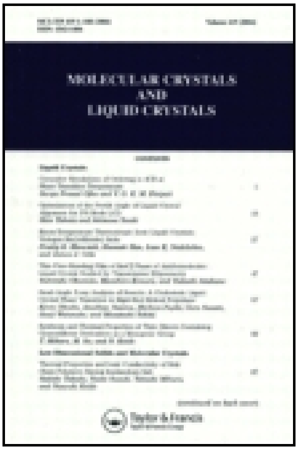

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Electronic Properties of DNA/CNT Chip on Si

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The effects of the electronic structure self-formation and charge transfer for the planar system of layers from DNA unwrapped double helix, DNA double helix, DNA unwrapped double helix with carbon nanotubes (CNT) in the separated sections with common bounds on the silicon substrate – DNA chip on Si were studied in detail. The electronic structure of DNA/CNT layer is formed as a result of changes of electron levels in adenine, cytozine, guanine and thymine which were directly revealed by UV-VIS and IR spectroscopy. The transport properties of such system were determined by the charge transfer through the barriers in the DNA double helix/unwrapped double helix and in the DNA unwrapped double helix/CNT heterostructures that were proved by tunneling spectroscopy investigations.

Keywords: nanoelectronics; DNA/CNT layer; UV-VIS; IR and tunneling spectroscopy

INTRODUCTION

Our hypothesis about possibility of the new electronic material construction by self-assembling of DNA/CNT layers bases on theoretical predicted[1] and experimental confirmed[2] facts that single DNA molecule and CNT are able to conduct electrical charges. Electronic properties study of DNA molecules and CNT in layers has a great significance in view of their using in DNA nanotechnology for the construction of "lab on a chip" electron systems. The results obtained could be used as basis for further development of the molecular computer engineering principles[3].

In this work some experimental results in support of proposed model for engineering of DNA chip were obtained. We have used the DNA/CNT layers adsorbed from DNA in NaOH solution with and without CNT on Si substrate. In the DNA/NaOH solution on Si substrate the regulated system of hydrogen bonds is transformed/ destroyed and the DNA molecule structure turns from double helix into chaotic ball structure. This change has a co-operative character. The DNA/CNT layer self-organization could be stimulated by this process. The UV-VIS and IR spectroscopy as well as tunneling spectroscopy were carried out for study the electronic structure of DNA/CNT, DNA double helix, DNA unwrapped double helix layers and charge transfer along these layers and through the barriers between these layers.

EXPERIMENTAL

Solution of DNA from calf thymus (1 g/l) in 0.4 n NaOH was used. The con-tent of adenine (A), guanine (G), cytozine (C) and thymine (T) were 29.0, 21.2, 21.2 and 28.5 mol.%, respectively. Single-walled CNT bundles were mixed with DNA/NaOH solution. The upper layer of this mixture as a single droplets were deposited on Si (100), quartz and KRS substrates and dried with and without 2 h irradiation of visible light (λ >500 nm) for the layer formation in the separated sections with common bounds on the Si substrate - for DNA chip on Si formation - as well as for the single layer formation on quartz and KRS substrates.

UV-VIS absorbtion spectra of single layers on quartz substrate between 200 and 850 nm were recorded on Hitachi 850 Spectra-fluorimeter. IR transmission and reflectance spectra of single layers on Si and KRS substrates were recorded between 400 and 4000 cm^{-1} on Specord M-80 Care Zeiss Jena spectrometer at T=293 K. The (I–V) characteristics of Pt/Ir tip – DNA (or DNA/CNT layer) – Pt/Ir tip structures were registered by Tunneling Spectrometer constructed in Kyiv University Laboratory.

RESULTS AND DISCUSSION

Structure of DNA, CNT in DNA and DNA/CNT layers

In the DNA/CNT layer the absorption peak wavelength increases on 3.83 nm in comparison with that one in DNA/NaOH layer, which correspond to decrease on 0.07 eV electron transiton enegry in DNA molecule. This may be caused by changing the hydrogen bonds under DNA/CNT interaction.

In the typical optical absorption spectra of the DNA layer the wide peaks were observed at around 259 nm based on the π–π^* transition of nucleic acids and are the same as for DNA in aqueous solution[4]. These results directly indicate that the DNA structure is not changed in the dried layer. In these spectra we also observed absorption increase in DNA layer adsorbed from DNA/NaOH solution in comparison with DNA layer adsorbed from DNA/Tris - HCl solution. This is known as hyperchromatic effect that testify the DNA unwrapping of double helix in chaotic ball structure in this solution and DNA has the same structure in the layer. It was also found that the optical density at 259 nm increases from 0.4×10^{-4} $M^{-1}cm^{-1}$ in the DNA/NaOH layer to 0.5×10^{-4} $M^{-1}cm^{-1}$ in the DNA/NaOH/CNT layer that corresponds to partial unwrapping the DNA double helix caused by DNA/CNT interaction. The peculiarity of typical optical absorption spectrum of DNA/CNT layer consists in changing of absorption peak wavelength which we relate to known electron transition in the DNA molecule from 258.50 nm to 262.33 nm in DNA/CNT layer. These results directly confirmed that the electronic structure of DNA/CNT layer is formed as a result of changes of electronic levels in nucleotide bases of DNA molecule under DNA/CNT interaction.

In typical absorption spectrum of DNA/CNT layer recorded between 300 and 850 nm we observed peaks with wavelengths corresponding to photon energies: 1.67, 1.86, 2.10, 2.56, 2.80 and 3.34 eV. They correspond to reported ones for the thin films of single-walled CNT prepared by both laser evaporation and electric arc methods in work[5]. Using this fact we could suppose that CNT structure does not change in DNA/CNT layer.

From typical IR reflectance/transmission spectra of DNA/CNT layer/Si structures (Fig. 1) using their comparison with spectra of Si substrate, DNA layer/KRS and Si/DNA/CNT layer structures we have found: a) the infrared active modes at 845, 870 cm^{-1} and 1512, 1583, 1596 cm^{-1} as the narrow peaks in the reflectance spectra. These frequencies differ from corresponding ones of graphite (868 and 1590 cm^{-1})[5]. One frequency 870 cm^{-1} is the same as predicted by recent calculations[6] for "armchair" CNT, another frequency (845 cm^{-1}) is smaller then predicted by the same calculations 850 cm^{-1} for "chiral" CNT. The frequencies 1512, 1583 and 1596 cm^{-1} correspond to also predicted by the calculations for "armchair" (1510, 1580 cm^{-1}) and "chiral" (1575 cm^{-1}) CNT and as for "zigzag" (1510 cm^{-1}) CNT (Fig. 1a, 1b); b) the features in the increasing of reflection in range (682-721) cm^{-1} as well as increasing of adsorption at 1458 cm^{-1} which originate in the spectrum of DNA/CNT layer/Si structure testify that structure of DNA is double helix unwrapping in DNA/CNT layer and presence of CNT with IR active phonons calculated for "zigzag" CNT (650 and 770 cm^{-1}); c) dominating line at 1374 cm^{-1} which is characteristic E_{1u} mode for "armchair" CNT[5]; d) between two lines 1374 and 720 cm^{-1} several weak and broad peaks were observed but we

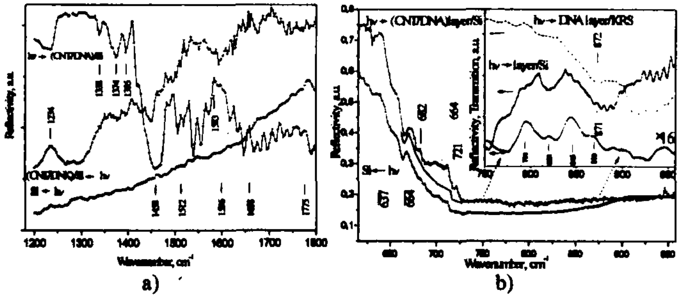

FIGURE 1 IR reflectance spectra of DNA/CNT layer/Si structure, Si substrate (a) and DNA/ CNT layer/Si, Si/DNA/CNT layer structure and Si substrate (b). The spectral regions are represented, where the IR active phonons are expected for "armchair", "zigzag" and "chiral" CNT from calculations[6]. The reflection angle is 75^0 to the normal (Brewster angle). Inset: IR reflectance spectrum of DNA/CNT layer/Si and IR transmission spectra of DNA/CNT layer/ Si and DNA layer/KRS. Absorption peaks of Si substrate are 630 and 664 cm^{-1}.

but we identified only a line at 870 and 845 cm^{-1}. IR active mode at 1234 cm^{-1} also corresponds to the calculated "armchair" CNT mode (1230 cm^{-1})[6]; e) detected lines at 1458, 1512, 1583, 1596, 1658 and 1775 cm^{-1} correspond to IR active phonons that expected for "armchair", "zigzag" and "chiral" CNT from calculations[6].

Presented identification is a continue of discussion concerning the question how many different types of CNT are in the bundle.

Electronic structure of the layers, transport in layers and heterostructures

For identification of conductivity types of CNT we used the values of optical transitions in CNT layer found from UV-VIS spectra (300-850 nm) and calculation results of the band structure of single wall CNT obtained using tight-binding model[7]. The features at 1.67, 2.56 and 2.80 eV we attributed to electronic transitions between pairs of singularities in semiconducting CNT. This fact and our results on the layer conductivity of structures of DNA double helix and unwrapped double helix with and without CNT on Si were used for formation of the planar system of these layers in the separated sections with common bounds on the Si substrate – DNA chip on Si. We created the system of heterostructures as DNA unwrapped double helix/CNT, DNA unwrapped double helix/DNA double helix and formed Pt/Ir tip – DNA (or DNA/CNT layer) – Pt/Ir tip nanostructures. For these nanostructures (Fig. 2a, d) as well as for layers from CNT (Fig. 2b) and from DNA unwrapped double helix with CNT (Fig. 2c) on (I-V) characteristics we found the following features: a non-linearity; diode behavior; negative differential resistance of heterostructure (Fig. 2a) with dependence on the voltage that is typical for resonance tunneling through double barrier; the irregularity in increasing of a current with the steps that are typical for Coulomb blockade (Fig. 2a, b, c) and for jumping transport of charge carriers (Fig. 2d). The part of these features can be caused by the electronic structure of these layers and interface in heterostructures. In order to study the electronic structure we have investigated the shape of the normalized differential conductance, dI/dV(V/I), that represents the shape of density of states (DOS) of the layer. It can be seen from normalized differential conductance - voltage curves there is a voltage gap at low applied bias (1.44 and 1.70 eV for CNT and DNA with CNT nanostructures, accordingly). The voltage dependence on the differential conductance as well as normalized conductance exhibits the clear peaks (Fig. 2b) that is typical for the DOS of CNT[7].

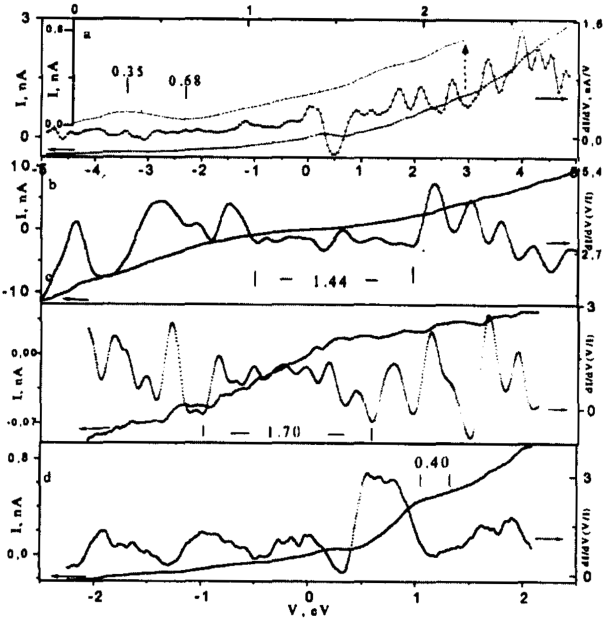

FIGURE 2 The typical (I-V), (dI/dV)-V and dI/dV(V/I)-V characteristics of DNA unwrapped double helix/CNT heterostructure (a), CNT layer (b), DNA unwrapped double helix layer (c) and DNA unwrapped double helix/DNA double helix heterostructure (d). dI/dV(V/I) is normalized differential conductance that represents the shape of DOS. The characteristics do not change principally under increase the distances between tips in the (50-100) μm range.

Acknowledgements

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