STRUCTURAL STUDIES OF MATERIALS

FEATURES OF THE FINE STRUCTURE OF THE X-RAY CKα EMISSION BANDS OF MULTIWALLED CARBON NANOTUBES


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The electronic structure of multiwalled carbon nanotubes of different diameters fabricated with and without the use of catalysts is investigated by means of ultrasoft x-ray spectroscopy. Nanodimensional narrowing of the CKα bands of nanotubes with lesser diameter is discovered. A dependence of the electronic structure of multiwalled carbon nanotubes on the type of the catalyst applied is established.

Keywords: carbon nanotubes, x-ray emission spectroscopy, electronic structure, valence band, hybridization

INTRODUCTION

Because of their structure, carbon nanotubes may be semiconductors and may also possess metallic conduction depending on diameter and chirality. They exhibit unusual magnetic properties, and may also be used as capillaries. Because of these distinctive properties of nanotubes, comprehensive investigations of their electronic structure, the feature which is largely responsible for these properties, are needed.

Theoretical investigations of the electronic structure of nanotubes [1-5], in particular, the density of electron states, are basically confirmed by the data of photoemission and x-ray emission spectroscopy. An increase in the density of states near the Fermi level at the ends of nanotubes due to the large quantity of disrupted bonds has been discovered [2] by studies of local photoemission spectra.

The x-ray emission CKα bands of nanotubes, which reflect the distribution of occupied valence states were used in [6] only for preliminary calculations of the density of p-states. At the same time, a dependence of the electronic structure of carbon nanotubes on the method used to produce them has been established [7]. From these data, no significant differences from graphite was found in the electronic structure of multiwalled nanotubes fabricated by an electric-arc method. On the other hand, in the CKα spectrum of multiwalled nanotubes fabricated using 2.5 mass% Co and 2.5 mass% Ni as catalysts, it was found that the intensity of high-energy states increases. In the view of the authors of [7], this growth is a consequence of the appearance of vacancies on the walls of the nanotubes. The appearance of vacancies will manifest itself in a decrease in the intensity of CKα bands and the formation of a special feature in the energy region corresponding to the sp2 hybrid states, by comparison with the spectrum of contaminated multiwalled nanotubes. In that study, however, the corresponding low-energy branch of the CKα spectrum was not detected, and the resolution ΔE = 0.5 eV probably prevented the detection of such a features in the near-peak region of the spectrum.

Thus, theoretical calculations and spectroscopic investigations have demonstrated the significant value of studies of the x-ray emission spectra of nanotubes of different radii and with varying number of walls as well as multiwalled nanotubes fabricated by means of low-temperature methods in the presence of Ni, Fe, or Co catalysts. In
view of above it is necessary to carry out a comparative investigation of the spectra of multiwalled nanotubes fabricated in the presence of these catalysts, though with a high content of the catalysts (30 mass% Ni, 33 mass% Fe, 11 mass% Co) before and after washing. The fine structure of the $C K_\alpha$ spectra of nanotubes of different diameters must also be studied.

**METHODS AND SUBJECTS OF STUDY**

X-ray spectrum investigations were conducted by an RSM-500 spectrometer at high energy resolution ($\Delta E < 0.2$ eV) and oil-free pumping through use of the NORD-250 Penning-type pumps to $10^{-4}$ Pa. In addition, to prevent “padding” of the $C K_\alpha$ bands from hydrocarbon vapors, a specially developed trap for freezing out these vapors around the anode was used. The samples were studied in different regimes ($I = 0.5-5$ mA, $U = 5$ kV); four or five surveys were conducted, the results of which were averaged. The energy position of the emission bands was determined relative to the $Cr L_1$ reference.

Fine multiwalled carbon nanotubes (Fig. 1) measuring 20-70 nm in diameter fabricated using iron (33 mass%), cobalt (11 mass%), and nickel (30 mass%) were investigated to arrive at a comparison with large multiwalled nanotubes measuring 140 nm in diameter. The fine nanotubes were produced in a low-temperature process of decomposition of carbon monoxide according to the Bell-Boudoir reaction:

$$2CO = CO_2 + C.$$  

The reaction occurs directly on catalysts belong to the iron group at temperatures from 460-470°C (Ni) and 490-500°C (Co). The state of the catalyst powder (e.g., size of particles, presence of impurities, degree of oxidation) is also of importance. In the experiments higher oxides of the corresponding metals (iron, cobalt, nickel) with particle sizes from 5 to 50 μm were used. Note that the rate of decomposition of carbon monoxide depends substantially on the presence of hydrogen in the gaseous medium. Gaseous hydrogen (about 2% of the total gas flow) was used.

One advantage of the process being considered here is that at such a low temperature there is no homogeneous condensation of carbon out of its vapors, as is usually observed in high-temperature processes in a methane or acetylene medium when both fullerenes and carbon soot particles are formed together with the nanotubes. In the process being used here this is excluded, and all the carbon segregations are only the product of decomposition of carbon monoxide on the catalyst. Thus, the product which is obtained does not require additional purification, which simplifies the entire process besides rendering it less expensive.

The structure of such formations is distinct and depends on both the conditions of the experiment and the type of catalyst. The most ideal multiwalled nanotubes are formed on a cobalt catalyst. Their diameter is from 10 to 30 nm, with length up to several micrometers. The quantity of catalyst in the nanotubes before and after cleaning is determined by chemical analysis.

**RESULTS AND DISCUSSION**

The $C K_\alpha$ emission bands of multiwalled nanotubes fabricated using Co, Ni, and Fe catalysts and subsequently washed from these catalysts were compared with the spectrum [7] of nanotubes synthesized with the participation of a mixture of 2.5 mass% Co and 2.5 mass% Fe (Fig. 2). The results show that the latter is most similar to the spectrum of
multiwalled nanotubes that have been produced in the presence of iron. In the spectrum presented in [7], however, the intensity of the \(a''\) and \(e\) peaks is significantly higher. Since in [7] the \(CK_{\alpha}\) emission band is presented only in the range 275-285 eV, it is not possible to compare the width of the spectra or to analyze the low-energy parts of the spectra. At the same time, the spectra of multiwalled nanotubes washed from Co and Ni differ even more from the results of [7]. This underscores the need to study the electronic structure of carbon nanotubes as a function of the catalyst metals that are used in fabricating the nanotubes.

From a comparison of the spectra that we have obtained (Fig. 2, curves 1-3), it is evident that the low-energy branch of the spectrum of a nanotube that has been washed from the cobalt catalyst differs substantially from the other branches, with the \(\alpha\) peak splitting to the build-ups \(a'\) and \(a''\) in a neighborhood of 275.5 eV. The fine structure of the \(CK_{\alpha}\) of tube that has been washed from the cobalt corresponds to the peak of the density of electron states obtained through a calculation of the electron structure of single-walled nanotubes. The \(sp\sigma(a')\) and \((sp\sigma + pp\sigma)\) hybrid states \((a'')\) are concentrated at these peaks. The near-peak build-ups \(b\) that may arise as a consequence of the formation of \(sp\)-hybrid bonds between the carbon atoms and atoms of the metals once the \(sp^2\)-orbitals overlap the high-energy \((3d + 4s)\) states appear in the spectra of all the cleaned multiwalled nanotubes. This isolation of the peaks is related to the difference between the energies of states that exist along parallel \(\sigma\)-bonds that are directed along the axis of the nanotube, and the bonds that are directed at oblique angles to the nanotube axis. This slight splitting is, however, observed only in the most thin multiwalled nanotube that has been washed from cobalt, with diameter around 20 nm, whereas in thicker nanotubes, with \(d \approx 40\) nm (washed from Ni) and \(d \approx 70\) nm (washed from Fe), it vanishes, since the curvature of multiwalled nanotubes decreases as their diameter increases, and the angles between the \(\sigma\)-bonds approach that typical in graphite and, consequently, the difference between the energies of the above states decreases.

In the near-peak region of the high-energy branch of the \(CK_{\alpha}\) bands, besides the \(c\) peak there are two other features of the bands, \(c'\) and \(d\). According to calculated data [5], the vertex of the \(CK_{\alpha}\) band of the multiwalled nanotube here reflects hybrid \(pp\sigma\) states to which \(pp\pi\) states, which may be described by two peaks separated by a deep minimum, are added upon rotation of the graphene sheet in the nanotube. This is a result of the fact that the \(\pi\)-overlaps in the direction of the axis of multiwalled nanotubes differ from those that are in the radial direction. In the radial plane within the nanotube, the \(\pi\)-overlap is greater, as a result of which the \(pp\pi\) states have lesser energy and intermingle with the \(pp\sigma\) states described by the computed peak to which the feature \(c'\) of the emission bands corresponds. The degree of \(pp\pi\) overlapping in the direction of the axis of multiwalled nanotubes both within the tube as well as on its surface is the same and less than within the multiwalled nanotubes in the radial direction. Therefore, the states that are present in the overlaps are concentrated at the computed maximum corresponding to the features of the \(d\) peak of the multiwalled nanotubes. The \(np_z\) states that overlap very slightly in the radial direction above the surface of the nanotubes are reflected in the highest-energy maximum \(e\).
From a comparison of the spectra obtained from multiwalled nanotubes of different diameters (Fig. 3), it is evident that with decreasing diameter of the nanotubes, their CKα bands contract in the high-energy region corresponding to the pπ states, that is, with \( d \approx 20 \) nm the CKα band is narrowest, and with \( d \approx 70 \) nm, broadest in the region of energies corresponding to both the maximum c and the feature d.

Since the CKα spectra of nanotubes that had been preliminarily washed from catalyst metals (in order to prevent interaction between carbon atoms and those of residual metals from influencing the spectral width) were compared, we obtained spectra of a nanotube that had been synthesized without the use of catalysts the diameter of which, \( d \approx 140 \) nm, was close to the diameter of a multiwalled nanotube that had been washed from iron. A comparison of these spectra showed that their parameters practically coincided. This attests to the fact that where the diameter of the tubes is greater than 70 nm, the overlap of the πpz orbitals is already practically the identical, a result which is reflected in the similarity of the spectra.

A clearly resolved peak e is apparent in the high-energy part of the spectra of all the nanotubes (282.5 eV); the intensity of this peak grows slightly in the series of washed nanotubes thus: Co → Ni → Fe. The increase in the intensity of the e peak caused by an increase in the population of the π-subband may be induced by the additional electron density introduced by the atoms of metals found within the nanotubes and interacting with the carbon atoms of the multiwalled nanotube. This type of variation of the intensity of the e peak may be related to the fact that the multiwalled nanotubes were cleaned free of the cobalt catalyst better than from the other metals.

To account for the influence of the type of catalyst on the electronic structure of the multiwalled nanotubes, let us compare the spectra of nanotubes before and after washing. Thus, the low-energy branch of the spectra varies to a significantly lesser extent than the high-energy branch (Fig. 4, line a). Following washing from cobalt, the intensity of the spectrum in the high-energy branch of the band decreases substantially, which leads to a contraction of the CKα band. This decrease is obviously related to the increase in the contribution to the energy distribution of the valance electrons of degenerare Cpz states belonging to ruptured bonds following removal of cobalt atoms. This attests to an arrangement of the cobalt atoms predominantly in the nanotube channel (Fig. 1a).

The spectra of multiwalled nanotubes that have been washed free of the iron catalyst and those that have not been washed free (Fig. 4, line b) are quite different. Thus, the intensity of the two peaks b and e of a tube that has been washed free of iron falls slightly, which attests to the formation of a small quantity of ruptured bonds upon removal of the metal both from the walls and from the channel of the multiwalled nanotubes (Fig. 1b).

A comparison of the CKα bands of nanotubes obtained with the participation of nickel and nanotubes that had been cleaned free of nickel (Fig. 4, line c) showed that these bands are practically identical. This is a consequence of the fact that nickel atoms are significantly more strongly bound with the carbon atoms of the nanotubes than are the cobalt or iron atoms, due to the formation of covalent-type binding states between the carbon and nickel in the walls of the synthesized nanotubes.
Since the narrowing in the low-energy branch of the spectrum is much less than in the high-energy branch, it may be claimed that it is precisely those bonds in which $C_p$ electrons participate that are the bonds that are ruptured as a consequence of decobalting. These carbon bonds may arise only with Co atoms that are found in the nanotube channels. The slight narrowing of the spectrum in the low-energy region attests to the very small number of breaks in the bonds of carbon atoms with cobalt atoms concentrated in the walls of the nanotubes.

After the nanotubes have been washed free of iron, their $C_K\alpha$ bands become narrow in the low-energy branch to a far extent than with the use of cobalt catalyst; this narrowing is substantially less in the high-energy branch. This indicates that significantly greater quantities of Fe catalyst are removed from the nanotube walls than if the Co catalyst is used; moreover, following synthesis of the nanotubes, far less Co catalyst than iron catalyst is found.

From an analysis of the spectra it follows that the interaction between the atoms of cobalt, iron, and nickel, on the one hand, and the carbon atoms of the nanotubes, on the other hand, differs substantially. Thus, let us compare the combined emission bands of multiwalled nanotubes that have not been cleaned free of the metals and that contain 11 mass% cobalt, 30 mass% nickel, and 33 mass% iron (Fig. 4, line d). The low-energy branches of the spectra of multiwalled nanotubes contaminated with cobalt and iron practically coincide in the range 267-275 eV. This attests to the existence of the same energy distribution of their valence states present in the $sp^2$ hybrid bonds of the lower half of the valence zone. At the same time, in the interval of energies 275 -277 eV the fine structure of the high-energy branch of the $C_K\alpha$ spectrum of a nickel-contaminated nanotube differs substantially from iron- and cobalt-contaminated nanotubes. This difference is due to the appearance of an additional, clearly resolved build-up $a''$ with energy position 275.5 eV along with the disappearance of the near-peak build-up $b$. The total width of the build-ups $a$ and $b$ in the spectra of nanotubes with iron and cobalt impurity is close to the width of the build-up $a''$ in the spectra of nanotubes contaminated with 30 mass% nickel. This indicates that in nickel-contaminated nanotubes, the low-energy $sp^2$ states mix with the $p_z$ orbitals, decrease their energy. This can occur only as a result of more energetically advantageous interaction between electrons of those states and other atoms. These atoms may be nickel atoms in which high-energy $(d + 4s)$ states hybridize with $sp^2$ orbitals that exist in the $\sigma$ bonds of the nanotube walls. As a consequence, $spd$ hybrid bonds will form between the nickel and carbon atoms. This must lead to additional splitting of energy levels and a decrease in their energy, which also manifests itself in a decrease in the energy of the build-up $b$ and its merging with the feature $a''$. In nanotubes that have been produced with the participation of nickel catalyst, nickel atoms are found predominantly on the tube walls. Upon washing of the nanotubes free of the Ni catalyst, the nickel atoms remain on the nanotube walls with no change in their quantity. This also underscores the practically complete coincidence of the $C_K\alpha$
emission bands before and after washing (Fig. 4, line c). This also serves to attest to the fact that the bond between these atoms and the atoms of the nanotubes is quite strong and is basically covalent in nature.

CONCLUSIONS

The following conclusions were arrived from a study by means of ultrasoft x-ray spectroscopy of the electronic structure of multiwalled carbon nanotubes of different thicknesses that have been produced through the use of different catalysts.

As a consequence of overlapping of $\pi p_z$ and $\sigma sp^2$ orbitals within the nanotubes, mixed ($\pi + \sigma$) binding states are formed. These states appear in the form of features in the density of states distinguished by energy position due to the different degrees of overlap of the carbon atoms orbitals in directions along the axis and in the radial planes within and above the nanotubes.

Nanodimensional narrowing of the $CK_\alpha$ bands is related to a decrease in the degree of $\pi$-overlap of $Cp_z$ orbitals over the surface of nanotubes as their diameters decrease.

Because of the appearance of $\pi$-type ($spd + Cp_z$) weakly binding states in the course of synthesis of nanotubes in the presence of iron and cobalt catalysts, as well as ($spd + Csp^2$)-covalently binding states with high binding energy, which are formed in the presence of the Ni catalyst, the cobalt atoms and, to a lesser degree, the iron atoms are situated between the walls of the nanotubes. Meanwhile, the nickel atoms are inserted into the walls of the nanotubes, as a consequence of which the nanotubes are washed free of iron and cobalt to a considerably better degree than from nickel.

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REFERENCES