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QUANTITATIVE ANALYSIS OF NANOSTRUCTURES

The interest to surface disordered phases in modern nanoelectronics and recent progress in the combination of visualization and simulation techniques are discussed. The role of modeling and studying the properties of nanoclusters on Si surface is emphasized. The applications of the Model Molecular Graphics Package to such nanostructures are demonstrated, its interactivity possibilities are considered. Mathematical background and computation results are presented for the Modified IEHT-α method, POTENTIAL package, and Graphic Package. The last one gives the 3D representation of the investigation of nanoclusters, processes of their formation through chemisorption and their final geometry. The results are important for nanotechnology.

Keywords: nanoclusters, model, quantum-dimensional system, visualization.

Обсуждаются причины интереса к поверхностно разупорядоченным состояниям в современной наноэлектронике и существующий прогресс среди методов визуализации и моделирования. Особое внимание уделяется роли моделирования при изучении свойств нанокластеров на поверхности кремния. Продемонстрировано применеиие пакета молекулярной графики Model Molecular Graphics Package к таким наноструктурам и рассмотрены его интерактивные возможности. Представлены математическое обоснование и результаты расчетов в программных пакетах Modified IEHT-α method, POTENTIAL package, и Graphic Package. Последний пакет позволяет в трехмерном представлении проводить исследования нанокластеров, изучать процессы их образования в результате хемосорбции и получать окончательную геометрию. Полученные результаты представляют интерес для нанотехнологий.

Ключевые слова: нанокластеры, модель, квантово-размерные системы, визуализация.

Обговорюються причини інтересу до поверхнево розупорядкованих станів у сучасній наноелектроніці та прогрес у розробці методів візуалізації та моделювання. Особлива увага приділяється ролі моделювання при дослідженнях властивостей нанокластерів на поверхні кремнію. Продемонстровано застосування пакету молекулярної графіки Model Molecular Graphics Package до таких наноструктур та розглянуті його інтерактивні можливості. Представлено математичне обґрунтування та результати розрахунків у програмних пакетах Modified IEHT-α method, POTENTIAL package та Graphic Package. Останній пакет дозволяє у тривимірному представленні проводити дослідження нанокластерів, вивчати процеси їх утворення в результаті хемосорбції та отримувати остаточну геометрію. Отримані результати є цікавими для нанотехнологій.

Ключові слова: нанокластери, модель, квантово-розмірні системи, візуалізація.

Introduction

Semiconductor surface forms a specific surface disordered phase (SDP) and the main peculiarities of modern nanoelectronic devices depend on the individual parameters of the surface phase. Furthermore, the reactions of atomic hydrogen (H), fluorine (F), chlorine (Cl) and bromine (Br) with Si surface are widely studied experimentally and many investigators observe the semiconductor SDP directly [1-3]. For the quantitative analysis of the creation of nanostructures like nanoclusters (NC) in Si and other solid materials the cluster distribution along the surface is necessary.

On the other hand, the recent progress in the combination of visualization and simulation techniques concurs in obtaining spectacular results in the investigation of chemical reaction mechanisms as well [4]. The traditional quantum chemical ab initio methods, based on the Hartree–Fock scheme became well-established in studies of the electronic and geometrical structure of solid NC's [1]. Therefore, the surface NC's as real objects and models of nanoelectronic materials for intellectual systems are of great interest.

Our Model Molecular Graphics Package (MMGP) is specially designed so as to allow us the high-level computerized visualization in molecular science. MMGP contains many interfaces with quantum chemical programs such as those of the semiempirical and molecular surface geometry generation that is based on an interatomic potential (for example, the modified Stillinger - Weber (MSW) potential).

In the paper the development and applications of the MMGP to the Si-NC structure is demonstrated. The MMGP generates detailed and easily interpretable and aesthetically attractive graphics representing models of molecular structures and related properties. The package offers a high level of interactivity through the use of the mouse and via a large set of menus and submenus organized in such a way that enables users to learn rapidly the basic operations leading to efficient visualization (see Fig. 1, 2).

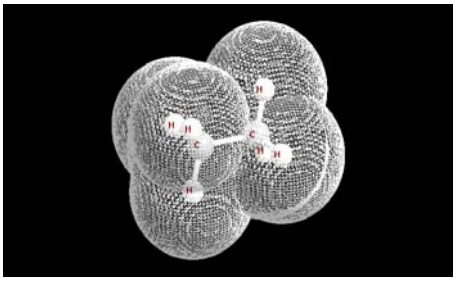

Fig 1. Map of the electron density distribution for the nanocluster.

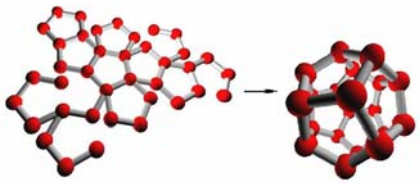

Fig.2. 3D - representation of the nanocluster formation.

For all the menu items, a help facility is implemented. Various representation options and attributes may be selected for adapting the visual output to personal needs and preferences: the molecular structures may be represented as discrete dots, and the global appearance may be modified via attributes such as background appearance, perspective or orthogonal projection, and others. The purpose of the MMGP is the interactive visual representation of three-dimensional (3D) models of molecular structures and properties for research. Due to the flexibility of the data- and program-structure, various chemical systems ranging from small compounds (clusters) to large macromolecules may be investigated; additional interfaces and tools can easily be implemented. The MMGP contains the tools that are necessary for the investigation and visualization of the results generated by the calculations with such an available program-package: Modified IEHT-α method, POTENTIAL package, Graphic Package.

Modified IEHT-α method

This is for semiempirical calculations of one-electron level energies, wave functions, and other parameters of electronic structure of NC. The estimation of the total energy of clusters that have different sizes follows

$$E_{tot} = \sum_{A \neq B} \frac{Q_A(\vec{r}_{AB}) - Q_A^*(\vec{r}_{AB})}{r_{AB}} + \sum_i g_i E_i - (E_{ee} + E_{exc}), \qquad (1)$$

$$E_{exc} = \sum_{A \neq B,\, \mu \neq \nu}^{all} \sum^{occ} \frac{1}{r_{AB}} v_{AB} \; S_{\mu\nu}^2 \qquad (2)$$

where ν_{AB} is a fitting parameter.

POTENTIAL package

This is a simulation program for calculations based on different types of interaction potentials. One of them is the modified Stillinger–Weber-type potential [2]. The Hamiltonian is

$$H(\vec{r}_1, \vec{r}_2 \ldots \vec{r}_N, \vec{p}_1, \vec{p}_2 \ldots \vec{p}_N) =$$

$$= \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j}^{N} V_{int}^{(2)}(\vec{r}_{ij}) + \sum_{i<j<k}^{N} V_{int}^{(3)}(\vec{r}_{ij}, \vec{r}_{ik}, \vec{r}_{jk}) \qquad (3)$$

where $\vec{r}_1, \vec{r}_2 \ldots \vec{r}_N$ are coordinates of the atoms, $V_{(2)int}$ is the twin potential (4); $V_{(3)int}$ is the tree-particle SW-potential

$$V_{int}^{(2)}(\vec{r}_{ij}) = \begin{cases} A\left(B\frac{1}{r_{ij}^p} - 1\right) exp\left(\frac{\Lambda}{r_{ij} - a}\right), \vec{r}_{ij} < 2{,}5\,\sigma_{AB} \\ 0, others \end{cases} \qquad (4)$$

$$V_{int}^{(3)}(\vec{r}_{ij}, \vec{r}_{ik}, \vec{r}_{jk}) = \Pi_{ijk} + \Pi_{kij} + \Pi_{jki}$$

$$\Pi_{ijk} = \Lambda\left(cos\,\theta_{jik} + \frac{1}{3}\right)^2 exp\left(\frac{\delta_{ijk}}{r_{ij} - a} + \frac{\delta_{ijk}}{r_{ik} - a}\right) \qquad (5)$$

where θ_{jik} is an angle, $\vec{r}_{ij}$ and $\vec{r}_{jk}$, $\vec{r}_{ij} = |\vec{r}_i - \vec{r}_j|$ is a vector between i and j atoms in units of the equilibrium distance between the nearest atoms in the structure ($\vec{r}_0$). For Si $\vec{r}_0$ = 2.351A (modified SW) and $\vec{r}_0$ =2.0951A (original SW). The energy unit equals to E = 2.1675 eV, i.e. $E_{Si\text{-}Si}$ in the Si crystal. The parameters of the modified SW- potential are presented in [3].

Graphic Package

Graphic Package is a geometrical program based on 3D-representation of the investigation of NC.

We report the results of test calculations for adsorption processes and optical properties of the closely packed and ball-like Si NC. Real surface objects may be constructed by introducing stereochemistry, i.e., the 3D atomic positions, and it is important to visualize them as molecular models with the usual rendering techniques leading to 3D perception. MMGP visualization allows investigators to emphasize at length the different aspects of molecular structure of surface: chemical topology, conformational details, etc.

We applied the MMGP to the Si-SDP. With the appearance of semiempirical methods, the calculation of the equilibrium geometry and visualization of quite large model became possible (N=125 Atoms). The calculated bond lengths of some surface are given in Refs. [5-7].

As one can see from these data, the calculated interatomic distances are in a quite good agreement with the experimental ones. Especially, the changes of the Si-Si bond from a small Si-NC (2-10 atoms) to big ones are accurately described. We find the energies of NC, binding energy per atom, and interaction energy of the systems «NC-SDP» are obtained for more stable geometry. Furthermore, the energetic positions and equilibrium distances as well as of silicon are described rather well.

Another example of the adsorption process and chemical reactions on semiconductor surfaces is the interaction with halogen atoms [6]. When using the model to represent the SDP, a choice has to be made about the NC size, that is, the number of atoms that are treated explicitly in the calculations, and the level of precision of the required computation. Fortunately, the chemisorption of atoms on SDP seems to be of local character. This fact is greatly supported by ab initio model calculations, and particularly by the calculations for the chemisorption of F and Cl on Si-SDP.

In our calculation the single NC contains 10-100 Si atoms representing the first four layers of the Si-SDP. We regard this model as hypothetical molecules (quasimolecules) and do try to compare the computed results (for example, magic numbers) directly to experimental data of the corresponding impurities in the solids or chemisorbed systems [1]. The mass spectra of charged NC's, where magic numbers are observed, are given in [3].

Taking into account the internal structure of the ball-like Si NC's we investigate theoretically the adsorbtion and scattering of light by them. The theory for the interaction of electromagnetic fields with local charge-carriers near boundary of the small spherical semiconductor microcrystals was presented in [8]. In [5, 8] the dipole moments of NC (using MMGP) and transition dipole moments for local bulk states and local exterior surface states were calculated. It was shown that the dipole moments of the transitions for local states of the Si NC are large compared to the typical values of transition dipole moments for Si-NC.

Conclusions

It is shown that the calculated energy and geometrical characteristics obtained by MMGP are in satisfactory agreement with the experiment and others ab initio calculations [1-8]. The present calculations show that the MMGP can be used to obtain a detailed and reasonably accurate description of various aspects of the small halogen – Si- NC. In view of the interest of physicists to the visualization of such NC, one may foresee that the data banks representing the major types of stable systems will soon be available. Therefore, it is important for a physicist to have at hand the computer tools allowing visualization and

generation of computational information. The combination of MMGP with molecular dynamics in connection with the technique of simulated annealing makes it a very useful tool for the determination of geometries of large NC. Reconstruction processes at Si SDP or amorphous solids can be studied also in this way.

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