O. Ananina, Ph.D,
E. Severina, post-grad. stud.
Semiconductor Physics Department, Physical Faculty,
Zaporizhzhya National University of Zaporizhzhya

HYDROGEN ADSORPTION ON THE DIAMOND C(111) SURFACE: QUANTUM-CHEMICAL SIMULATION

The interaction of atomic hydrogen with the C(111) surface is the subject of the present work. Two configurations of the surface have been studied – C(111)-1x1:H and C(111)-2x1:H. The hydrogen adsorption on the diamond surface C(111) have been studied with the help of semi-empirical method of quantum-chemical modeling MNDO (MOPAC) and ab-initio Hartree-Fock method (PC GAMESS).
Keywords: diamond C(111) surface, hydrogen adsorption, cluster, computer simulation, MNDO (Modified Neglect of Differential Overlap), ab-initio method.

Introduction. Interest from both a fundamental and an applicative perspective has stimulated much research in diamonds interfaces and adsorption of different atoms and radicals on diamond surfaces. In particular, considerable attention has been directed at the study of the hydrogen adsorption on C surfaces. Hydrogen terminated diamond surfaces exhibit unique properties: negative electron affinity and high p-type surface conductivity under appropriate conditions [2]. Also the interaction of atomic hydrogen with the C(111) surface have been studied due to their importance in the CVD process [8]. H atoms not only can preferentially etch away graphite component and assure the smoothness of diamond surfaces, they can also terminate the surface C atoms to maintain the sp^3 hybridization so that graphite formation can be prevented [9]. Consequently, the interaction between H and diamond surfaces becomes an important issue for both diamond technology and surface science study [3, 4].

Mitsuda et al. [5] studied the effects of addition atomic hydrogen to the reconstructed C(111)-2x1 surface from both LEED and second harmonic generation (SHG) techniques. They discovered that the transition (2x1)→(1x1) to occur at approximately 5% of the saturation hydrogen coverage. Chin et al. [1] confirmed this result and found that C-H stretch mode for the begins to transforms (2x1) to (1x1) structure was slightly up-shifted in energy as compared to the fully hydrogenated C(111)-1x1:H surface. It means, that this surface structure is some different that the fully relaxed or fully hydrogenated surface. That a small fraction of a monolayer of chemisorbed hydrogen has implications for impurity stabilized surface diamond structures.

Many theoretical and experimental works have been performed in the reaction of H with diamond surfaces by using various methods. But for today the interaction of H atoms with surfaces C(111) is the unknown mechanism of the (2x1) to (1x1) transformation induced by hydrogen adsorption on a diamond surface, along with the structure of an intermediate metastable surface reconstruction that appears in the initial stages of hydrogen absorption on the (2x1) structure.

Results and discussion. Investigations of diamond surfaces C(111) were performed on the diamond nanoclasters C123H79, which used as a models for C(111)-2x1:H and C(111)-1x1:H surface simulation (fig. 1). The broken bonds of the carbon atoms at the edge of the clusters (i.e., the bonds leading into the bulk of the diamond crystal) were saturated with hydrogen atoms (the univalent pseudoatoms model). In our calculations, all carbon atoms were freely optimized, and the hydrogen atoms (the so called hydrogen bowl) were fixed.

The calculations were performed using the semiempirical quantum-chemical techniques contained in the MOPAC software package and the Hartree–Fock (ab initio) methods of the PC GAMESS package. The Hartree-Fock method was used as a basis for solving the Roothaan equations. In determining the optimized geometry of the system corresponding to the minimum energy, the method of Davidson-Fletcher-Powell was applied. In the system stationary points, the gradients on the atoms did not exceed 3 kcal/Å. We calculated the energy of the clusters, the atomic bond orders, the population of atomic orbitals and the molecular, localized orbitals.
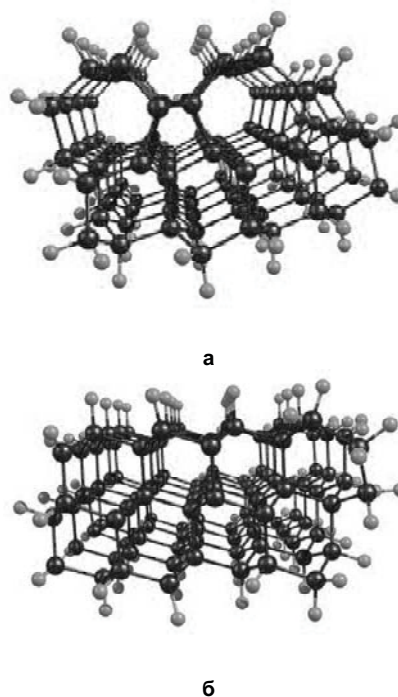

Fig. 1. Clusters, modeling the hydrogen terminated C(111) surfaces:
a) the Pandey-chain reconstructed C(111) -2x1:H surface,
b) the "ideal" structure C(111) -1x1:H

These clusters reproduce reconstructed diamond C(111)-2×1 surface with the chain reconstruction as proposed by Pandey [6] and the ideal C(111)-1x1 surface respectively. We constructed cluster to model ideal C(111)-1x1 the following way: all of the carbon atoms in these clusters are positioned at the diamond lattice sites, i.e., at distances of 1.54 Å from one to another. The angle between the C–C bonds amounts to 109.47º. Then, from the "ideal" structure C(111) was obtained the cluster with the reconstructed geometry 2x1.

The most probable reconstruction of the C(111) surface (occurring at higher temperatures) is the 2x1 – π - bonded Pandey chain structure. The exposed C atoms form upper and lower zig-zag chains that run in parallel across the surface. Surface structure composed of a topmost layer of carbon chains with mostly sp^2 character and a next layer of carbon chains with mostly sp^3 character. We find that this

structure C(111)-2×1 is highly asymmetric: on the first layer a relatively strong buckling Δz=0.17 Å is present [7].The atoms belonging to the top chains is undimerizied.

Search for the stable configurations of a monohydride form for the diamond surface (111) leads to two forms differing in geometry and electronic state: C(111)-2x1:H and C(111)-1x1:H. In case of C(111)-2x1:H the total cluster energy is by 15.12 eV higher than in case of C(111)-1x1:H. The unreconstructed C(111)-1x1:H surface was found to be lower in energy than the Pandey-chain reconstructed C(111)-2x1:H surface by 0.84 eV per surface C atom.

The analysis of molecular orbital compositions were carried out. Properties of the possible of two forms of hydrogen terminated surfaces on a diamond C(111) surface with different geometry, electronic properties and energy of formation is presented in the table 1.

Table **1**

Geometric, electronic and energy parameters of the C132H79 diamond surface C(111) cluster (Fig1. a-b)

claster	C-C, Å	C-H, Å	q (Csuf), e
C(111)-2x1:H	1.55	1.086	1 layer: -0.054 ÷ -0.056 2 layer: +0.008÷ +0.016
C(111)-1x1:H	1.55	1.086	1 layer: -0.044 ÷ -0.049 2 layer: +0.016÷ +0.02
claster	q (H), e	Ea, eV	Eb, eV
C(111)-2x1:H	+0.044 ÷ +0.055	1 position- 0.2 2 position- 0.45	1position- 3.4 2position- 3.1
C(111)-1x1:H	+0.041 ÷ +0.042	0.16	3.7

Ea (eV) – the activation energy of the hydrogen atoms adsorption on the clean surface C(111);
Eb (eV) – the binding energy of the hydrogen atoms on the clean surface C(111).

Hydrogen saturation of dangling bonds on the surface C(111)-1x1 and C(111)-2x1 of carbon atoms leads to a redistribution of the surface charge: the charge on the hydrogen atoms is +0.4e÷+0.5e and the charge on the carbon atoms is -0.4e÷-0.5e (on the clean C(111)-2x1 surface q(C)= -0.01÷-0.02e, on the clean C(111)-1x1 surface q(C)= -0.02÷-0.03e).

Hydrogenated diamond (111)-1x1:H has an "ideal" structure, with the surface carbon atoms very near their bulk-terminated positions. The nearest-neighbor C-C distance is 1.55 Å. Each surface carbon is bonded to a single hydrogen atom, and the C-H bond vector is perpendicular to the surface plane. The main difference between the clean and monohydrogenated C(111)-2x1 structures is in the bond length along the chains, which is 1.46 Å and 1.56 Å respectively. Increasing the length of the bond between the carbon atoms in the chains on the monohydride surface leads respectively to a decrease of the distance between the rows of chains – 3.33 Å (was 4.37 Å). In both cases, there is a formation of the covalent carbon-hydrogen bonds, which have a length of 1.086 Å.

To simulate the hydrogen adsorption processes, the reaction coordinate calculation was used. The hydrogen atom is located at a distance of 6 Å from the surface and the gradual approach of the H atom to the surface of the cluster in the process of calculating the reaction coordinate.

On clean ideal surface diamond C(111) we are not found preferential adsorption centers. The activation energy of adsorption H on any atom of surface C(111)-1x1 is equals Ea=0.16 eV, the binding energy C-H is Eb=3.7 eV. Because the chain of the surface C(111)-1x2 have a slope, on the reconstructed surface adsorption mostly will take place at the higher atoms (1position): Ea=0.2 eV, Eb=3.4eV (fig.2).
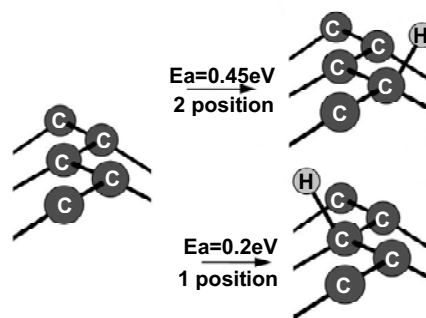

Fig. 2. The results of hydrogen adsorption on the clean diamond C(111)-2x1 surface
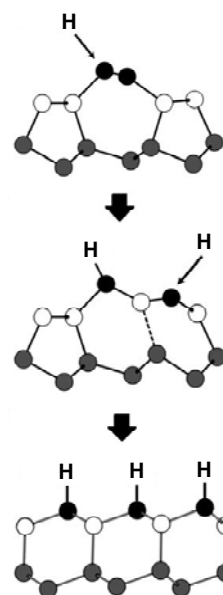

Fig. 3. The hypothetical mechanism transformation process from C(111)-2x1 to C(111)-1x1:H

Black color shows atoms of the first layer, white – the second layer, gray – the third layer.

Conclusion. Hydrogenation of the surface leads to formation two configurations: a metastable (2x1) configuration with Pandey chains and a stable (1x1) configuration that is very close to bulk-terminated geometry. For both configurations bond length C-C is about equal to the interatomic distance in the bulk. Hydrogen terminates the surface C atoms to maintain the sp^3 hybridization. We find that the most probable monohydride form for the surface diamond (111) is C(111)-1x1:H. So, in the case of the hydrogen termination of the diamond (111) surface, the surface dangling bonds stabilizes without any noticeable relaxation of the carbon atoms, in contrast to the C(100) surface.

We proposed the mechanism of the (2x1) to (1x1) surface transformation induced by hydrogen adsorption on a diamond surface (fig. 3). Most probably adsorption of the hydrogen atoms on the reconstructed surface of diamond with (111)-2x1 will occur selectively, mainly in the upper atoms of the surface chains.

REFERENCE:
1. *Chin R. P.* Vibrational spectra of hydrogen on diamond C(111)-(1x1) / R. P. Chin, J. Y. Huang, Y. R. Shen et al. // Phys. Rev. B, 1992. – Vol. 45, № 3. – P. 1552–1524.

2. *Garrido J. A.* pH sensors based on hydrogenated diamond surfaces / J. A. Garrido, A. Härtl, S. Kuch et al. // Appl. Phys. Lett., 2005. – № 86. – P. 073504(1)–073504(3).

3. *Nichols B. M.* Photochemical functionalization of hydrogen-terminated diamond surfaces: a structural and mechanistic study / B. M. Nichols, J. E. Butler, J. N. Russell and R. J. Hamers // J. Phys. Chem, 2005. – Vol. 109, № 44. – P. 20938–20947.

4. *Marsili M.* Tight-binding calculations of quasiparticle wave functions for C(111)2x1 / M. Marsili, O. Pulci, F. Bechstedt and R. D. Sole // Phys. Rew. B., 2005. – Vol. 72. – P. 115415(1)–115415(5).

5. *Mitsuda Y.* Interactions of deuterium and hydrocarbon species with the diamond C(111) surfaceSurf. / Y. Mitsuda, T. Yamada, T. J. Chuang et al. // Surf. Sci. – Vol. 257, Iss. 1–3. – P. L633–L641.

6. *Pandey K. C.* New pi-Bonded Chain Model for Si(111)-2x1 Surface / K. C. Pandey // Phys. Rev. Lett., 1981. – Vol. 47, № 26. – P. 1913–1917.

7. *Severina E.* Diamond C(111) surface reconstruction / E. Severina // Sci. Lett. of Acad. Soc. of Michal Baludansky, 2014. – Vol. 2, № 1. – P. 122–125.

8. *Su C.* Hydrogen chemisorption and thermal desorption on the diamond C.111. surface / C. Su and K.-J. Song, Y. L. Wang, et al. // J. Chem. Phys., 1997. – Vol. 107, № 18. – P. 7543–7558.

9. *Zhigilei L. V.* Intermediate metastable structure of the C(111)/(1x1)H-C(111)/(2x1) surface phase transition / L. V. Zhigilei, D. Srivastava and B. J. Garrison // Phys. Rew. B., 1997. – Vol. 55. – № 3. – P. 1838–1843.

Ананьїна О., канд. фіз.-мат. наук,
Северина О., асп., каф. фізики напівпровідників, Фізичний факультет
Запорізький національний університет

АДСОРБЦІЯ ВОДНЮ НА ПОВЕРХНІ АЛМАЗУ С(111): КВАНТОВО-ХІМІЧНЕ МОДЕЛЮВАННЯ

Процеси взаємодії атомарного водню з поверхнею С(111) є об'єктом даного дослідження. Було розглянуто дві конфігурації поверхні – С(111)-1x1:Н and С(111)-2x1:Н. Вивчення адсорбції водню на поверхні алмазу С(111) здійснювалось за допомогою напівемпіричного методу квантово-хімічного моделювання MNDO (MOPAC) і ab-initio методу Хартрі-Фока (PC GAMESS).

Ключові слова: поверхня алмазу С(111), адсорбція водню, кластер, квантово-хімічне моделювання, МНДП (модифіковане нехтування диференціальним перекриттям), ab-initio.

Ананьина О., канд. физ.-мат. наук,
Северина Е., асп., каф. физики полупроводников, Физический факультет
Запорожский национальный университет

АДСОРБЦИЯ ВОДОРОДА НА ПОВЕРХНОСТИ АЛМАЗА С(111): КВАНТОВО-ХИМИЧЕСКОЕ МОДЕЛИРОВАНИЕ

Процессы взаимодействия атомарного водорода с поверхностью С(111) являются объектом данного исследования. Было рассмотрено две конфигурации поверхности – С(111)-1x1:Н и С(111)-2x1:Н. Изучение адсорбции водорода на поверхности алмаза С(111) осуществлялось при помощи полуэмпирического метода квантово-химического моделирования MNDO (MOPAC) и ab-initio метода Хартри-Фока (PC GAMESS).

Ключевые слова: поверхность алмаза С(111), адсорбция водорода, кластер, квантово-химическое моделирование, МПДП (модифицированное пренебрежение дифференциальным перекрытием) , ab-initio.

V. Andrusenko, stud.,
I. Bekh, PhD, S. Novak, stud.
Faculty of radiophysics, electronics and computer systems,
Taras Shevchenko National University of Kyiv

SIMULATION OF NEURAL NETWORKS BY THE ANALOG CALCULATING MACHINE (ACM) (IN THE TASK OF APPROXIMATION OF MATHEMATICAL FUNCTIONS)

By means of environment of design NI Multisim realized and investigated ACM which is modeling Rumelhart's perceptron that is presently most investigational. Using ACM was obtained approximated mathematical function sin (x). Analysis of approximation showed that ACM meets implemented to the task and meet the stated accuracy of the simulation function.

Keywords: neural network, Rumelhart's perceptron, approximation of function, analog calculating machine.

Introduction. For a long time people tried to explain, as functions their own thinking. Neurobiologists and neuroanatomists attained considerable progress in the study of cerebration. Prospecting a structure and functions of the nervous system of human, they much understood in the "wiring" of brain, but small learned about his functioning. In the process of researches it turned out, that a brain had stunning complexity: billion of neurons, each of that is connected with hundreds or thousands others, form the system that far exceeds our brave dreams about super computers. A concept "artificial neural network" was first entered in 40's years of last century [6]. On logical level an artificial neural network designs activity of the nervous system of human and animals. The formal neurons united in network can decide tasks that traditionally behave to the area of "human activity" (for example recognition of patterns and even making decision on the basis of incomplete information). Especially interesting is ability of neural networks to study and memorize information that reminds human's intellection. Therefore in early works of research of neural networks a term "artificial intelligence" was often used.

Short time ago interest to artificial neural networks quickly grew. They took up specialists on such distant areas, as a technical constructing [8], physiology [7] and psychology [1]. This interest is clear: an artificial neural network, essentially, is the model of the natural nervous system, that is why creation and study of such networks allows to know much about functioning of the natural systems. Other important property of neural network is reliability [3]: even if a few elements will work wrong or break ranks, however, a network will be able to give out correct results, but with less exactness.

Some types of neural networks have the ability to generate an abstract image on the basis of a few input signals [5]. For example, it is possible to teach a network, giving the sequence of the twisted images of letter of "A". After studies a network will be able to generate the letter of "A" without distortions, namely the network can generate it that she never given.

Neural networks can execute the enormous amount of various tasks most widespread from that is: nonlinear approximation of multidimensional functions, prognostication of development of processes that depend on many the