Analysis of the band structure of tetrahedral diamondlike crystals with valence bonds: Prediction of materials with superhigh hardness and negative electron affinity

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In the present paper, an analysis of the energy gap E_{gap}, work function X, lattice constant L, and some other characteristics of the tetrahedral diamondlike crystals was performed in the framework of tight-binding band-structure theory. Comparison with experimental data for diamondlike carbon films illustrates a good agreement with the obtained results, providing the possibility to estimate indicated parameters using the relation: $E_g + X = 5.3$ eV $- E_v$. The materials with extreme properties (hardness, exceeding that of natural diamond; high values of negative electron affinity, etc.) have been predicted.

From calculations of the dependence of the energy bands on the lattice constant L (i.e., on the characteristic distance between atoms in lattice $d \sim L$) for tetrahedral configurations performed by Shockley, Kimbell, Slater, Joannopoulos, Pauling, Philips, and Harrison,[1–8] we can see, that this dependence is nearly the same for all cubic crystal materials of the fourth group in the periodical table of elements: carbon-diamond, silicon, germanium, tin in cubic modification, as well as mixtures of cubic crystals such as SiC, SiGe, and probably, others, like GeC, GeSn, SiSn, SnC, or three-component materials like $Si_xC_{1-x}Ge$, Si_xC_xSn, etc. Moreover, even alloys of elements of the third to fifth groups with cubic lattice in the case of valence-bond domination obey the above-mentioned dependence. Figures 1 and 2 illustrate this for different materials whose data on energy gaps E_{gap} and lattice constants L were mainly taken from literature.[9–15] A good agreement between experimental data and theoretical curves is seen.

Let us consider this question qualitatively in more detail. The last calculations of the electron and mechanical parameters of face-centered cubic (FC-cubic) crystals with complex bonds (valence and ionic) were performed by a number of authors (Animalu, Chelicovsky, and Cohen, Pantelides, and Liu and Cohen)[15–18] in linear combination of atomic orbitals in (LCAO), tight-binging and pseudopotential approximations, with pseudopotential being considered not small. In this case Fourier components of the matrix elements of the bond energy corresponding to **k** oriented along [111] in k-space proves to be dominating. Then energy of metallic, valence, and ionic bonds can be calculated from the matrix elements of the atomic interaction: $H_{12(21)} = \langle Y_a | H | Y_b \rangle$. If we designate the matrix element of energy as $\varepsilon_s = \langle Y_a^S | H | Y_a^{S*} \rangle = \langle Y_b^S | H | Y_b^{S*} \rangle$ and $V_2 = -H_{12(21)} = \langle Y_a^P | H | Y_b^P \rangle$, then energy of the conduction band E_c (C-band energy) in some approximation can be calculated, in accordance with,[8] as antibonding states energy ε_a

$$E_c \equiv \varepsilon_a = (\varepsilon_s + V_2),$$

and energy of the valence bonds as bonding states energy ε_b

$$E_v \equiv \varepsilon_b = (\varepsilon_s - V_2).$$

This gives the covalent energy gap

$$E_g = E_c - E_v \cong \varepsilon_a - \varepsilon_b = 2V_2. \qquad (1)$$

In the case of bi- or more component crystals nonsymmetry of bound electrons density takes place, and the "ionic" component of the energy band can be taken into account[15] using an approximation for electronegativity of elements X_A, X_B, and L, Pauling relation for the degree of ionicity[6,7]

$$I = E_{gi}^2 (E_{gh}^2 + E_{gi}^2)^{-1},$$

or proposed by Harrison through matrix element V_2 (valence) and V_3 (ion bonds)
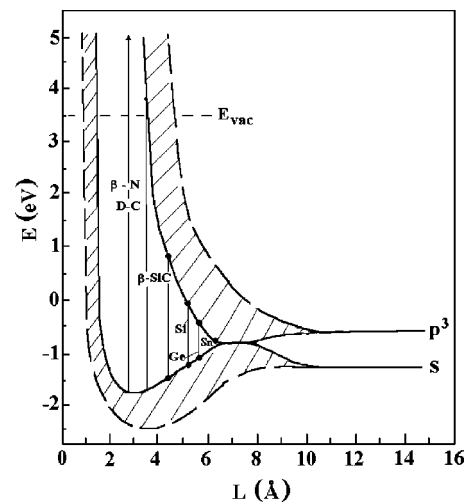
$$I_i = V_3 (V_2^2 + V_3^2)^{-1/2}.$$

FIG. 1. Energy bands for FC-cubic crystal modification of fourth group element of the periodical system as result of the sp-3 hybridization of valence electron orbitals, in dependence of the lattice constant L.[1–6]
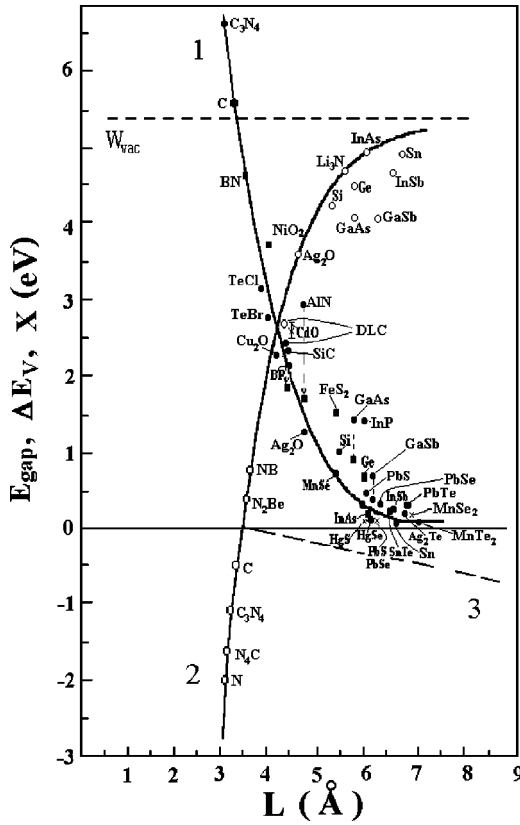
FIG. 2. Theoretical dependences of the energy gap E_{gap} (1), electron affinity X (2), correction value ΔE_v (3, dotted lines), and experimental data for different cubic crystal materials (points) as a function of the lattice constant L. On the left part of Figs. 1 and 2 the parameters for set of hypothetical materials are shown.

Quantative calculations of matrix elements have been performed in the scheme of extended bands for different matrix elements: $ss\sigma$, $sp\sigma$, $pp\sigma$, $pp\pi$ bonds

$$V_{ll'm} = \eta_{ll'm} \frac{h^2}{m^* d^2} \sim 1/d^2 \qquad (2)$$

and for pure covalent tetrahedral crystals the factor $\eta_{ll'm}$ is equal correspondingly to 1.39; 1.88; 3.24; and 0.93.[8–15] Hence, the energy gap will decrease in accordance with a simple relation

$$E_{gap} \sim 1/d^2, \qquad (3)$$

where $d \sim L$ is interatomic distance, $L = 2d/\sqrt{3}$ is lattice constant. Some differences for various substances will also depend on the electron effective mass m^*.

As to the mechanical properties of such semiconductor crystals, they are determined by elastic energy[8]

$$E_{el} = \tfrac{3}{4} (C_{11} - C_{12})\Delta X^2 \sim A/L^5, \qquad (4)$$

where C_{11}, C_{12} are the elastic constants, ΔX is the deformation of bonds. The values of $(C_{11}-C_{12})$ are equal to 9.5; 1.0; 0.8; and 0.44 for $C(D)$, Si, Ge, and Sn, respectively.[8] In accordance with the above equation, very sharp dependence
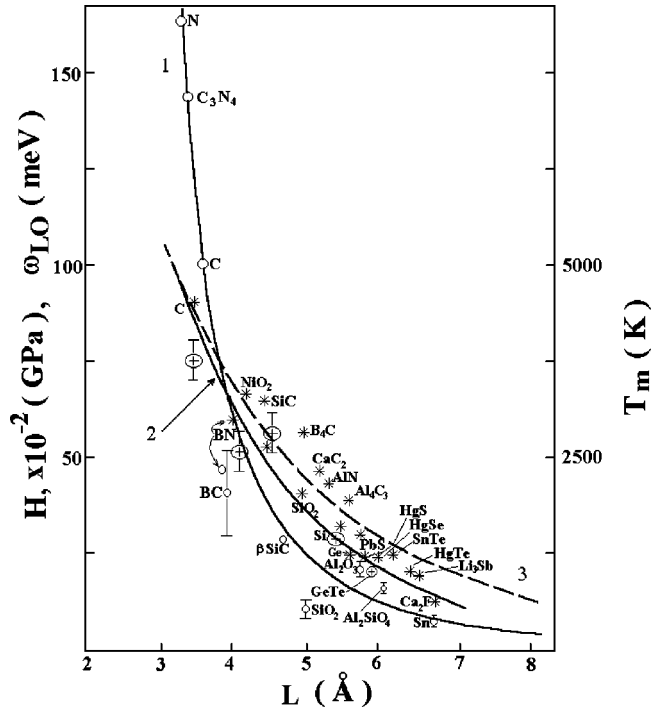

FIG. 3. The dependences of mechanical hardness (in GPa, scale Wicklers—open circles, points—experimental, solid line—theoretical curve $\sim L - n$), melting temperatures T_m, (stars) and optical phonon energy wph (crossed circles) as a function of the lattice constant L.

$E_{el}(d) \sim 1/d^5$ is predicted (Fig. 3, curve 1). For mixture bands (ioncovalent) more complicated dependence for elastisity modulus has a place, as proposed by Phillips, Liu and Cohen, Phylips, and Korsunkskii and Pepekin[7,18–20]

$$E_{el} = (20 - 2.2\alpha_{I_i})/L^{3.5}. \qquad (5)$$

So, in a rather general case, sharp dependence on d of energy gap, optical-phonon frequency, ω_{ph}, melting temperature $T_{melt} \sim$ the energy of bands $E_{gap}(\sim 1/d^2)$, and mechanical properties such as hardness ($H \sim 1/d^{3.5-5}$) has been predicted. We demonstrate the applicability of this formula to many materials, in particular, to cubic crystals. In Fig. 3 summarized data are presented [theoretical curves: 1-H $\sim 1/L^{3.5}$, 3-$T_m \sim 1/L^2$, 2- experimental curve for $\omega_{ph}(L)$].

Of course, the highest value of hardness, (~ 10 Mbar) as well as the energy gap and negative electron affinity X for valence-band crystals until now was observed for diamond carbon. Nevertheless the discussion on such order values (or even higher) has appeared in some publications, which in fact were based on relations for basic parameters of lattice constants L (3)–(5).[18–23] Below we will discuss this problem on the basis of calculations of the dependence of the band structure on the lattice constant, as shown in Figs. 2 and 3.

The additional results can also be obtained from Fig. 1, if one estimates the other important characteristic such as elec-

tron affinity X (i.e., the optical work function), which in energy scale is the distance between the conduction band and vacuum level (the latter, of course, is the same for all materials): $X = W_{vac} - E_{gap}$. The theoretical curve for $E_{gap}(L)$, $X(L)$, predicted from Fig. 1, and experimental points are presented in Fig. 2. Besides good agreement of theoretical curves with the experimental points this curve demonstrates also the maximum possible value for X to be ~ 5 eV for known cubic crystals. As a result, the next general expression involving E_g and X was obtained

$$E_g(L) + X(L) = 5.35 - \Delta E_v \ \text{(eV)} \approx 5.5 \ [\text{eV}], \quad (6)$$

where $\Delta E_v \sim (L - L_D)/2L[\text{eV}]$ (here L_D is the minimum value of L) being a small correction (<0.5 eV) determined as the dependence of valence-band edge on the lattice constant, i.e., it is equal to zero for diamond, about 0.25 eV for Si and Ge, and about 0.5 eV for Sn (see Figs. 1 and 2). Thus, knowing the value of E_{gap}, we can calculate from Eq. (1) the value of the optical work function X. In particular, it is possible to predict low values of X for a set of crystals for $Cu_2O(X \sim 3 \text{ eV})$, $Ag_2O(X \sim 3.5 \text{ eV})$, $NB(X \sim 1 \text{ eV})$, $CdO(X \sim 2.5 \text{ eV})$, $C_3N_4(X \sim -1 \text{ eV})$, etc., as well as propose the corrections of the E_g for a set of important, but not yet studied enough, materials with FC lattices, such as $Ag_2Se(E_g \sim 1.2–1.7 \text{ eV})$ $HgSe(E_g \sim 0.4–0.6 \text{ eV})$, and $TiO(E_g \sim 2.8–3 \text{ eV})$ (instead of 0.15 eV).[14]

Let us consider now such materials as diamondlike carbon composites $C:H_n$, enriched with tetrahedral sp-3 chemical bonds,[12,13,18–27] for which Eq. (10) is also valid. The reason for that is that the optical spectroscopy measurements clearly demonstrate the existence of the forbidden gap, i.e., noticeable values of E_{gap}, which can vary from about tenths of eV to more then 4 eV.[11–13] The relation between effective E_{gap} and X is also fulfilled to within 0.5 eV: $E_{gap} + X = 5$ eV was obtained by Robertson,[11] $E_{gap} + X_T = 4.5 - 5.5$ eV also was obtained in our works.[12,13] So, for these cases it is possible to estimate the indicated quantities from relation (1) and, in addition, some technology parameters like hydrogen content, refraction index n, etc., can be estimated.[22–24]

Calculations of the effective lattice constants from the data of valence radii of atoms r as $L = r \times 4/\sqrt{3}$ have been performed for the following compositions: CH_4, SiH_4, and GeH_4. Respective data are following: $L = 4.32$, 5.25, and 5.33 Å. This means that tetrahedral compositions of the elements of fourth group with hydrogen atoms have substantially larger sizes than carbon (diamond)—by a factor of up to 2. These values are even higher for H-enriched diamond-like CH_2 and CH_3 composites, where L reaches about 5.5 Å and E_{gap} can be predicted to be 1 eV or even less. Thus, from the value of E_{gap} it is possible to roughly estimate the molecular configuration of the CH_x composites.

Another extreme case is connected with the opposite situation—when minimum possible lattice constant L as well as maximum E_{gap}^{max} and negative electron affinity X_{max} for FC (face centered) valence materials have a place. These values can be calculated from the position of the valence-band mini-

mum $E_v(L)$, where the maximum possible value of gap (being proportional to $1/L^2$) $E_{gap}^{max} = 8 - 10$ eV and lattice constant $L = 2.6$ Å is predicted, (see Figs. 1 and 2). The real material with such properties is nitrogen (or C_3N_4) cubic crystal, which can be obtained under special conditions (very high temperatures, high pressures, existing face-cubic seeds). In particular, $d_{N-N} = 1.1$ Å, $L = 2.54$ Å. Besides, electron affinity here has an unusually large negative value: $X_N = -(1.3 \pm 0.5)$ eV and hardness is twice as large as for natural diamond. Material with such extreme parameters seems to be important also for vacuum microelectronics due to the large negative values of electron affinity X.

In Figs. 2 and 3, we present the set of the such predicted superhard materials with tetrahedral FC (cubic) configuration. Note, that some of them can have not perfect crystal lattices, namely, rather deformed FC-configuration, nevertheless with dominating valence bonds and, hence, with rather large hardness due to small values of interatomic distances d. The main candidates for this is crystal materials on the base of C(IV) N(V) and B(III) [may be, in some cases also O(V), Be(II), and Li(I)] which have rather strong chemical bonds and small valence radii of atoms. Some of such compositions, indicated in Figs. 2 and 3, are those: C_3N_4, BN, $C_{3-x}Si_x$, N_3C_3O, AlN. The most perspective are the modifications of the "nitrogen diamond," when in the center of the tetrahedrons carbon C atoms are located, and in the corners of tetrahedrons are nitrogen atoms N (also considered by Liu and Cohen[18] and Korsunskii and Pepekin.[20]) In our paper, we propose the approach for a wider circle of materials on the base of general plots $E_{gap}(L)$, $X(L)$, and $E_{gap}(X)$. Because the lattice constant L for the N-based crystal will be ~ 1.1 times less, than for pure diamond, in accordance with the relation for elastic parameters (4), (5), the hardness of this crystal has to be about two times larger (as demonstrated in Fig. 3). Melting temperature will increase to $T_m \sim 5000 - 5500$ K, energy of optical phonons - up to $\omega_{ph} \sim 150$ meV, negative electron affinity X also has to be extremal $\sim -(2-3)$ eV and energy band gap has to reach $E_g \sim (7-9)$ eV. So, these crystals have to be appoximately twice as fast as the fastest natural materials and they will have other unique parameters, not indicated in previous publications. Note, that the physical reason for negative electron affinity is very small interatomic distance so, appearance of large repulsion between the electrons. This leads to the push out of free electrons from crystal.

In conclusion, in this paper we describe the analysis of the importance in vacuum micro- and nanoelectronics energy parameters such as the work function (electron affinity), energy gap E_g, and lattice constant L in the framework of the known band-structure theory. A comparison between our paper and reference experimental data, in particular, for the diamondlike carbon films, illustrates rather good agreement with the the obtained theoretical dependences: $E_{gap}(L)$, $X(L)$. This gives us the possibility to predict the composites structure of the hydrogen-enriched diamondlike carbon films, obtain the work function X from values of E_{gap}, and vice versa: $E_{gap} + X = 5.3$ eV $- \Delta E_v$, as well as predict materials of cubic crystal configuration with unique properties (the highest melting temperature, the largest optical phonon energy, and the largest negative electron affinity).

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