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Dedicated to Professor Valer Fărcăşan at his 85th anniversary

ELECTRONIC PROPERTIES OF THE ZIGZAG CARBON-NITRIDE NANOTUBES

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ABSTRACT. The influence of possible defects of atoms due to deviations from the 1:1 stoechiometry inside of zigzag carbon-nitride nanotubes has been considered in this paper. PM3 calculations demonstrate that small quantities of nitrogen incorporated into carbon nanotube lead to thermodynamic instability relative to the pure carbon nanotubes.

This doping of the carbon nitrogen nanotubes does not significantly modify the bands in the vicinity of the Fermi level and these tubes are semiconductors.

Keywords: *carbon-nitrogen nanotubes, semiempirical calculations, electronic properties and oscillator strengths.*

INTRODUCTION

Since their discovery [**1**], carbon nanotubes and related materials have attracted much interest due to their many exceptional properties. Recently, nitrogen doping of carbon nanotubes has gained increasing attention [**2, 3**]. Up to date, only small quantities of nitrogen (<10%) have been incorporated experimentally into carbon nanotubes and filaments [**4-10**].

In this study we determined the structural, energetic and electronic properties of the (10,0)CN nanotubes with deviations from the 1:1 stoechiometry. Plots of density of states have carried out the electronic properties analysis.

METHOD OF CALCULATIONS

Carbon-nitrogen nanotubes with zigzag geometry have been considered theoretically by performing *PM3-RHF* [**11**] type semiempirical molecular orbital calculations by using Spartan '02 package [**12**].

The densities of states (*DOS*) have been calculated by the extended Hückel tight-binding method using BICON-CEDIT package [**13**]. Calculations of the oscillator strength were carried out using ICON-EDIT package [**14**].

RESULTS AND DISCUSSION

Enthalpy of formation

The structure of the basic *(10,0)C* nanotubes was taken from reference [**15**]. This tube has been virtually doped with 0, 1, 2, 3, 4, 5, 10, 20, 30, 40 or 50 nitrogen atoms. After geometry optimization we found that the carbon-nitrogen distances vary between 1,39 and 1,41Å, the C-N-C angles ranging from 117-120^0 and the N-C-N angles between 119 and 123^0. These values are in agreement with the experimental results, [**16**].

Figure 1 shows the dependence of the enthalpies of formation of the carbon nitrogen nanotubes with the nitrogen content (*x*). It comes out that the carbon nitride nanotubes are thermodynamically unstable with the increasing of *x*. This might explain the synthesis of carbon-nitride nanotubes containing no more than 13%N [**17**].

Density of states

The density of states obtained for *(10,0)C* nanotubes are shown in **Figure 2a**. From the partial *DOS(E)* plot it can be seen that the lowest bands (valence bands) are composed of *C(2s)* derived states and the conduction bands are consisted of *C(2p)* derived states.

When the band gap is not very large, usually ranging from 0,5 to 3,0eV, the material is a semiconductor, while an insulator has an E_g>3eV [**18, 19**].

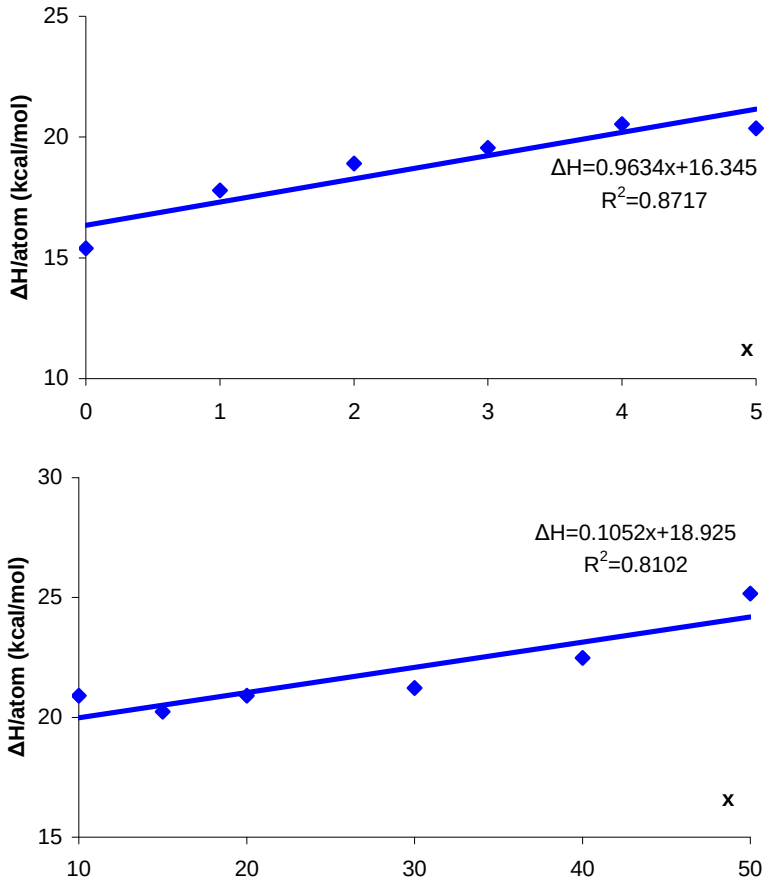

Fig. 1. Enthalpy of formation (per atom) as a function of nitrogen content (x) for (10,0)$C_{100-x}N_x$ tube.

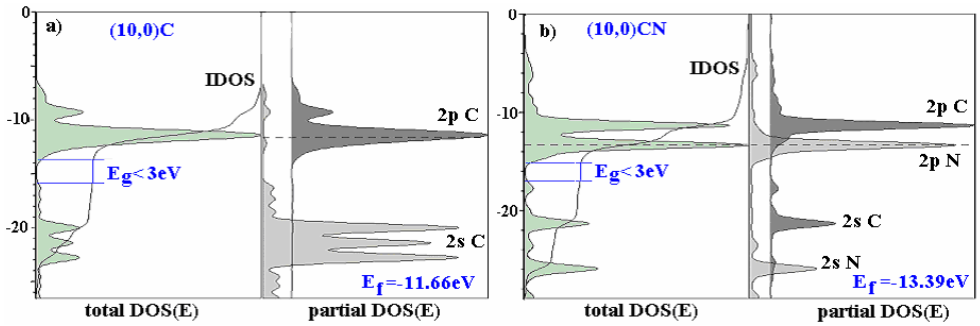

Fig. 2. The total, partial *DOS* and *IDOS* diagrams for (10,0)C and (10,0)CN tube.

The total DOS(E) and integrated DOS (*IDOS*) diagram confirm that (10,0)C nanotube is a semiconductor, which is in agreement with the experimental results published by Dresselhaus [**20**].

The total DOS and the N(2s, 2p), C(2s, 2p) contributions for (10,0)CN tube (with the 1:1 stoechiometry) are given in **Figure2b**. The partial DOS(E) plot shows that the lowest band is derived N(2s), C(2s) orbitals and conduction bands are composed of 2p orbitals of the nitrogen and carbon, respectively. Because the band gap energy is 2eV the nanotube is a semiconductor.

Clearly, in all cases displayed in **Figure 3**, the doping with nitrogen maintains the semiconductor character of the tube. Doping of the tube leads to a lowering of the Fermi level to the valence bands of the undoped tube. In the lowest unoccupied bands of the undoped tube new bands are formed. These bands correspond to the formation of an acceptor level in semiconductors with very low dopant concentration. The Fermi level is not located in the middle of Van Hove singularities which is an indication that the overlap is not very strong [**21**].

These date suggest that carbon nanotubes with small quantities of nitrogen give the same response as a tube with a closer to 1:1 stoechiometry and such tubes could be used as nanodevices.

Electronic transition

One spectral quantity that can be obtained is the oscillator strength of the electronic transitions, *f*, [**22**]. Oscillator strengths of approximate 1 signify intense transitions, while oscillator strengths of rough 0.001 denote weak transitions, [**23, 24**]. The highest values of oscillator strengths for the (10,0)&1,2,3,4N tubes lie between 0.80 (4553.8 cm^{-1}) and 0,95 (4027.9 cm^{-1}) shown intense transitions, **Table 1**.

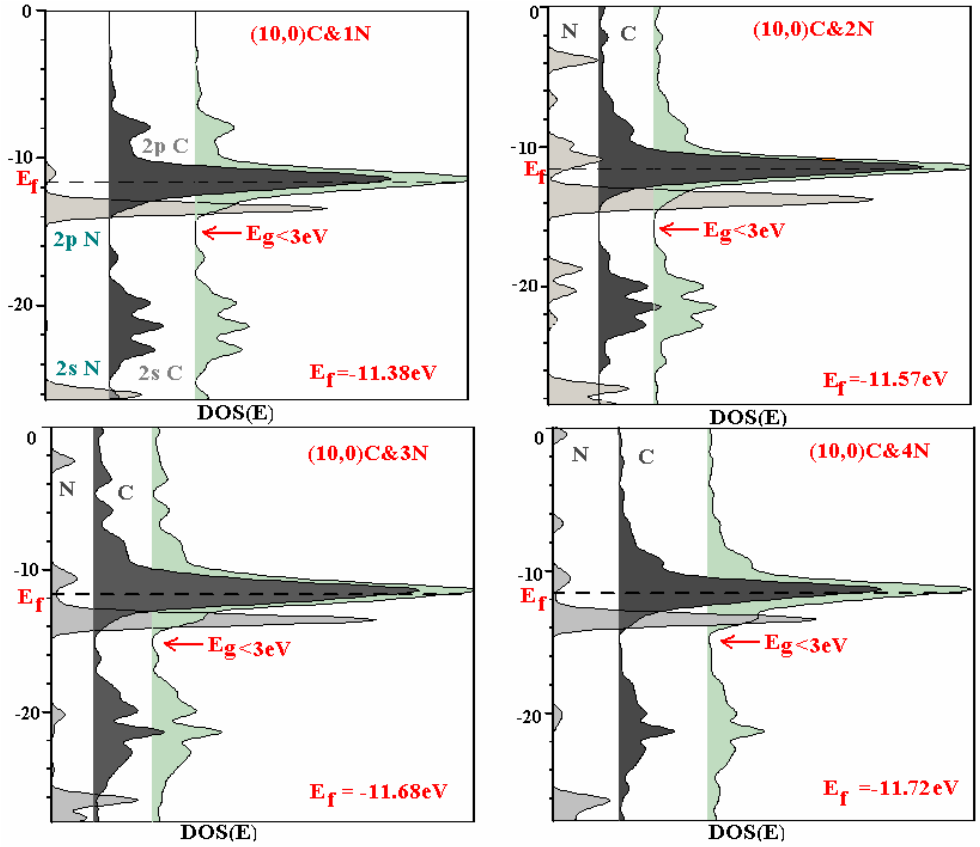

Fig. 3. The total and partial *DOS* diagrams for (10,0)C&xN tube where x =1, 2, 3, 4.

Table 1.

Calculations of oscillator strengths, *f*, wave numbers, *ú* and gap energy, E_g, for *(10,0)* nanotubes (values of *f* >0.1).

tub	ú (cm^{-1})	E_g (eV)	f	Electronic transition bring from filled to unfilled levels
(10,0)C	4764.0	0.6	0.14	homo-5→lumo+5
(10,0)C&1N	4105.6; 4755.7; 2221.9	0.5	**0.94** 0.34 0.23	homo-1→lumo+4 homo-3→lumo+4 homo-2→lumo+1
(10,0)C&2N	3950.7 2359.8 4914.2	0.5	**0.91** 0.26 0.25	homo-1→lumo+5 homo-2→lumo+2 homo-3→lumo+5
(10,0)C&3N	9743.7 10521.3 3909.2 11799.8 11022.2	0.6	**0.80** 0.57 0.38 0.23 0.22	homo-2→lumo homo-4→lumo homo→lumo+1 homo-4→lumo+1 homo-2→lumo+1

tub	ú (cm^{-1})	E_g (eV)	f	Electronic transition bring from filled to unfilled levels
(10,0)C&4N	4027.9 4127.0	0.5	**0.95** 0.25	homo→lumo+5 homo-1→lumo+5
(10,0)C&5N	4638.6	0.6	0.17	homo-1→lumo+5
(10,0)C&10N	2850.5	0.5	0.16	homo-3→lumo+1
(10,0)C&20N	7018.3	0.9	0.23	homo-3→lumo+4
(10,0)C&30N	8856.6 5192.3 12850.0 6879.1	1.1	0.40 0.27 0.23 0.20	homo-1→lumo+5 homo-2→lumo+2 homo-4→lumo+5 homo-4→lumo+2
(10,0)CN	6945.2 2281.6	0.9	0.43 0.21	homo-4→lumo+5 homo-2→lumo

The results are in agreement with the electronic density states plots shown in **Figure 3**, which denote the splitting of the Van Hove singularities corresponding to C orbital derived states.

CONCLUSION

All carbon nitride nanotubes are thermodynamically unstable relative to their carbon analogues and their stability decreases with the increasing of the nitrogen content. The $C_{100-x}N_x$ tubes have semiconductor properties for all x = 0-50.

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