DIPOLE MOMENTS OF COMPONENTS OF A NANOCLUSTER SUBSYSTEM

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The article presents the results of the analysis of the components of film heterojunction – nanoclusters using silicon as an example. The formation of the nanocluster subsystem of heterojunction with nanoclusters – quantum-sized objects – opens wide possibilities for the creation of modern functional nanoelectronic devices. Within the framework of the electron density functional method, a parameterization is proposed that allows the mechanical, electrical, and optical characteristics of nanoclusters to be determined with sufficient accuracy. The results of calculations of the dipole moments of silicon nanoclusters with different topologies are presented. The relationship between the dipole moment and the internal structure of nanoclusters observed in experiments is considered. The influence of changes in the angles of interatomic chemical bonds on the properties of nanoclusters is analyzed. The proposed approach allows us to control and manage the properties of film heterojunctions with nanocluster subsystem.

Keywords: heterojunction, nanocluster, dipole moment, nanocluster subsystem.

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1. Introduction

Modern research in the field of functional electronics is mainly aimed at reducing the geometric dimensions of devices and increasing their reliability and efficiency [1, 2]. In this context, clarifying the fundamental properties of nanotechnological components of new-generation electronic and computer equipment, in particular quantum-sized systems – nanoclusters (NCs) is an extremely important task [3 - 5]. The idea of forming a clustered phase in the form of a nanocluster subsystem (NCS) from atomic NCs seems fruitful here [6]. Our research proves that NCs are capable of functionally modifying the properties of matter [7]. In this context, solving specific problems related to the determination of the physicochemical characteristics of NCs is of particular interest. The article sets the task of evaluating the dipole moments of silicon NCs. An effective solution to this problem is possible by conducting a comparative analysis of the results of experiments obtained by atomic force and scanning electron microscopy methods [8] with the results of mathematical modeling based on modern methods of quantum chemical approximation [5, 6]. Solving this problem opens up new prospects for determining the optical characteristics of systems that exploit the unusual manifestations of the photoelectric and spectral properties of NCS [7]. In particular, these are film heterojunctions and devices based on them.

2. The mathematical model and approximation

We present a method for modeling the atomic, electronic, and phonon structure of NCs based on the electron density functional (EDF) method. The modeling process takes into account the gradient expansion within the framework of the local electron density approximation [5, 6]. In the parameterized electron density functional (PEDF) method that we propose, several empirical parameters are used. This calculation scheme allows us to study fairly large NCs with sufficiently good accuracy of results. In addition, PEDF allows dynamic processes to be studied using a standard molecular dynamics procedure. The PEDF approach is based on the approximation of molecular orbitals as a linear combination of atomic orbitals (MO LCAO), i.e., in the representation of wave functions Ψ as:

$$\Psi(\vec{r}) = \sum_{\mu} C_{\mu} \cdot \varsigma_{\mu}(\vec{r}),$$

where C_{μ} are atomic orbital (AO) decomposition coefficients, μ is an addition index for all

NC AOs, $\varsigma_\mu(\vec{r}) = N_\mu r^{n^*-1} e^{-\alpha_\mu r} Y_{lm}$ are basis wave functions, i.e., $\Psi(\vec{r}) = \sum_\mu C_\mu \cdot \varsigma_\mu(\vec{r})$, $\vec{r}$ is electron's radius vector, $\vec{r_j} = \vec{r} - \vec{R_j}$, N_μ is a normalizing constant, $\vec{R_j}$ is a radius vector of the *j*-th nucleus of the NC, α_μ is a parameter determined by the algorithm described in [6], Y_{lm} are spherical harmonics, n^*, l, m – effective, orbital, and magnetic quantum numbers, respectively. The use of the MO LCAO method leads to standard equations, where the matrix elements $(H_{\mu\gamma} =< \varsigma_\mu|\hat{T}|\varsigma_\upsilon >)$ of the Hamiltonian and the overlap matrix $(S_{\mu\gamma} =< \varsigma_\mu|\varsigma_\upsilon >)$ AO NC are determined. In the PEDF method, the Hamiltonian of the model system has the form:

$$H = \hat{T} + V_{ef}(\vec{r}), \tag{1}$$

where $\hat{T}$ is the kinetic energy operator, $V_{ef}(\vec{r})$ is the effective potential that determines the state of the electron in the model NC. Let us assume that $V_{ef}(\vec{r})$ is a superposition of the potentials of isolated atoms $V_j^0(\vec{r})$:

$$V_{ef}(\vec{r}) = \sum_{j=0}^{N} V_j^0(\vec{r}), \tag{2}$$

where N is the number of nuclei in the model NC. As shown in [6], the approximation of the potential $V_{ef}(\vec{r})$ in the form (2) agrees with the expression for the matrix elements of the Hamiltonian

$$H_{\mu\gamma} = \begin{cases} < \varsigma_\mu|\hat{T} + V_j^0 + V_k|\varsigma_\upsilon >, \mu \cap \upsilon \in \{j, k\} \\ 0, \quad otherwise \end{cases}$$

where V_k is a potential that takes into account electron-nuclear interaction. The Hamiltonian operator matrix includes 2-part matrix elements $(H_{\mu\nu}, S_{\mu\nu})$, which are calculated precisely using a self-consistent procedure. This is an important advantage of PEDF. The matrix elements of the Hamiltonian and the overlap matrix allow us to determine the wave function and energy terms of the studied NC. According to approximations, all matrix elements depend on inter-nuclear distances. Therefore, for each pair of atoms in NC, the matrix elements are calculated only once with a step of $0{,}1a_B$, where a_B is the Bohr radius. Using analytical formulas for numerical integration, it is possible to interpolate the calculated values to convert the integrals into the real coordinate system of the NC model studied.

Most of the calculation time is spent on performing the matrix diagonalization procedure. The formulated approximations lead to characteristic equations. The accuracy of the results can be improved by using basis wave functions and potentials that correspond to slightly "compressed" rather than free atoms. Such "compression" can be achieved by introducing an additional repulsive potential in the form of $\left(|\vec{r}|/r_0\right)^p$, where r_0 is the equilibrium interatomic distance, $\vec{r}_j \equiv |\vec{r} - \vec{R}_j|$, p is a variation parameter, into the potential energy of the Hamiltonian (1) to optimize the parameters included in the PEDF method when performing test calculations of the zone structure of crystals [5]. The main effect of the potential additive of this type is, on the one hand, to dampen the long-wave part of the basis wave functions and, on the other hand, to preserve the shape of this function near the equilibrium point r_0. In particular, for the NC model with carbon and silicon atoms, the value p=2 was used. Variation of the parameter p slightly changes the energy and geometric characteristics of the model system. The equilibrium interatomic distances r_0 were compared with the calculated data obtained by the effective semi-empirical MIEHT-alpha method [6].

Calculations have shown that for semiconductor models, the approximation $r_0 = r_{cov}$, where r_{cov} is the covalent radius of an atom, is quite good. In addition, numerical analysis also allowed us to obtain values for different effective quantum numbers (n*). This comparison allowed us to obtain an optimized set of basis wave functions ζ_μ . Let us write an expression for the total energy of the model NC:

$$E\,[\rho(\vec{r})] = \sum_i \epsilon_i \; - \frac{1}{2}\left[\sum_{j \neq j'} \int d^3 r V_{eff}\,\rho - \int d^3 r V_{Ex}\,\rho\right] + E_{ec}$$
$$- \frac{1}{2}\int d^3 V_{ec}\,\rho + E_N$$

where V_{Ex} is external potential (potential of nuclear interaction for electrons), ϵ_i is single electronic energy spectrum, $\rho = |\Psi|^2$ – electron density, E_{ec} – potential exchange-correlation energy, V_{ec} – exchange-correlation potential, E_N – potential repulsive energy of nuclei. Representation of electronic density and potential as a superposition of atom-like components: $\rho = \sum \rho_j$, $V = \sum V_j$, allows you to record the total energy in such way:

$$E\,[\rho(\vec{r})] = \sum_i \epsilon_i \; - \frac{1}{2}\sum_{j \neq j'} \int d^3 r V_j\, \rho_{j'} - \frac{1}{2}\sum_{j \neq j'} \int d^3 r V_j\, \rho_j \frac{Z_j}{r_j} + \frac{1}{2}\sum_{j \neq j'} \int d^3 r \tilde{V}_{ec}\, \rho_{j'} + E_N \tag{3}$$

where Z_j is charge of the nucleus of the *j*-th atom of NC, $\tilde{V}_{ec}$ – exchange-correlation correction for the corresponding atomic-like approximation, ρ_j – electron density localized on the *j*-th atom of NC. To represent $\tilde{V}_{ec}$ in terms of E_{ec} and V_{ec}, the method described in [5] was used.

Let us consider the case of large interatomic distances. Then the energy of electron-nucleus interaction contributes more to the sum (3) than the strong interatomic repulsion. Due to the screening potential, the two-center terms vanish. Therefore, $\int d^3 r V_j\, \rho_{j'} = 0, j \neq j'$. Additionally, let us assume that $\int d^3 r \tilde{V}_{ec}\, \rho_{j'} = 0$. Taking these approximations into account, the energy $E[\rho(\vec{r})]$ is estimated using formula (3). On the other hand, the energy E_j of the isolated *j*-th atom is calculated using the EDF method. Then, the energy of a single chemical bond between NC atoms is estimated using the formula:

$$\varepsilon_b = E - \sum_j E_j \tag{4}$$

where ε_b is chemical bond energy, $E \equiv E[\rho(\vec{r})]$. Taking into account the formula for evaluating E_j from [5], as well as expression (3) for determining E, we rewrite relation (4) in terms of the single-electron energy spectrum:

$$\varepsilon_b = \sum_i \varepsilon_i - \sum_j \sum_{nj} \varepsilon_{n_j} \tag{5}$$

where ε_{n_j} is single electron energies estimated in the EDF method. Note that the expression (5) is strict only for large interatomic distances. In the PEDF method, instead of calculating the E_{ec} energy through the total energy $E[\rho(\vec{r})]$ of the NC model using formula (4), the following approximation is used:

$$E_b^{approx} \approx \varepsilon_b + \frac{1}{2}\sum_{j \neq j'} \Delta E_{jj'}$$

where $\Delta Ejj' = \varepsilon_b - E_b^{EDF}$ for the corresponding values of diatomic molecules. The proposed approximation for estimating the energy of chemical bonds is used in traditional strong coupling methods [1]. However, in the PEDF method, the correction corresponds to the short-range energy range, i.e. where the empirical estimates used in the strong coupling method are ineffective. Taking into account the PEDF approach, as well as the MO LCAO decomposition coefficients C_μ and derivatives $\partial H_{\mu\nu}/\partial x_j$, $\partial S_{\mu\nu}/\partial x_j$, let us determine the force acting on the m-th atom:

$$F_m = \sum_{i}^{all\,MO} \sum_{\mu} \sum_{\gamma} C_{i\mu} C_{i\gamma} \left[-\frac{\partial H_{\mu\gamma}}{\partial x_j} + E_i \frac{\partial S_{\mu\gamma}}{\partial x_j} \right] + \sum_{i \neq j} \frac{\Delta E_{jj'}}{\partial x_k}$$

If the forces F_m acting on the atom are determined, then a molecular dynamics (MD) study of specific NC models can be performed.

3. Discussion of the results of calculations of NC characteristics

Relaxation effects were taken into account in the MD modeling process. First, the initial spatial configuration of atoms was entered. Next, boundary conditions were set, i.e., the method of calculating the energy of atoms near the boundary between the NC and the surrounding matrix. Several approaches are possible here: periodic boundary conditions, introduction of pseudoatoms (so-called passivates of broken chemical bonds in the NC). The relaxation procedure itself includes three ways of changing the atomic configuration in the NC volume: rigid displacement of an atom (atoms); introduction of additional atoms or formation of vacancies (defect configurations); atomic relaxation. Rigid displacement consists in the displacement of one atom relative to another without changing the coordinates of individual atoms. As a result, the mutual arrangement of atoms is determined, which corresponds to the minimum energy and their interaction. Atomic relaxation consists of the individual displacement of atoms. The "history" of some semiconductor NC models corresponded to 1 picosecond (when hundreds of thousands of iterations were performed).

For silicon (46 silicon atoms) – Si_{46}, germanium Ge_{46}, and carbon C_{46}, as test calculations, the comprehensive compression modulus (B), linear expansion coefficient (C_L), and equilibrium interatomic distance (r_0) were obtained (Table 1). As can be seen, there is good agreement with the experimental data. Using a molecular dynamics approach within the PEDF method, estimates of changes in the lengths of interatomic chemical bonds in NC were made. It was found that the change in the length of chemical bonds depends on the degree of hybridization of Group IV atoms.

Table 1

Characteristics of NC Si_{46}, Ge_{46}, C_{46}

NC	$B\times10^{12}$, Erg/cm^3		$C_L\times10^{-6}$, grad^{-1}		r_0, Å
	PEDF	Exp [4,9]	PEDF	Exp [4,9]	PEDF
Si_{46}	1,00	0,988	0,41	0,233	2,34

Ge_{46}	0,753	0,772	5,07	6,0	2,83
C_{46}	5,35	5,45	1,43	1,20	1,785

We used the PEDF and MIEHT-alpha methods to analyze the physicochemical characteristics of spherical (checkered) polyhedral NC (Si-PNC) of silicon. The calculated energy and geometric characteristics of such NC were determined using optimized basis wave functions, namely: STO-3G and HF/3-21G basis (within the framework of PEDF). Using this basis set of wave functions, the geometric parameters of Si_{60}-NC, which has I_h symmetry, were obtained (Table 2). For comparison, the results of calculations using the semi-empirical MIEHT-alpha approach [6] are presented.

Table 2

Geometric characteristics of the polyhedral NC Si_{60}, symmetry I_h

Basic wave functions used	$r_{66}, \overset{0}{A}$	$r_{56}, \overset{0}{A}$	$\Delta r, \overset{0}{A}$	$d, \overset{0}{A}$
MIEHT- alpha	2,189	2,226	0,037	12,7
STO-3G PEDF	2,067	2,152	0,085	11,8
HF/3-21G PEDF	2,213	2,301	0,088	11,6

Optimization by energy state proves that polyhedral (checkered) silicon NC with 60 atoms is constructed from 12 five- and 20 six-atom cyclic NC rings (5-AC and 6-AC). The diameter *d* of the entire structure and the interatomic distances in 5-AC and 6-AC were calculated. It was found that the results of interatomic distance estimates depend on the type of basis wave function sets used. It is shown that when modeling a polyhedral NC, the “sticking” of planar pentagonal atomic rings (5-AC) is an energetically disadvantageous process, since it increases the deformation stress of the NC as a whole. An increase in the number of neighboring 5-ACs with a constant number of 6-ACs leads to compression of the structure, thereby reducing its stability. This is confirmed by calculations of smaller diameter NCs containing fewer silicon atoms than the Si_{60}-type NC, which has I_h symmetry.

For example, a checkered NC with 50 atoms (Si_{50}) having D_{5h} symmetry is less stable than the polyhedral NC Si_{60}. The difference in energy is 0.0868 eV. A similar effect was obtained for the polyhedron Si_{30} with C_{2V} symmetry: 0.252 eV, as well as Si_{24} – D_3: 0.404 eV. The results of the calculations indicate a high probability of synthesis of Si_{60} (I_h) nanocluster polyhedral. As shown by quantum chemical calculations, the total and specific energies of silicon-based nanoclusters (Si-NC) in the ground and excited states, according to the mathematical model presented above, the compaction of the structure is associated with a change in the hybridization of chemical bonds.

Experiments measuring the properties of neutral and ionized silicon NCs in the gas phase (ranging in size from 2.5 to 40 angstroms) confirm not only the existence of “magic numbers” for structural elements but also confirm the possibility of transition from a diamond to a more compact structure of NCs up to 15 angstroms in size [8]. We have found that energetically favorable Si-NCs are those containing up to ten silicon atoms and characterized by cubic octahedral or icosahedral symmetry. Estimates of the electron density of such NCs give a band gap width of less than 1.1 eV.

Moreover, the change in the density of electronic states during the transition to “primordial” tetrahedral Si-NCs leads to zero bandgap width. This result indicates the manifestation of metallic properties of such NCs. The results presented below expand the possibilities of studying the “degree of metallization” of silicon-based NCs, opening up new opportunities for identifying measurable macroscopic parameters and calculated microscopic data. This task is also of interest because of the connection with high-performance mass spectrometry data, where a size distribution for Si-NCs (up to 20 atoms) was obtained in an ion trap (ref. [4, 6]). The magic numbers that were discovered for Si-NCs with the number of silicon atoms ranging from three to 29 back in the late 1980s reflect the divergence of their physicochemical properties. At that time, it was experimentally shown that sublimation from the silicon surface is accompanied by the injection of not individual atoms, but whole Si-NPs with six or ten silicon atoms.

It should be noted that tetrahedral symmetric (similar to crystalline silicon, c-Si) NCs are characterized by paramagnetic properties due to their characteristic large number of broken chemical bonds. Theoretical estimates of the specific energy of NCs consisting of ten atoms (Si_{10}) within the framework of PEDF indicate that the NC fragment (which appears to have been torn out of the crystal lattice of the substance) is energetically unstable. We define such an NC as “firstborn”.

Broken chemical bonds also exist on clean surfaces of bulk silicon. Therefore, the energy of the formed broken chemical bonds can cause reconstruction of the semiconductor surface. For example, (7×7) reconstruction of the Si(111) surface reduces the number of broken chemical bonds by 60%. A decrease in the concentration of broken chemical bonds reduces the chemical activity of the system. Our theoretical analysis shows that the geometric reconstruction of Si_{10} NC also passivates broken chemical bonds. Thus, the degree of oxidation of Si-NC allows us to conclude not only about the chemical activity of these structures, but also about the density of the geometric “packing” of atoms in NC. Incidentally, Raman spectroscopy [6] and electron microscopy [7] show that dense packing of atoms in NCs is more typical for metallic than for covalent structures.

Moving on to medium-sized NCs (up to a hundred atoms), the situation becomes more complicated. As the number of atoms in the NC configuration increases, it becomes necessary to introduce additional approximation conditions into the calculation methods. But, on the other hand, an effective analogy arises, which is associated with the existence of carbon framework structures – quite large (and sometimes giant) quasi-molecules, a new allotropic form (in addition to the long-known carbon forms: diamond and graphite) [6, 9, 10]. The calculation proves that NC containing 27 silicon atoms are highly likely to be polyhedral and characterized by an ellipsoidal shape. Those NC containing a larger number of atoms (60, 78, and more) have a spherically symmetric checkerboard structure. The existence of small polyhedral Si-NC in a specific organic matrix environment does not contradict spectroscopic experiments [6, 7] and experiments on the photoionization of NC [8].

The polyhedral Si NC (PNC) with up to 20 silicon atoms that we have considered show that it is precisely such structures that can be considered constituent elements of more massive NC. Small NC – Si_6, Si_{10} – are quite stable configurations. In addition to polyhedral NCs, there are two most energetically favorable configurations of Si_{10} NC. Their stability is associated with optimal spatial symmetry. The geometric structure of such NC differs from the symmetry of polyhedral NC. Such isomers have fairly similar energy characteristics. Therefore, the probability of the existence of these NC (rather than polyhedral) as isolated fragments is quite high. Polyhedral NCs have a high atom packing density: some of the atoms have a coordination number exceeding four. Such structures, in terms of their characteristics, are closer to the high-pressure metal phase, i.e. structures of the tin type (beta-Sn).

Theoretical estimates of NCs of various configurations show that the energy required to create a densely packed polyhedron with 10 silicon atoms corresponds to an energy of 5.0 eV. We have shown that during the transition to a densely packed NC structure, there is a significant increase in the number of chemical bonds between atoms: from 12 (polyhedral structure) to 24 (two other isomers) [8]. This indicates that additional broken chemical bonds arise during a certain conformational reconstruction of NC. The mechanical stress of unreconstructed broken chemical bonds contributes to the emergence of mechanically brittle NCs. Another consequence of the structural reconstruction of NC is the emergence of interatomic chemical bond hyperhybridization, which leads to a change in the symmetry of NC.

4. Hybridization of AO and dipole moments of NC

When evaluating the total energy of a compound, the first step is to assume that the atoms in the NC have ideal tetrahedral coordination: that is, the four sp^3-hybridized atomic orbitals (AO) belonging to each Si atom (centered, for example, at point $\vec{R}_i$) are directed toward the four nearest neighboring atoms ($\vec{R}_j$). Although for surface atoms, the degree of hybridization χ_{ij} of each AO differs from the bulk value (χ_{ij} = 3), because the ideal tetrahedral geometry is disturbed here by the reconstruction (relaxation) of the NC. Deviations from the ideal arrangement of atoms (i.e., the tetrahedron) cause a change in the value of the corresponding parameter: $\chi_{ij} \neq 3$. The value of χ_{ij} was determined through the connection order matrix $P_{\mu\nu}$ and the decomposition coefficients of AO C_i for a specific MO Ψ_i:

$$\chi = \sum_{\mu=1}^{p} P_{\mu\mu} \Big/ \sum_{\mu=1}^{s} P_{\mu\mu}, \text{ where } P_{\mu\nu} = \sum_{i=1}^{occ} g_i C_{i\mu} C_{i\nu}. \tag{6}$$

The dependence $\chi(n)$, where n is the number of atoms in the NC, for central and peripheral Si atoms has a non-monotonic dependence. AO rehybridization can be quantitatively estimated from the ratio for hybridization energy (ε_{ij}^{hybr}):

$$\varepsilon_{ij}^{hybr} = \frac{\varepsilon_s + \chi_{ij}\varepsilon_p}{1+\chi_{ij}} - \left(Q_i \cdot E_{ee} + e^2 \cdot \sum_{k \neq i} \frac{Q_k}{|R_j - R_k|}\right) \tag{7}$$

where ε_s, ε_p are electron energies at s-AO, p-AO, respectively (ε_s =–13,55 eB, ε_p =–6,52 eV); Q_i is charge localized on an atom centered at point $\vec{R}_i$; e is elementary electric charge; E_{ee} is energy of interatomic interelectronic correlation (electron-electron interaction) on sp^3-AO (for Si, this energy is equal to E_{ee} = 8,39 eV).

The energy ε_{ij}^{hybr} depends on the morphology of the NC. Additional effects related to the change in ε_{ij}^{hybr} are the effects of changing the localization of electron density on atoms due to its redistribution on the atoms of the NC structure, i.e. the emergence of an ionic component of interatomic chemical bonding in the NC. Additionally, this includes the component of interatomic (Madelung) interaction and interorbital components. The charge on a silicon atom in the NC (Q_i) can be determined by the degree of polarization (α_{ij}) of the NC as a whole. The polarization of the NC depends on its morphology (i.e. the type of symmetry) and is determined by the geometric arrangement and number of atoms in the NC (Fig. 1). For four sp^3-hybridized atomic orbitals that provide the chemical bond of the silicon atom with its nearest neighbors, the degree of polarization was estimated by the ratio:

$$\alpha_{ij} = \frac{1}{2} \cdot \frac{\varepsilon_{ij}^{hybr} - \varepsilon_{ji}^{hybr}}{\sqrt{E_{ij}^2 + 0{,}25\left(\varepsilon_{ij}^{hybr} - \varepsilon_{ji}^{hybr}\right)^2}} \tag{8}$$

where E_{ij} are matrix elements of the Hamiltonian NC between two atomic orbitals participating in hybridization, directed from one atom ($\vec{R}_i$) to another ($\vec{R}_j$).

The functional dependencies of polarizability (α) and dipole moment (D) on the number of atoms in the NC (*n*) obtained by us are non-monotonic, as illustrated in Fig. 1 and Fig. 2. Note that the numerical value of D depends on the spatial arrangement of atoms in the NC, unlike polarizability, whose value does not change significantly for the relaxed or unrelaxed state of atoms in the NC.

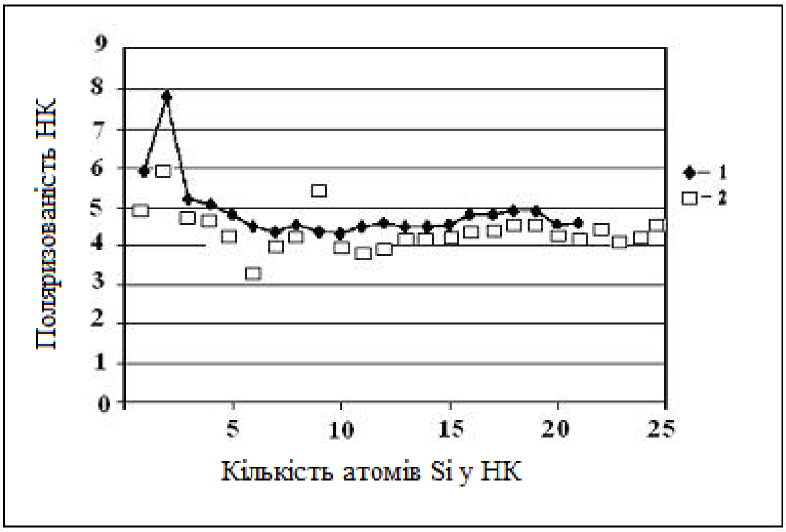

Fig. 1. Dependence of polarization vs NC dimensions:
1 – calculation result [4], 2 – calculation result using the PEDF method.

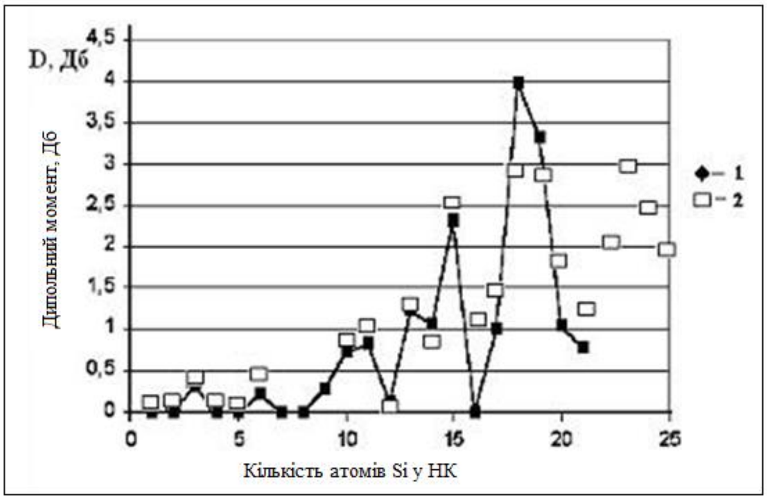

Fig. 2. Dipole moment (D) NC-Si$_n$, as a function of its size (n).
1 – calculation result using the MIEHT-alpha method,
2 – calculation result using the PEDF method.

Our theoretical diagnosis of the energy spectrum of NCs involved not only studying changes in interatomic distances, but also angles between chemical bonds of neighboring atoms, or NC fragments. It turned out that the strength of chemical interaction increases with decreasing angles in parallel with the usual radial shortening of the chemical bond. This allows us to conclude that radial forces are significant only for the closest neighbors. From our point of view, the transition from the covalent to the metallic stage of Si-NC existence corresponds to a change in the angles between the chemical bonds for the nearest neighboring atoms, namely: θ=60º – metallic phase, θ~110º – covalent.

We analyzed the effect of changes in the angles of interatomic chemical bonds on the properties of NC. Calculations showed that the shift of electron density from the silicon atom Si to the halogen (X) causes a decrease in the angle between neighboring chemical bonds in small NCs of the SiF_4 type from 109º28' to 104º31'. A hydrogen atom or halogen (fluorine, chlorine, iodine, and bromine) has a significantly higher electronegativity than a Si atom. Therefore, any chemical bond between silicon atoms located near a halogen atom is deformed and polarized. This causes an increase in the frequency of oscillation of the Si-Si chemical bond and enhances the absorption of radiation with the corresponding wavelength. This halogen-induced phenomenon can be used in studies of the Si-Si chemical bond lattice in amorphous silicon saturated with halogens.

5. Conclusions

The results of our research can be systematized as follows. First. A mathematical model for calculating characteristics of NCs based on the EDF method in a parameterized approximation - the PEDF - has been proposed. Test calculations prove the high level of reliability and efficiency of the proposed mathematical approach. Second. The relationship between dipole moments and the internal structure of NCs observed in experiments ([8], ref. [4-6]) is considered. The influence of various factors on the dipole moment of silicon NCs is illustrated. If there are rotational structural fragments in the NC, then the total dipole moment of such a nanocluster compound will depend on temperature, because an increase in temperature affects the intensification of the free rotation of atoms in the NC.

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