

SENSITIVITY OF ELECTRON ENERGY LOSS SPECTROSCOPY TO ION IRRADIATION OF CARBON NANOTUBES

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Introduction

Carbon nanotubes (CNTs) are interesting objects for research and they are promising objects for nanotechnology. Unique properties of CNTs make it possible to produce functional elements for nanoelectronics (for example, diodes, transistors) out of CNT fragments. It is also possible to build quantum zero- and one-dimensional structure and to fabricate nanolasers, operated in different ranges of spectrum.

Ion irradiation is relatively simple technique, which gives good opportunity to controllably modify CNT structure and to change CNT physical properties.

In this work, the effect of dependence of plasmon spectra on CNT properties and specific experimental parameters was used to study interaction of Ar ions with single-walled (SWNTs) and multi-walled carbon nanotubes (MWNTs). They were obtained by reflection energy loss spectroscopy (EELS). Auger spectroscopy was used to control condition of CNT surface.

Experimental

The samples of both SWNTs and MWNTs were used in these experiments. MWNTs were prepared by the arc-discharge evaporation [49] and were produced by the closed joint-stock company «Astrin», Saint-Petersburg, Russia. MWNTs were approximately 10 nm in diameter and approximately 10 μ m in length. SWNTs were prepared by the electric-arc-discharge synthesis. The SWNTs were 1.2 - 1.6 nm in diameter and 1 - 10 μ m in length.

The samples of SWNTs and MWNTs were periodically irradiated by argon ions (Ar⁺) *in situ* in the spectrometer chamber. The Ar⁺ energy was 1 keV. The maximum dose of Ar⁺ irradiation (Q) was 360 μ C/cm².

Each irradiation of a sample was followed by Auger spectra measurement in the mode of constant absolute energy resolution $\Delta E = 0.6$ eV in order to determine the concentration of argon absorbed in the near surface region of the sample [1].

Energy loss spectroscopy of reflected electrons was used: energy of the primary electrons was 1 keV, the incident angle of the primary electron beam and the registration angle were 45°, the diameter of the beam on the sample was approximately 1 mm, the analyzer aperture was 12°. Absolute energy resolution ($\Delta E = \text{Const}$) was 0.2 eV when the transmission energy was 10 - 25 eV.

Results and discussion

A detailed analysis of the π - and $\pi + \sigma$ -plasmons before and after different doses of Ar⁺ irradiation of carbon MWNTs and SWNTs was done. The primary steps of Ar⁺ interaction with the surface and the volume of SWNTs and MWNTs were studied. At small doses of Ar⁺ irradiation, generation of defects in the CNT walls predominates over their recombination. However, particulars of these processes are different for SWNTs and MWNTs [2,3].

Regularities of change of π -plasmon energy E_π and FWHM δE_π under ion irradiation were determined for both SWNTs and MWNTs. The E_π value decreases and δE_π value increases with increase of dose of Ar⁺ irradiation at small values of Q ($Q < Q_0 = 60$ μ C/cm²), when the rate of absorption is the highest [4].

Classical theory of dispersion and absorption was used for preliminary interpretation of the observed results. Two possible ways of plasmon interaction with defects generated under ion irradiation were discussed qualitatively. First, the generated defects deform atomic structure of CNT surface and volume and hence modify electronic properties. According to model of "inflexible bands" that causes a change of interband transition energy. Second, irradiation initials significant scattering of plasmons on the defects. The scattering is the most intensive when de Broglie wavelength of plasmons is equal to the distance between the defects. The details of the scattering are different for SWNTs and MWNTs. For SWNTs, the scattering of energy of interband π - π^* transition was calculated from experiment

data to be $1.8 \text{ eV} \leq \overline{E}_n \leq 4.3 \text{ eV}$. The upper limit ($\overline{E}_n \approx 4.3 \text{ eV}$) is close to the interband π - π^* transition energy at the extreme point M of Brillouin zone of graphite. For MWNTs, the scattering of $\overline{E}_n$ is not so significant ($\overline{E}_n = \sim 5 \text{ eV}$). The atomic structure of MWNTs is similar to structure of multi-layer bent graphite crystal. Smaller scattering of interband transitions energies $\overline{E}_n$ in MWNTs occurs probably due to "three-dimensional ordering" of MWNT structure (diameter of MWNTs is greater than diameter of SWNTs). Induced by ion irradiation, defects are generated only in interlaminar space. Thus, the process of defect formation in MWNTs and in SWNTs is different.

The interaction of π -plasmons with carbon atoms of MWNTs changes drastically when Q becomes greater than $50 \mu\text{C}/\text{cm}^2$ ($Q \geq 50 \mu\text{C}/\text{cm}^2$). According to the experimental observations, concentration of absorbed Ar was $\sim 2.5\%$ when dose of irradiation Q was $50 \mu\text{C}/\text{cm}^2$. It was supposed, that the distance between absorbed Ar atoms and distance between defects induced by irradiation are comparable with a half of de Broglie ($\lambda_B \approx 200 - 230 \text{ nm}$) wavelength in MWNTs. This fact can explain additional plasmon resonance scattering on the defects.

It was shown, that complex π + σ -plasmon should at least four components with different intensities: two quasi-surface plasmons (longitudinal and transverse) and two quasi-volume plasmons (longitudinal and transverse). Only one plasmon of the four exhibits dependence of its energy on the dose, while the other three do not. It varies from 19 to 23 eV during ion irradiation. In case of transverse plasmon G_L ,

concentration of excited electrons is about twice as greater than it is for plasmon G_2 . Relative areas $S_{G1}/S_{0\text{elastik peak}}$ and $S_{G2}/S_{0\text{elastik peak}}$ of plasmon peaks G_1 and G_2 were calculated. Ratio S_{G1}/S_{G2} is ~ 6.3 for SWNTs and ~ 2.1 for MWNTs. Relative area of plasmon peak G_2 is almost the same for both SWNTs and MWNTs. Contribution of excited electron orbital movement in the energy π + σ -plasmon could cause, that $S_{G1}/S_{G2} = 6.3$ for SWNTs. The further study is needed to explain this behavior of π + σ -plasmons.

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