

posite polymer films having good perspectives for applications in plasmonics, optoelectronics and sensor technologies.

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NANOSENSOR APPLICATIONS OF CARBON NANOTUBE FILMS

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In this report we would like to concentrate on a new generation of the icing condition resistive sensors that we have developed. These sensors are based on the adsorption of a molecular thin layer of water on the surface of carbon nanotubes (CNTs) and on the detection of the first order phase transition of water into ice. This transition is very well detected as a result of non-monotonous dependence of the resistance of the sensor vs. temperature in the vicinity of the freezing point due to a virtual “field effect transistor” effect. Carbon nanotube films, assembled in the resistive films with highly developed surface are considered to be extremely sensitive to the adsorption of polar H₂O molecules.

There have been a significant number of commercial and general aviation airplane accidents caused by icing conditions. In particular, there was a disaster in the Air France Flight 447 from Rio de Janeiro to Paris – a routine international flight on June 1, 2009. It appeared that three pitot tubes failed simultaneously. They were unable to cope with the storm conditions facing Flight 447. Accident investigators believed that super-cooled water in the clouds – well below freezing, but too pure to turn into ice – had disabled the pitot tubes. Since 2003, there have been around forty incidents involving frozen pitot tube on A330s or the similar A340s. The cause of the Comair Flight 3272 crash in Buffalo on February 12, 2009, was identified as a failure to meet operating standards in icing conditions. The regulations recommend pilots fly manually in icing conditions, and require they do so in severe icing conditions. Without flying manually, pilots may be unable to feel changes in the handling characteristics of the airplane, which is a warning sign of ice buildup. That is why the detection of icing built up on the early stage (or even better) warning on the approaching to dangerous situations is a vital component of safety flying in the icing conditions. Unfortunately, modern sensors of icing conditions (optical, or piezo-devices) are based on the detection of the actual (significantly thick) layers of ice formed on the sur-

faces. The accumulation of the ice layer is a fast process, and detection of the massive ice formation is too late for the safety of the aircrafts.

We have developed a method of assembling of multi wall carbon nanotube (MWCNT) films of arbitrary thickness for sensor applications. This method involves slight oxidation of carbon nanotubes, and does have several major advantages over the conventional methods of carbon nanotube assembling via their functionalization. The assembled carbon nanotube films are dense, homogeneous and strong on the macro-level, but internally they consist of disordered structure of self-assembled carbon nanotubes, forming conductive medium, as it is seen in the Fig. 1. Based on our experience of multi-wall CNT characterization [1, 2], we were able to investigate them at fixed values of humidity and the temperature variation.

We have found that the adsorption of the water vapor at the temperatures close to freezing conditions generates a specific non-monotonous dependence of the resistance of the sensor vs. temperature.

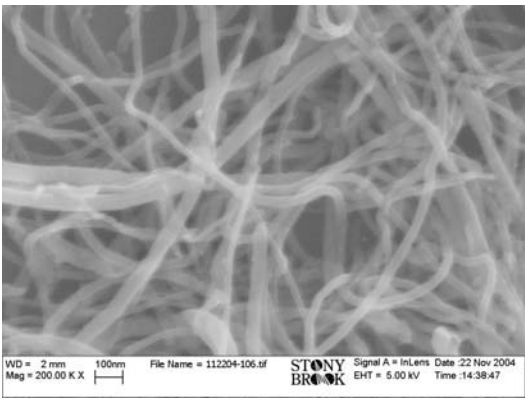


Fig. 1. – SEM picture of the morphology of carbon nanotube film

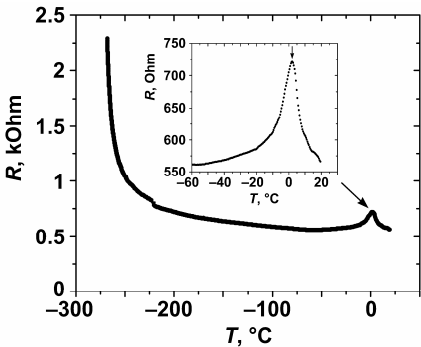


Fig. 2. – Temperature dependence of the resistance of the MWCNT layer in the presence of water vapors. Note, the max of the resistance is located in the nearest proximity to the water freezing point at $T = 0^{\circ}C$

The intensive precipitation of the water vapor, when the temperature is decreasing, results in the increasing of the resistance of the nanosensor, due to the “field effect” created by the adsorbed polar water molecules on the surface of slightly charged CNT tubes. Further decreasing of the temperature passing the freezing point results in sudden drop of the resistance (“lambda-point”-type curve at the phase transitions of the first order) – see the insert in the Fig. 2 – due to the water transition to nonpolar ice crystal. As a result, the “field effect” disappears, and the resistance of the carbon nanotubes decreases again.

In order to verify, if the positions of the peaks correspond to the humidity (dew point or frost point), we did temperature scans at different controllable values of the humidity. The dependences of the resistance of the CNT sensor measured at fast temperature scan at different humidity levels and temperature variations from approx +50 $^{\circ}C$ down to -50 $^{\circ}C$ are plotted in the Fig. 3. The temperature dependences of the resistance of the CNT sensors measured at the slow temperature scan ($\leq 0.01^{\circ}C/sec$ in the cryo-cell of our own design) are shown in the Fig. 4. As can be seen at the Figs. 3 and 4, if the temperature drops down, a significant resistance increase takes place, following by the max point of the resistance and sudden resistance drop due to the ice formation.

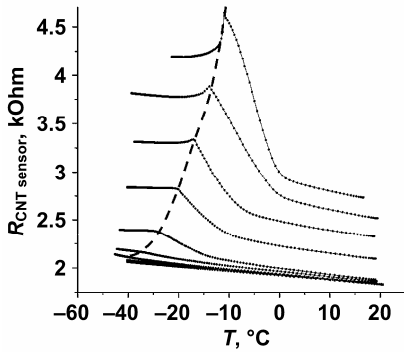


Fig 3. – The resistance of the CNT sensor vs. temperature at different humidity levels at the fast temperature scan of ~ 1 °C/sec

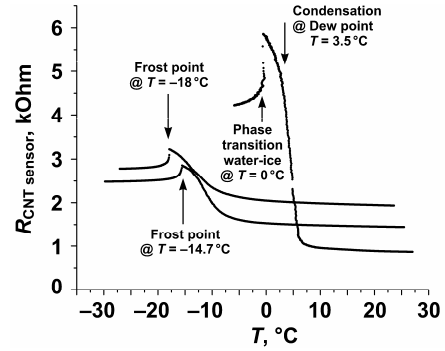


Fig. 4. – Temperature dependences of the resistance of the CNT sensors measured at the slow temperature scan ≤ 0.01 °C/sec in the cryo-cell of our own design

There is a significant difference in the observation of the dew points and the frost points using CNT sensors. If we observe T_{dew} , which is higher than the freezing point, we observe significant resistance increase due to condensation. Then the saturation occurs, and at the freezing point is characterized by a sudden resistance decrease. In the meantime, if we observe frost points instead, while the temperature decreases, the condensation corresponds to the frost point.

In order to verify, if the phenomenon takes place specifically on the carbon nanotube surface only, or not, we did an observation of the same phenomenon on the surface of 3D sponge-like graphene material (Fig. 5). The same type of the nonmonotonous behavior was found there (Fig. 6). This confirms the generality of the “field effect” of the polar molecules adsorption on carbon with sp^2 hybridization.

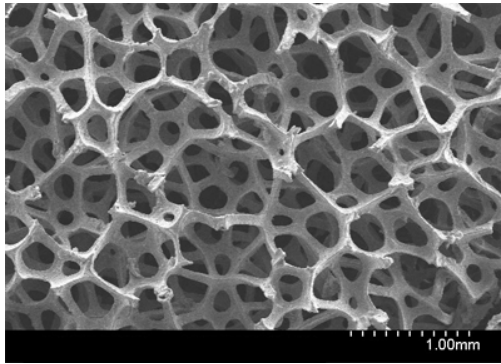


Fig. 5. – 3D sponge-like graphene material

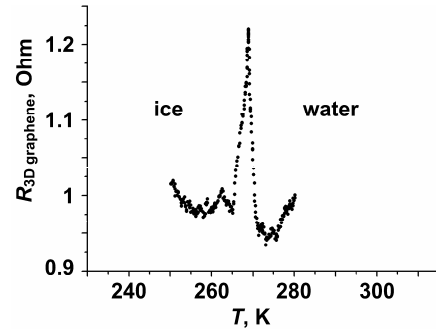


Fig. 6. – The nonmonotonous behavior of the resistance was found in the 3D graphene material as well as in CNT resistive films

As a conclusion, we summarize that carbon nanotube layers could be utilized as inexpensive and effective sensors of icing conditions, suitable for applications in aviation and different industries, with totally different background of operation in respect to the standard sensors of humidity [3–5]. Clear observation of the specific peaks on the dependences of the resistance of the CNT sensors while the temperature variation at different fixed humidity levels is a clear confirmation of the feasibility of the CNT sensors as an icing condition sensor. Icing in the humid conditions occurs at the abrupt resistance drop (after rising) of

the CNT sensor (maximum of the resistance vs. temperature). Instrumentally, the icing condition could be easily detected as a result of the observation of the first derivative of the resistance vs. temperature passing zero value ($dR/dT = 0$) at the specific value of humidity.

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SPATIO-TEMPORAL LOW DIMENSIONAL SYSTEMS AND NANOSTRUCTURES

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Since the Conference is devoted to “the Materials and Structures in Modern Electronics” we would like to present a brief review of some of our results on low dimensional and spatio-temporal structures.

CURRENT OSCILLATIONS IN SEMICONDUCTORS

We observed spontaneous low frequency current oscillations in polycrystalline Si [1, 2], amorphous Si [3–8], semi-insulating semiconductors [9–11] and *n*-type [12–13] GaAs. We did confirm a method of obtaining information on deep levels in semi-insulating GaAs and in Fe-compensated InP by analyzing the temperature dependence of low frequency current oscillations (Fig. 1, 2). From the power density spectra peaks the extraction of the Arrhenius plots of $\log(T^2/2f)$ versus $1/T$ gave us an activation energy of 0.47 eV for the main peak in InP and 0.75 eV in GaAs (Fig. 3). The method is complementary to the other deep level spectroscopy techniques and the information is obtained more easily on levels which exhibit field-enhanced trapping. In the meantime, the current oscillations in *n*-type GaAs (Fig. 4) [12–13] show an activation energy of hopping conductivity in this material.