any traditional metallic conductors. However, as the structure of currently produced fibres has not yet been fully controlled this anticipated conduction is still not possible. The current fibres can comprise nanotubes of random lengths, chiralities and number of walls [4–7]. The CNTs can be defected and the whole structure – disordered having e.g. misalignments or areas of poor condensation as well as impurities or dopants [5,7–9]. All these aspects will decidedly influence the current flow in the fibres.

Full characterisation of the complex morphology of every assembly requires laborious, statistical microscopic measurements and it is very difficult to predict the electrical properties of the given fibre and thus judge the efficacy of its production process [4]. Therefore, any straightforward technique aiding the electrical characterisation of the fibres in correlation with their morphology, would be highly useful. An interesting method for such purpose is the measurement of the dependence of the electrical resistivity of the fibres on

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temperature. Generally, the resistance of the CNT assemblies drops with decreasing temperature down to a crossover temperature T_0, below which it starts increasing [5–7]. It has been reported that the best quality fibres (less disordered, pure) and/or highly doped ones retain most of their conductance at the lowest temperatures and can have T_0 as low as 40 K, which gets them close to crystalline metals [5,10,11]. Other fibres have considerably decreased conductance at the lowest temperatures and higher T_0 – even well above room temperature [5,6,12,13], similarly to conductive polymers and disordered semiconductors/metals. The latter similarities caused that most of the theoretical models used so far to describe resistance–temperature (*R*–*T*) characteristics of CNT fibres/assemblies were adopted from these materials and therefore concentrate only on the semiconducting parts of the *R*–*T* curves.

Kaiser was the only author who approached the fitting of full *R*–*T* curves [14–17]. The characteristics were fitted with several types of equations which were the combinations of linear metallic term, expressions describing fluctuation assisted tunnelling (FIT), the resistivity of a quasi one-dimensional (1D) metal and 2D or 3D variable range hopping (VRH). This approach although enabled the fitting of the *R*–*T* curves in the whole range of temperatures, did not allow to mark T_0 temperature and characteristic minimum in resistance. Moreover, no systematic correlation between the structure of the CNT assemblies and chosen models was presented so the interpretation of these results is difficult. Following the approach of Kaiser, Behabtu et al. [18] found that the fits may be ambiguous and e.g. both FIT and VRH models could fit their data. The studies of other authors were also not conclusive. Vavro et al. [5] and Yanagi et al. [6], who studied only the semiconducting parts of the characteristics, indicated that gradual changes of the structure/doping of the samples leads to the progressive alterations in the resistance–temperature characteristics and the fitting models which changed from 1D VRH through 2D and 3D VRH, intermediate exponential behaviour to weak localisation. However, these authors did not discuss the use of FIT model. Finally, Salvato et al. [19] showed that the semiconducting parts of their CNT fibres *R*–*T* curves should be fitted both with 3D VRH and FIT, below/above a doping-dependent transition temperature, respectively. When testing our CNT assemblies we also observed that the use of the above mentioned models is often ambiguous. More importantly, however, this approach does not allow the extraction of all information included in the full *R*–*T* characteristics.

Our paper presents *R*–*T* characteristics measured for the fibres directly spun from floating catalyst chemical vapour deposition (CVD) furnace [8,20] at varying process conditions. We find clear correlations between the structure of the fibres and their *R*–*T* curves and propose a new framework model which can be used for all the CNT fibres in the whole range of temperatures and aid the interpretation of experimental results.

2. Experiment

The CNT fibre samples for testing were directly spun from floating catalyst CVD furnace. In this process a hydrocarbon, ferrocene, sulphur precursor and hydrogen are introduced into the hot zone of the furnace. At temperatures above 1000 °C the hydrocarbons and ferrocene crack releasing carbon atoms and iron particles, respectively. With the aid of sulphur and hydrogen, iron particles form small clusters which become catalysts. The carbon atoms arrange on the top of catalysts and the nanotubes grow suspended in the hot zone of the furnace. Further, the nanotubes are extracted from the furnace with a use of a metal rod, to which they stick trailing other nanotubes along. The extracted material is then condensed using acetone spray and collected on a rotating spindle. As shown previously, any change in parameters of the process may result in the modification of the morphology of the fibres [4] and thus their electrical properties. Fig. 1(a) presents resistance–temperature characteristics, measured for 17 as-made fibre samples, which came from four types of processes. The first process used carbon disulphide as a sulphur precursor and methane as a hydrocarbon (3 samples). Other

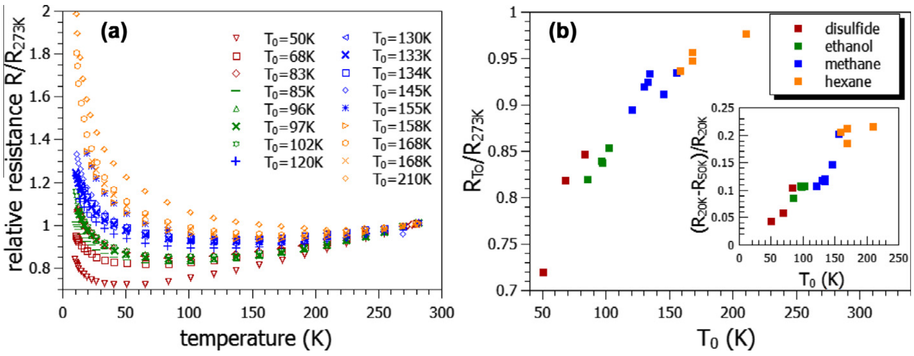

Fig. 1 – (a) Resistance changes as a function of temperature for 17 samples of various CNT fibres spun directly from the CVD reactor. Resistance values are referenced to the resistance of a given sample at 273 K. The symbol colours refer to the fibre production process (red – methane/carbon disulphide, green – ethanol/thiophene, blue – methane/thiophene, orange – hexane/thiophene). (b) Analysis of the data presented in (a) showing the dependence of the resistance at the crossover temperature – R_{T_0} related to the resistance of a given sample at 273 K – R_{273K}, against T_0. (inset) The dependence of the difference of resistance at 20 K – R_{20K} and at 50 K – R_{50K} for a given sample related to R_{20K} against crossover temperature T_0. (A colour version of this figure can be viewed online.)