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LETTER

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Structural, elastic and electronic properties of isotropic cubic crystals of carbon and silicon nanotubes: Density functional-based tight binding calculations.

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Atomic models of cubic crystals (CC) of carbon and graphene-like Si nanotubes are offered and their structural, cohesive, elastic and electronic properties are predicted by means of the DFTB method. Our main findings are that the isotropic crystals of carbon nanotubes adopt a very high elastic modulus B and low compressibility β , namely $B = 650$ GPa, $\beta = 0.0015$ 1/GPa. In addition, these crystals preserve the initial conductivity type of their “building blocks”, i.e. isolated carbon and Si nanotubes. This feature may be important for design of materials with the selected conductivity type.

Introduction : Since Iijima’s report [1], carbon nanotubes (C-NTs) have been the subject of growing interest due to their potential applications in nanoelectronic devices. A wide variety of C-NTs-based materials, such as “bundles” or “ropes”, films (*buckypaper*) and tubular crystals, have been prepared or theoretically proposed and their mechanical and electronic properties were intensively examined, see for example Refs [2-5]. Let’s note that as carbon NTs possess extremely anisotropic properties (for example, typical Young’s moduli of single-walled C-NTs are about $Y \sim 800$ -1200 GPa, whereas their shear moduli are $G \sim 20$ -40 GPa), these *non-covalent* (molecular) materials, where the tubes are bonded *via* weak van der Waals forces, are *essentially anisotropic* systems. In addition, the association of single nanotubes into condensed systems leads to sharp changes in their intrinsic electronic properties as the symmetry is lowered [4].

Recently, the theoretical models of *isotropic* carbon materials in form of 2D and 3D *ordered covalent networks* of C-NTs (2D - square, hexagonal; 3D - cubic, diamond-like *etc.*) were constructed using T, X, Y - like tubes cross-junctions as nodes [6]. However, synthesis of such hypothetical systems will be very problematic.

In this paper we propose atomic models of *isotropic non-covalent* cubic crystals (CC) of carbon nanotubes. Using cubic crystal of (4,4)C-NTs as an example, structural, cohesive, elastic and electronic properties of such materials are examined by means of the density-functional-based tight-binding method (DFTB). The results obtained are discussed in comparison with a cubic crystal constructed from the same (4,4) silicon nanotubes (Si-NTs). As carbon and silicon NTs have rather different mechanical and electronic properties [2,3,5,7], comparison

of such CC should be of interest, in particular, in view of the high attention which is paid now to silicon-based nanomaterials.

Structural models and method of calculations : The proposed atomic model of ordered non-covalent cubic crystals of nanotubes is presented in Figure (1). These crystals may be considered as generated by three aligned systems of parallel tubes which are located orthogonally to each other along x , y and z axes so that the nanotube crossbar junctions are bonded *via* van der Waals interactions.

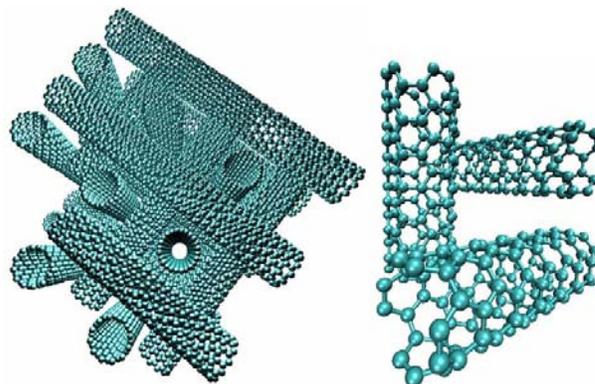


Figure (1) : (*Color online*) Fragment of the proposed isotropic cubic crystal of C, Si nanotubes (*left*) and elemental cell of cubic crystal composed from *armchair* (4,4) C-NTs (*right*).

In our numerical simulations we have focused on single-wall *armchair* (4,4) carbon nanotube as an example. The unit cell of the corresponding cubic crystal of these C-

NTs ((4,4)C-NT-CC), which includes three fragments of infinite-long tubes located at a distance of ~ 0.3 nanometers (the so-called van der Waals gap) as depicted in Figure (1), contains 336 carbon atoms. Accordingly, the unit cell of a similar cubic crystal of *armchair* (4,4) silicon NTs ((4,4)Si-NT-CC) contains 288 Si atoms. Note that in the construction of the above (4,4) silicon NT we used a Si graphene-like sheet.

Our calculations were performed within the DFTB method [8], which was well tested for the simulations of various carbon and Si nanostructures. The dispersion-corrected modification of DFTB with the implementation of an empirical dispersion term parameterised in the framework of the UFF method was used for correct description of weak Van-der-Waals interactions [9].

As a result, we have evaluated and analyzed a set of physical parameters of the proposed cubic carbon and silicon tubular crystals such as optimized lattice parameters (a), density (ρ), bulk moduli (B), compressibility (β), formation energies (E_{form}), as well as total and partial density of states (DOS).

Cubic crystal of carbon nanotubes. At the first step, we have evaluated the equilibrium lattice parameter of the examined (4,4)C-NT-CC, where the initial constructed crystal structure has been fully relaxed with respect to atomic positions; the result is presented in Table (1). Note that the optimized atomic geometries of carbon nanotubes in the constructed crystal and for isolated (4,4)C-NT coincide well: no appreciable distortions of the tubes walls in CC are present, and the difference in the corresponding C-C distances in (4,4)C-NT and (4,4)C-NT-CC is negligibly small.

Table (1) : Cohesive energies (E_{form} , in eV/Å), lattice constants (a , in Å), mass density (ρ , in g/cm³), and radii of nanotubes (R , in Å) for the cubic crystals of carbon and silicon nanotubes according to DFTB calculations.

System	$-E_{\text{form}}$	a	ρ	R
(4,4)C-NT-CC	0.108	17.22	1.31	2.79
(4,4)Si-NT-CC	0.222	23.25	1.07	4.37

Next, we have examined the stability of the proposed crystal. For this purpose the cohesive energy (E_{coh}) of CC has been calculated with respect to the isolated nanotubes as: $E_{\text{coh}} = 1/3\{E_{\text{tot}}(\text{CC}) - 3 E_{\text{tot}}(\text{NT})\}$, where E_{tot} are the total energies of the cubic crystal and “free” nanotubes at their optimized geometries. In this way, a negative value of E_{coh} indicates that it is energetically favorable for the given nanotubes to form a stable crystal. The results (Table 1) show that E_{coh} is negative, *i.e.* the formation of the predicted crystal is favorable.

One of the most interesting results obtained seems to be the elastic characteristics of the proposed tubular material, Table (2). According to our calculations, the bulk modulus B of the (4,4)C-NT-CC is very high (about 630 GPa), *i.e.* it is higher than for crystalline diamond (438-467 GPa [10]) as well as for many other synthesized or predicted carbon nanomaterials, see Table (2). Comparable values of the bulk moduli ($B \sim 462$ -546 GPa) were reported [11] for high-pressure samples of carbon nanotubes and C_{60,70} fullerenes – from 530 GPa to 1 TPa see [13].

Table (2) : Bulk moduli (B , in GPa) and compressibility (β , in 1/GPa) of the proposed cubic crystals of carbon and silicon nanotubes in comparison with diamond and some hard carbon nanomaterials.

System/References	B	β
(4,4)C-NT-CC	630	0.00159
Diamond [10]	438-467	0.00228-
aggregated diamond nanorods [13]	491	0.00214
anisotropic 3DC ₆₀ polymer [12]	288	0.00204
phase of pressed carbon NTs [11]	462-546	0.00347
phase of pressed C ₆₀ [14]	530	0.00216-
		0.00183
		0.00187
(4,4)Si-NT-CC	180	0.00556

However, as distinct from the suggested isotropic cubic crystal with sp^2 -type of C-C bonding, the structures of the above-mentioned materials have been not identified and should be anisotropic and the mixed sp^2 - sp^3 bonding type should be expected.

On the other hand, the suggested cubic crystal (with $\rho = 1.3$ g/cm³) exhibits the maximal modulus (and minimal compressibility) among other known carbon materials with comparable density: for example, the bulk moduli for hyperdiamond and hyperlonsdaleit C₂₈ (with $\rho \sim 1.1$ g/cm³) are much smaller: $B = 45.5 - 45.9$ GPa, for so-called supergraphite C₃₆ (with $\rho \sim 1.4$ g/cm³) $B = 64$ GPa *etc.*, see Ref. [15].

Let us discuss the electronic properties of the cubic crystal (4,4)C-NT-CC. Its total and partial densities of states (DOSs) in comparison with DOSs of the isolated *armchair* (4,4) carbon nanotube are shown in Figure (2).

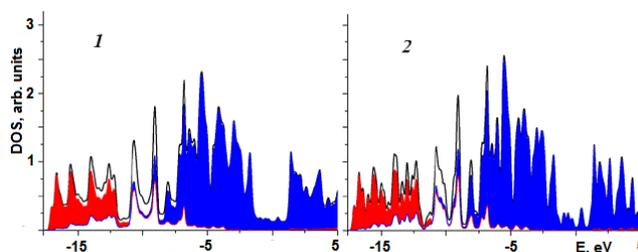


Figure (2) : (Color online) Total (full line) and partial C 2s (red) and C 2p (blue) densities of states (DOS) for: 1 - isolated *armchair* (4,4) nanotube and 2 - cubic crystal of (4,4)C-NTs.

As is seen, the (4,4)N-NT in accordance with earlier results [4,6,12] is metallic-like and exhibits a DOS “plateau” near the Fermi energy E_F . In the assembling of these NTs into a crystal, the tube-tube interactions lead to some degeneracy of the bands near the E_F and to the formation of local DOS peaks in this energy region, but the metallic-like type of cubic crystal is retained. This situation differs from the reorganization of the band structure of metallic-like carbon tubes within the “bundles”, when stronger interactions between parallel-aligned tubes lead to the opening of a gap at the Fermi level and the “bundles” exhibit a semiconducting behavior, see review [4].

Cubic crystal of silicon nanotubes. The results obtained for the isostructural cubic crystal of (4,4) Si nanotubes are summarized in Tables (1, 2). For this system, the atomic structure of isolated (4,4)Si-NTs is retained; the negative E_{coh} is indicative of a possibility of existence of such nanotubular crystal. The predicted bulk modulus ($B \sim 180$ GPa) of the (4,4)Si-NT-CC is about 3.5 time smaller than for the C-NT-based crystal. This result reflects the well-known fact that the stability of silicon nanotubes formed by rolling of Si graphene-like sheets decreases (as compared with carbon nanotubes), as Si atoms prefer the sp^3 hybridization.

The isolated *armchair* (4,4)Si-NT exhibit metallic-like properties, see [7]. As can be seen from Figure (3), the electronic properties of the (4,4)Si-NT-CC, as compared with individual Si NTs, also remain practically unchanged, i.e. they are metallic-like.

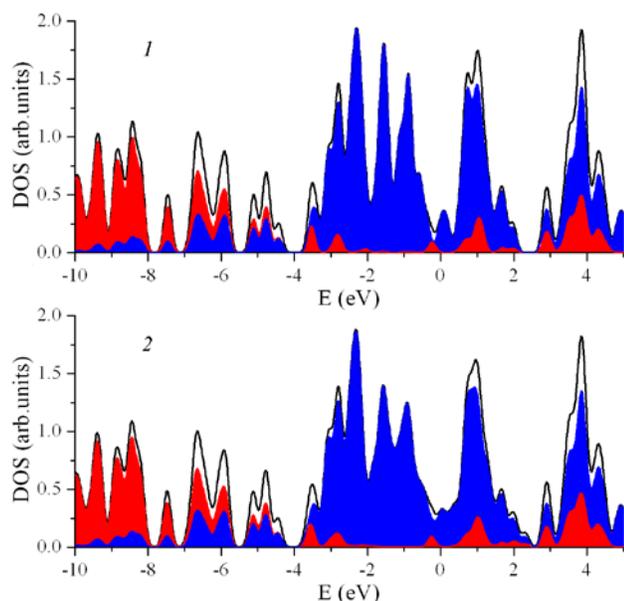


Figure (3) : (Color online) Total (full line) and partial Si 3s (red) and Si 3p (blue) densities of states (DOS) for: 1 - isolated *armchair* (4,4) nanotube and 2 - cubic crystal of (4,4)C-NTs.

Conclusions. The isotropic non-covalent tubular crystals were proposed and their structural, elastic, cohesive and electronic properties were predicted by means of the DFTB method. We showed that these low-density carbon tubular crystals will be energetically stable systems, which will adopt elastic modulus B higher than for crystalline diamond and comparable with the known superhard carbon nanomaterials. The examined crystals of C and Si nanotubes preserve the initial conductivity type of their "building blocks", i.e. isolated carbon and Si nanotubes. In our opinion, the obtained feature, i.e. preservation by the crystal of the conductivity type of the starting individual NTs, may be important for design of materials with the selected conductivity type.

Finally, the realization of such crystals can be described as consecutive "stacking" of perpendicular single layers of carbon NTs on the ordered system of vertically - aligned nanotubes located at a required distance from each other. Such systems (*the so-called vertical-aligned arrays*

of C-NTs) have been successfully prepared, see [16]. Probably, in this way, a wide family of tubular crystallites could be prepared, among them there could be crystals of other symmetries (for example, hexagonal), crystals of multi-walled tubes or crystals of tubular "bundles", as well as "mixed" crystals of various inorganic NTs, for example, BN, BCN, AlN etc. nanotubes.

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