

ABOUT AUGER-SPECTRUM FOR SINGLE-WALLED CARBON NANOTUBES

A.P. Dementyev^a, V.A. Ignatchuk^b, E.P. Krinichnaya^c, B.E. Muradyan^c, B.P. Tarasov^c

^a RRC «Kurchatov Institute», Moscow, Russia

^b Institute of Hydrogen and Solar Energy, P.O. Box 195, Kiev-150, 03150 Ukraine

^c Institute of Problems of Chemical Physics, Chernogolovka, Russia

Introduction

Electron structure for single-walled carbon nanotubes (SWNTs) is a subject for numerous theoretical researches [1-7]. Such interest in SWNTs was caused by their unique structure and properties [8]. In spite of the fact that there are plenty of theoretical works in literature, data about AUGER-spectra for well characterized SWNTs [9] are practically absent. Though AUGER-spectroscopy of a high energy resolution may give unique information about a local electron structure for a solid [10]. Such a contradiction is explained first of all by impossibility to extract individual SWNTs in the number sufficient for the AUGER-spectrum survey.

The paper sought to produce the sample with basically SWNTs on its surface and measure AUGER-spectrum for such a sample with a rather high energy resolution. It was also interesting to compare the obtained spectrum with the spectra for graphite and C₆₀ fullerite - carbon materials accessible in a "pure" form (practical absence of impurities, known structure) and whose AUGER-spectra are rather well described.

Details of the experiment

The samples containing SWNTs were produced by the electric arc sputtering of graphite cores containing the mixture of cobalt and nickel powders. The mixture is known (see, for example, [11]) to be the most effective catalyst for the process of SWNT producing. The calculated part of

a catalyst in the sputtering core was 10 mass %, and one nickel atom falls at three cobalt atoms. Sputtering was carried out in a helium atmosphere (p=650 Torr). The discharge current was 100 A at a voltage of 20-30 V.

The carbon material produced after sputtering was divided into the parts depending on the place where that material was at the opening of the chamber cooled to room temperature. Raman spectra for some of the taken samples are shown in Figure 1. It is known (see, for example, [12]) that Raman spectra for SWNTs are characterized by a narrow G peak with a maximum at 1592 cm⁻¹ and a shoulder at 1570 cm⁻¹. Besides that in Raman scattering spectra for SWNTs the "respiratory" mode may be observed in 150-200 cm⁻¹ region. The position of a maximum for such a stripe (ω , cm⁻¹) is connected with a tube diameter (d, nm) by a ratio $\omega=223.75/d$ [13]. For the investigation of AUGER-spectra we chose the sample whose Raman spectrum is shown in Figure 1 (number 4). That sample is characterized by a rather high SWNT content with d=1.35 nm.

Measurement of Raman spectra was conducted by Jobin-Yvon S-3000 spectrometer. Ar⁺-laser was used for the spectrum exiting.

AUG-spectra were recorded by MK II VG Scientific spectrometer. Spectra were excited by Al K α radiation (hv=1486.6 eV). Samples for the investigation were prepared by pressing an investigated powder in the indium foil.

Experimental results and discussion

A photo-electron spectrum for the investigated sample is shown in Figure 2. The lines conditioned by carbon, indium and oxygen are seen on the spectrum. Similar spectra were also obtained for the other powders. Therefore the main part of metal particles, included in the content of investigated powders, is covered with carbon shells which hinder a free photoelectron egressing from the metal atoms. Photoelectron egressing from the opened sections of metal particles is extremely slight because of a small part of such sections in the analysis zone, and a shady effect conditioned by SWNTs "growing" from those particles [14] and rising above the other particles which form a carbon shell. O1s peak ($E_b=531$ eV) concerns an oxide on the indium surface, not CO groups on the carbon material surface, because such groups are characterized by a higher value of E_b (532.5 eV [15]).

AUGER-spectra for graphite, SWNTs and C_{60} fullerite are shown in Figure 3. The right highly energy boundary of a spectrum for SWCNTs is situated between the fullerite and graphite ones. Kinetic energy of AUGER-electrons may be described proceeding from the energies for the electron bonds on inner levels E_b [10]:

$$E_{kin}(KVV')=E_b(K) - E_b(V) - E_b(V') - U_{ef}(V,V'),$$

where U_{ef} - energy of interaction between two holes. If all E_b values are measured relative to Fermi level of a spectrometer, then $E_{kin}(KVV')$ was also determined relative to Fermi level of a spectrometer or to the sample being in contact with it. For a graphite AUGER-spectrum $U_{ef}(\sigma,\sigma)=5$ eV, $U_{ef}(\sigma,\pi)=1.5$ eV and $U_{ef}(\pi,\pi)=0$ eV [16]. Probably $U_{ef}(\sigma,\sigma)$ and $U_{ef}(\pi,\pi)$ values for fullerite and nanotubes are slightly differed from given values for graphite. However undoubtedly $U_{ef}(\pi,\pi)$ value is closed to zero, at least for nanotubes with a metal tube conduction.

On the whole the position of a highly energy AUGER-spectrum boundary for nanotubes between graphite and fullerite ones agrees with theoretical calculations of a electron structure for those compounds. It is known, that nanotubes may be both metal ($k=0$), and semiconductors (other k values) [6], depending on k integral index defined by geometric structure of a tube. The width of a prohibited zone for nanotubes - semiconductors is decreasing while their diameter is increasing. For the investigated sample an average SWNT size is 1.35 nm, as it was noted above. According to the calculations given in the work [6], for such nanotubes the width of a prohibited zone does not exceed 0.2 eV if they are semiconductors. It is often observed that the nanotube uniting in the bunches decreases the width of a prohibited zone much more [7].

For C_{60} fullerene molecule HOMO(h_u) - LUMO(t_{1u}) interval is 2.15 eV (see, for example, [17]), and for a solid fullerene energy slit is within 1.6 - 1.8 eV limits [18].

Therefore, a spectrum calibration relative to Fermi level assumes that kinetic energies of AUGER-electrons from the π -zone must be situated in the row $E_{kin}(\text{graphite}) > E_{kin}(\text{nanotube}) > E_{kin}(C_{60})$ what we observe at the experiment. However, proceeding from the consideration, $E_{kin}(\text{nanotube})$ must be closer to $E_{kin}(\text{graphite})$ than to $E_{kin}(C_{60})$. The only reasonable explanation for π -boundary shift of AUGER-spectrum for an investigated sample to the fullerite is that fullerene-like tops (ends) of nanotubes contribute to AUGER-spectrum very much. Indeed, at the soft powder pressing in the indium carrier nanotubes, growing from the metal particles, are being deformed. After deenergizing the nanotubes, due to their elasticity, are higher than the rest of the small particles being part of an investigated sample. Therefore nanotubes contribute to the spectrum of an induced electron emission most of all.

Our further work will be devoted to extracting a two-hole density of busy states from the experimental AUGER-spectrum which is a convolution of a true AUGER-one with that of electron energy losses, and interpreting characteristic properties of that state density with allowance for results of calculations for a nanotube electron structure.

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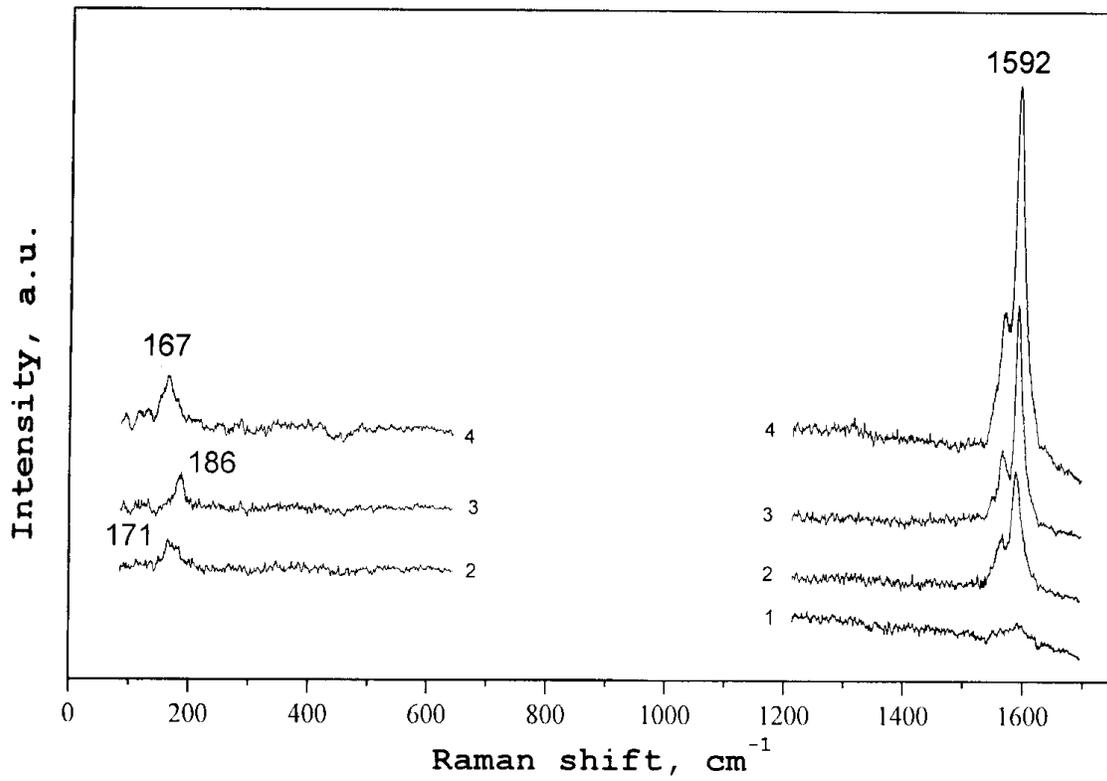


Figure 1. Raman spectra for four powders produced at the sputtering of graphite-cobalt-nickel electrodes.

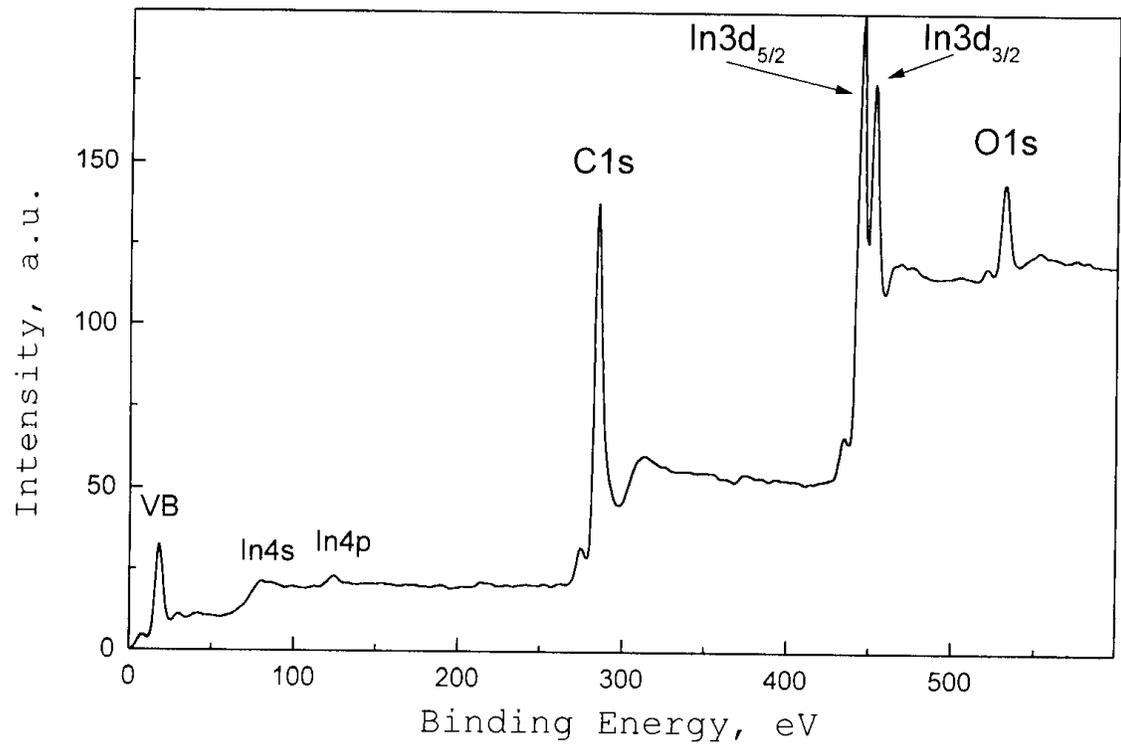


Figure 2. Survey spectrum for the powders produced at the electric arc sputtering of a graphite electrode with a cobalt-nickel catalyst.

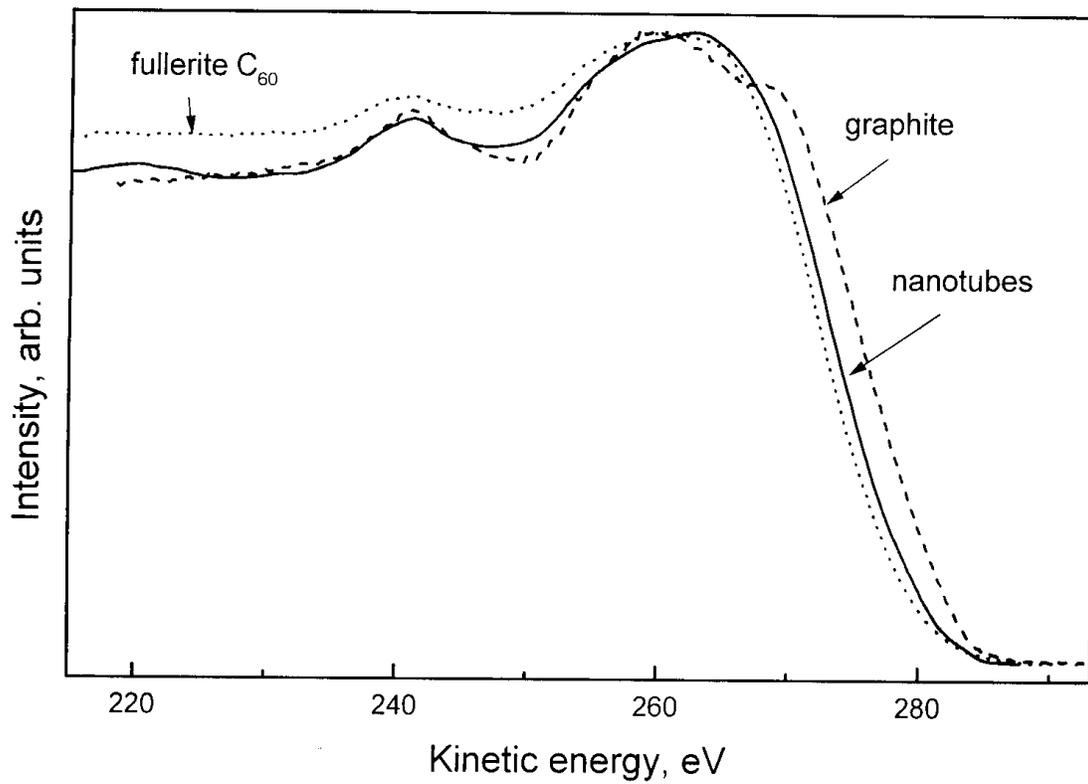


Figure 3. AUGER-spectra C(KVV) for graphite (1), SWNTs (2) and C₆₀ fullerite (3).