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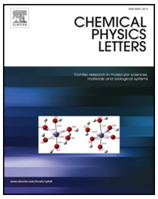

Research paper

Unusual conductivity temperature dependence of multiwalled carbon nanotube thin film

Kamil Kędzierski[a,*], Karol Rytel[a], Bolesław Barszcz[a,b], Anna Gronostaj[a], Łukasz Majchrzycki[c], Danuta Wróbel[a]

[a] *Faculty of Technical Physics, Poznan University of Technology, 60-965 Poznan, Poland*
[b] *Institute of Molecular Physics, Polish Academy of Sciences, 60-179 Poznan, Poland*
[c] *Center of Advanced Technology, Adam Mickiewicz University, 61-614 Poznan, Poland*

HIGHLIGHTS

- MWCNT thin film conductivity model was analyzed using DAE concept.
- The film is characterized by conductivity model crossover at 120 K.
- Model crossover from VRH to thermal expansion model is reported for the first time.
- Investigations enabled estimation of the MWCNTs coefficient of thermal expansion.

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ABSTRACT

The Multiwalled carbon nanotube (MWCNT) thin films has been formed on PVC substrate using Langmuir-Blodgett technique as highly promising material for optoelectronics. The layers were annealed at 367 K which has led to significant electrical resistance decrease. The resistance of the obtained layer was investigated in wide temperature range showing the dependence significantly different from that observed for the layers created using CNTs of smaller diameter. The reason of the unusual conductivity temperature dependence is most probably the difference in thermal expansion coefficients of MWCNTs and the polymer combined with relatively high stiffness of the nanotubes with such large diameter.

1. Introduction

Limited resources of indium tin oxide and its price fluctuations compels to search for alternative materials suitable for transparent electrode production [1]. Moreover, modern electronics requires a new kind of transparent and conducting materials which are able to create flexible electrodes. Due to their charge transport properties a carbon nanotubes (CNTs) are highly promising material to fulfill the requirements [2]. On the other hand the CNTs relatively high absorption coefficient in visible spectrum range [3] forces the manufacturing of the thin film electrodes. Many different methods of CNT thin films creation have been developed so far: dry routes of aerosol-depositing, spin/spray-coating or transfer printing and many others [4]. Some of the best methods for the CNT thin films creation are vertical and horizontal transfer from the air-water interface which are known as Langmuir-Blodgett (LB) and Langmuir-Schaefer (LS) techniques, respectively. The methods do not require vacuum or an inert atmosphere and simultaneously allows to create highly organized layers at nanometric level with a large surface area [5,6]. Furthermore, the thickness of the film can be controlled by means of multiple transfers. It has been shown that the CNT layers prepared in the LB and LS processes can be used in surface acoustic wave sensors [7], transistors [8], as highly catalytic activity material [9], photodetectors [10], and transparent conductive films [11]. Therefore we decided to use the LB method to create a CNT thin film on flexible substrate and investigate its electrical properties.

The main goal in creating transparent electrodes is to reach as low as possible electrical resistance (less than 100 Ω/square) combined with high light transmittance in visible range (more than 90%). CNT layers electrical and transmission parameters are comparable to the indium thin oxide (ITO) on flexible substrate – see for example [12]. However, the light transmission to electrical resistance ratio remains insufficient when compared with ITO on glass [13]. One of the steps to improve the

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* Corresponding author.
E-mail address: kamil.kedzierski@put.poznan.pl (K. Kędzierski).

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CNT thin films electrical properties is to study the nature of their conductivity which can be understood by proper model determination. The ballistic and diffusive types of conductivity were reported for individual single wall carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT), respectively [14,15]. On the other hand for the SWCNT LB layers a nonlinear current (*I*) *versus* voltage (*V*) characteristics are usually observed [5] and it can be described by a Poole-Frenkel (PF) model [16,17]. However the PF conductivity is particularly evident for the semiconducting CNT layers [18]. Furthermore, the nonlinear *I-V* characteristics are recorded when gap between the electrodes for measurement is comparable with CNT length – the conductivity of individual nanotube plays a dominant role. In case of significantly longer gap the CNT-CNT interconnections have the dominant influence on the whole layer conductivity which results in linear current *versus* voltage characteristic. For example Yahya et al. show the perfectly linear *I-V* characteristics for the single wall CNT LB film at room temperature with 0.2–1 cm gap experimental setup [19]. Moreover, for the layers created from multi-walled carbon nanotubes (MWCNTs), which are mostly metallic, the *I-V* characteristics are linear [20]. When the gap between the electrodes is significantly longer than average CNT length we may consider the CNT layer as a strongly disordered system where the charge “hops” between the nanotubes through the potential barrier. In that kind of a hopping conductivity a strong resistance *versus* temperature dependence is observed [21]. Our previous studies related to single and multi-walled carbon nanotube LS films have revealed that good fits to the measured resistance *versus* temperature characteristics can be obtained using the variable range hopping (VRH) conductivity model [22]. On the basis of the relationship between resistance and resistivity $R \sim \rho$ we can express the $R(T)$ relation in the VRH model as:

$$R(T) = R_0 \exp\left(\left(\frac{T_0}{T}\right)^p\right) \tag{1}$$

where R_0 is a pre-exponential factor, T_0 is a characteristic temperature which is proportional to system disorder and p is an exponent related to the conduction dimensionality of the sample and the density of states of energy at the Fermi level [21]. The VRH conductivity was observed for MWCNT mats [23] and bulk MWCNT composites [24].

Moreover during the experiment the sample expands and contracts as a result of temperature changes which can lead to the modification of the conducting path. That suggest the appropriateness of consideration of a conductivity model based on the piezoresistive effect (PRE) proposed by Knite et al. [25] and adapted to thermal expansion effect by Chin et al. [24]. The resistance can by described be the following expression:

$$\ln(R(T)) = \ln(R_{01}) + A\alpha T + B(\alpha T)^2 + C(\alpha T)^3 + D(\alpha T)^4 \tag{2}$$

where R_{01} is an initial resistance, α is a coefficient of thermal expansion and A, B, C and D are constants.

In fitting procedure of the experimental R(T) characteristics the Arrhenius plot modified to the VRH model is very useful. However the linear dependence of $\ln(R^{-1})$ *versus* $T^{-1/4}$ may be misinterpreted [21]. Therefore we have decided to provide the conductivity analysis by the Differential Activation Energy (DAE) concept as proposed by Hill [26].

$$\frac{\partial \ln(R(T))}{\partial (k_B T)^{-1}} = p k_B T_0^p T^{1-p} \tag{3}$$

where k_B is the Boltzmann constant. The DAE approach is powerful tool for the conductivity model analysis because the DAE smooth increase with temperature indicates the VRH conductivity. The wide plateau in the DAE *versus* temperature plot shall be observed in the case of a nearest neighbor hopping (NNH) or a band conductivity (BC). When the DAE value decrease with temperature or changes chaotically it indicates a crossover between the models or mixed conduction [27].

2. Experimental

The thin films of multiwalled carbon nanotubes (MWCNTs) of external diameter 120–170 nm and length about 5 μm (Sigma Aldrich) prepared by chemical vapor deposition (CVD) are studied. The film is created by vertical lifting of the MWCNT layer floating on the water-air interface, by the means of Langmuir-Blodgett (LB) technique. The floating layer preparation is realized by the modified method described in our previous paper; the MWCNT suspension and floating film preparation are described in details in supplementary materials and in [28]. Moreover, the standard surface pressure *versus* trough area isotherm and compressibility modulus were shown in the supplementary materials in Fig. S1. The layer is transferred on the flexible 0.15 mm thick polyvinyl chloride (PVC) foil. In our previous work [28] we proved the weak LB transfer ratio of the MWCT layer on the quartz substrate. However, in this paper we present the results of investigations of layers transferred on the PVC substrate where LB method allows to create large scale homogenous film. We believe that the better MWCNTs adhesion to the PVC and hydrophobicity of the substrate caused much better transfer compared with transfer on the hydrophilic quartz. Furthermore, in contrast to the most commonly studied Langmuir-Blodgett CNT films [29] we investigate the film obtained in a single transfer process (monolayer instead of multilayer).

The electrical resistance measurements are performed using a standard four-probe method. The contacts are made from a silver wire (diameter of 40 μm) and attached to the sample using silver paint. The distance between the electrodes is about 5 mm. Direct current is supplied by a Keithley 220 programmable current source and the voltage is monitored with a Keithley 182 sensitive digital voltmeter. In order to measure resistance *versus* temperature (R(T)) the sample is immersed in a continuous flow helium cryostat (Oxford Instruments, Optistat CF). Temperature is controlled and stabilized using an ITC 503 temperature controller (Oxford Instruments). The measurements are done using four current values (-4, -2, 2, and 4×10^{-8} A) at each temperature point. The R(T) characteristics are recorded during cooling from 290 K to 10 K and during heating from 10 K to 290 K. In the next step the samples are transferred to external drying chamber and annealed to 367 K for 30 min and cooled back to 290 K. Then, the measurements are repeated for the annealed samples from 290 K to 10 K and from 10 K to 290 K in the cryostat.

Microscopic images (SEM) are recorded by means of a Helios NanoLab 660 FEI scanning electron microscope operating at 1 kV in the immersion mode. Conductive carbon tape is used to ensure electrical contact between the layer and measuring table. The images are collected near the connection to avoid charging of the surface.

3. Results and discussion

The light transmittance of investigated film is 57% and 53% for the as deposited and annealed film at 550 nm wavelength, respectively; transmittance spectrum for the film is shown in supplementary materials (Fig. S2). The surface resistance at 20 °C is about 480 kΩ/square and after annealing the film at 367 K the surface resistance drops down to about 120 kΩ/square. The conductivity ratio (definition is given in supplementary materials and in [30]) growth almost four times in the annealing process – from 0.0012 to 0.0042 for the as deposited and annealed film, respectively. Fig. 1 shows the film resistance change during annealing process and temperature of the sample (details of this experiment are given in supplementary materials). The resistance increases with temperature by 70% and when the sample temperature reachs about 360 K we observe sharp drop of the resistance to 85% of initial value. During further annealing the resistance decreases slightly. Eventually after cool down the sample the resistance decreases to about 70% of its initial value. The resistance drop presented in Fig. 1 is not that significant as for the other tested samples however the current flow during annealing can change the state of affairs. The CNT resistance