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The Choice of Silicon Nanostructures for CH_4 Detection: *Ab Initio* Calculation

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The paper focuses on the *ab initio* theoretical study of the silicon nanostructures' sensitivity to adsorption of CH_4 molecules. The electronic properties of porous silicon, silicon nanoclusters in a vacuum, silicon nanowires, and nanoscale silicon film are examined. The analysis of results shows that silicon nanofilm is most sensitive to CH_4 adsorption as compared with nanoclusters, nanowires, and porous silicon.

Роботу присвячено теоретичному дослідженню методами з перших принципів чутливости кремнійових наноструктур щодо адсорбції молекул CH_4. Вивчалися електронні властивості наступних наноструктур: пористий кремній, нанокластери кремнію у вакуумі, кремнійові нанодроти та наномасштабна плівка. Аналіз результатів показує, що нанорозмірна кремнійова плівка найбільш чутлива до процесу адсорбції в порівнянні з іншими досліджуваними об'єктами.

Работа посвящена теоретическому исследованию методами из первых принципов чувствительности кремниевых наноструктур к адсорбции молекул CH_4. Изучались электронные свойства таких наноструктур: пористый кремний, нанокластеры кремния в вакууме, кремниевые нанопроволоки и наномасштабная плёнка. Анализ результатов показывает, что наноразмерная кремниевая плёнка наиболее чувствительна к процессу адсорбции по сравнению с другими исследуемыми объектами.

Key words: silicon, nanostructure, CH_4 molecules, *ab initio* calculations.

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1. INTRODUCTION

Gas sensors are widely used in various fields of human activity. In par-

ticular, the harmful gases (such as CH_4, CO_2, NO_2 and others) sensors are in large demand. There are observed trends in reduction of gas sensors and searching for new materials to create them.

Thus, much attention is devoted to the sensory properties of carbon nanostructures—nanotubes and graphene [1, 2, 3]. The authors of [1] experimentally documented the changing of electrical resistance of the examined nanotubes after adsorption of CH_4 and CO_2 gas molecules. It has been noted that this sensor has good sensitivity and short response time. However, after CO_2 adsorption, the sensor has not been fully recovered. The authors explain the change in conductivity by the shift of the valence band of nanotubes, which leads to appearing of the *p*-type semiconductor.

The authors of [2] experimentally investigated the sensory properties of graphene on the adsorption of vapours of ethanol, methanol, chloroform and other gases. In addition to changes in electrical resistance (which is different for different gases by value and by sign), the shift of the noise spectra of graphene has been observed. Therefore, by fixing these two options, one can achieve a high selectivity of single-transistor graphene sensor and use it to define a wide range of gases.

In Ref. [3], the sensory properties of nanopatterned graphene on adsorption of NO_2 have been experimentally examined. The nanopatterned samples showed sensitivities for NO_2 of more than one order of magnitude higher than for non-patterned graphene. The NO_2 concentrations as low as 300 ppt. were detected with an ultimate detection limit of tens of ppt.

Another area of research covers the sensory properties of nanocrystalline oxides ZnO, SnO_2, In_2O_3, TiO_2 and its composites [4, 5].

Thus, in Ref. [4], it has been experimentally demonstrated the role of quantum dots of SnO_2 in detecting low concentrations of methane (CH_4) at a relatively low temperature of $\cong 150°C$ with high response ($S \cong 3.5\%$) and response time below 1 min. These SnO_2 nanoparticles exhibited a strong sensing response to CH_4 in comparison to the annealed sample.

The paper [5] experimentally investigates the sensory properties of ZnO nanoparticles on atmospheric gases N_2, O_2 and CO_2. In addition to changing the electrical conductivity, the changes of examined material photoluminescence under the influence of gases were observed. It has been detected relationship between air pressure and photoluminescence.

Two-dimensional semiconductors are also interesting for gas sensing [6, 7]. In Ref. [6], it has been investigated the sorption ability of $Ge_{20}Se_{80}$ thin films applied as active layers of quartz crystal microbalance (QCM) for NO_2 gas sensing. It has been experimentally demonstrated that the introduced gas molecules interact electrostatically with the chalcogen atoms of the host material and initiate some degree

of structural changes in it.

Authors of [7] investigated the role of quantum confinement on the performance of H_2 sensors based on two-dimensional InAs membranes. They found the strong thickness dependence, with ~ 100× enhancement in the sensor response as the thickness is reduced from 48 to 8 nm.

Other promising materials for the construction of gas sensors are nanowires. In paper [8], the analysis of researches in this area, the classification of sensor materials, the methods of synthesis and comparison of sensory properties are given. This group of materials can be divided into nanowires of metal oxides, polymer nanowires, metal nanowires and silicon nanowires.

Silicon-based gas sensors are of great interest because they may be easily integrated to electronic circuits [8].

Thus, we can distinguish the following main lines of gas sensors evolution: reduction of the size, the transition to the nanoscale and increasing of selectivity and sensitivity. In addition to the empirical selection of sensor parameters, theoretical studies are effective for better understanding the nature of sensory properties, and may indicate directions for improving gas sensor.

2. MODELS AND METHODS OF CALCULATION

The aim of this work was the *ab initio* theoretical study of the silicon nanostructures sensitivity to adsorption of CH_4 molecules. All calculations were performed using the author's source code [9], which implements the Car–Parrinello quantum-mechanical dynamics, the density functional theory with local density approximation [10, 11], and norm-conserving *ab initio* pseudopotential of Bachelet–Hamann–Schlüter [12].

The ground states of the electron-nuclear systems were detected by means of the self-consistent solution of the Kohn–Sham equations, because electronic variables only were determined with the atomic cores fixed. Following Kohn–Sham approach, electronic density was written down in terms of occupied orthonormal one-particle wave functions:

$$n(\mathbf{r}) = \sum_i \left|\psi_i(\mathbf{r})\right|^2 . \quad (1)$$

The point on the surface of potential energy in the Born–Oppenheimer approximation was determined as a minimum energy functional with regard to the wave functions:

$$E\left[\{\psi_i\},\{R_j\},\{\alpha_\nu\}\right] = \sum_i \int_\Omega d\mathbf{r}\psi_i^*(\mathbf{r})\left[-\frac{\hbar^2}{2m}\nabla^2\right]\psi_i(\mathbf{r}) + U\left[\{n(\mathbf{r})\},\{R_j\},\{\alpha_\nu\}\right], \quad (2)$$

where $\{R_j\}$ are coordinates of atomic cores; $\{\alpha_\nu\}$ are any external influences on the system.

In the generally accepted formulation, minimization of the energy functional (2) with respect to one-particle orbitals with additional orthonormal constraint on the one-particle orbitals $\psi_i(\mathbf{r})$ results in the Kohn–Sham one-particle equations:

$$\left\{-\frac{\hbar^2}{2m}\nabla^2 + \frac{\partial U}{\partial n(\mathbf{r})}\right\}\psi_i(\mathbf{r}) = \varepsilon_i\psi_i(\mathbf{r})\,. \qquad (3)$$

The distribution of electrons along the energy zones for Γ-state was found by means of numerical calculation of derivative $\lim\limits_{\Delta E\to 0}\Delta N/\Delta E$ (where ΔN is a number of the allowed states for the ΔE interval of energy). The one-particle energy spectrum was obtained from calculation of the eigenvalues of the Kohn–Sham matrix. In accordance with ideology of the electronic density functional, the occupied states at absolute zero temperature were defined (states of valence zone and states in the gap zone, which are related to the defects). It allowed defining position of Fermi level, based on the last occupied state, their number being half the number of electrons (due to ignoring the spin of the electron). Attention should be paid to the fact that the Γ-point for superlattice calculations has the meaning of the Baldereschi mean-value point [13], which represents all vectors in the Brillouin zone.

3. RESULTS OF CALCULATION AND THEIR DISCUSSION

The atomic basis of the unit cell, which reproduces artificial translational symmetry of the system, consisted of 64 silicon atoms. By setting the different vacuum gap widths in the directions of the coordinate axes, various nanostructures of silicon were simulated: porous silicon, silicon nanoclusters in a vacuum, silicon nanowires and nanoscale silicon film. Coordinates of the atomic basis have not been optimized. We investigated the changes in the electronic structure of these materials after the adsorption of CH_4 molecules.

Figure 1 shows the partial valence electrons density distribution in the studied systems for a range of 0.7–0.8 of the maximum value. For all of nanostructures, the rearrangement of the electronic density after the gas molecules adsorption may be seen. The appearance of charge jumper between molecules and silicon nanostructures is observed. The analysis of the intensities of these interactions shows that silicon nanofilm is the most sensitive to the adsorption process; in this case, the highest values of the electron density are located around the adsorbed molecule. One can also observe the influence of the molecule to the distribution of electronic density inside the nanostructure.

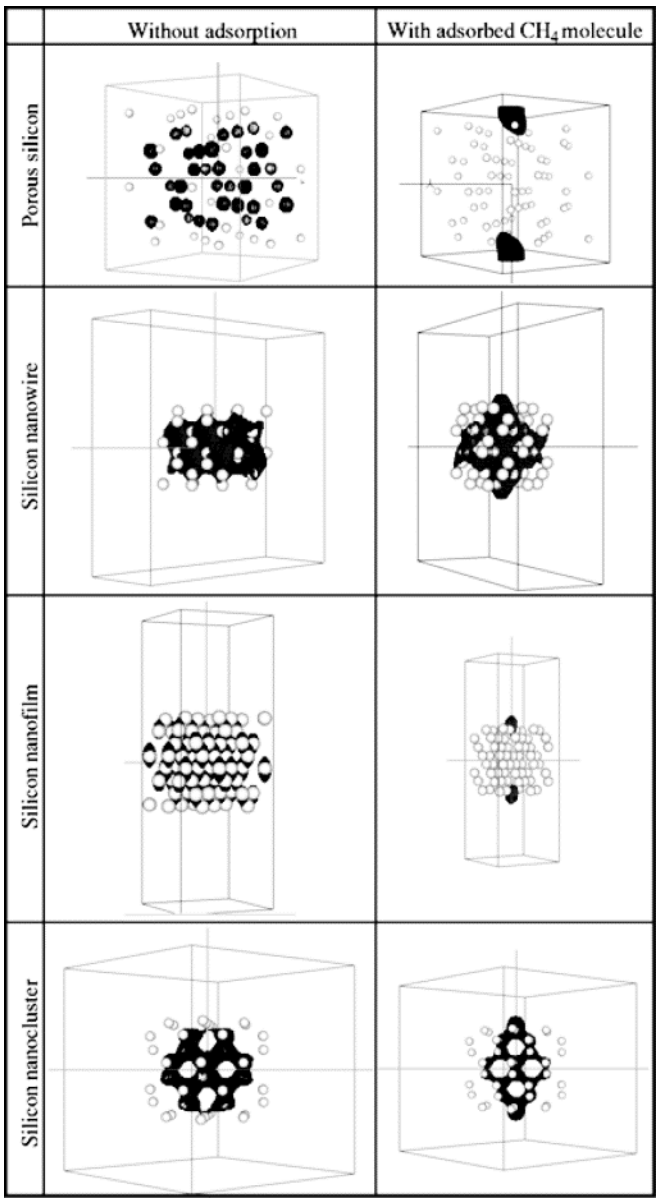

Fig. 1. The valence-electrons' density distribution in different examined nanostructures. The valence electrons density in the range of 0.7–0.8 of its maximum value is shown.

For example, in nanoclusters (see Fig. 1) in the absence of adsorbed molecules, the electronic distribution was symmetric with respect to the centre of the cluster, but, after the adsorption, it takes asymmetric

shapes' stretched in the direction of the adsorbed molecules.

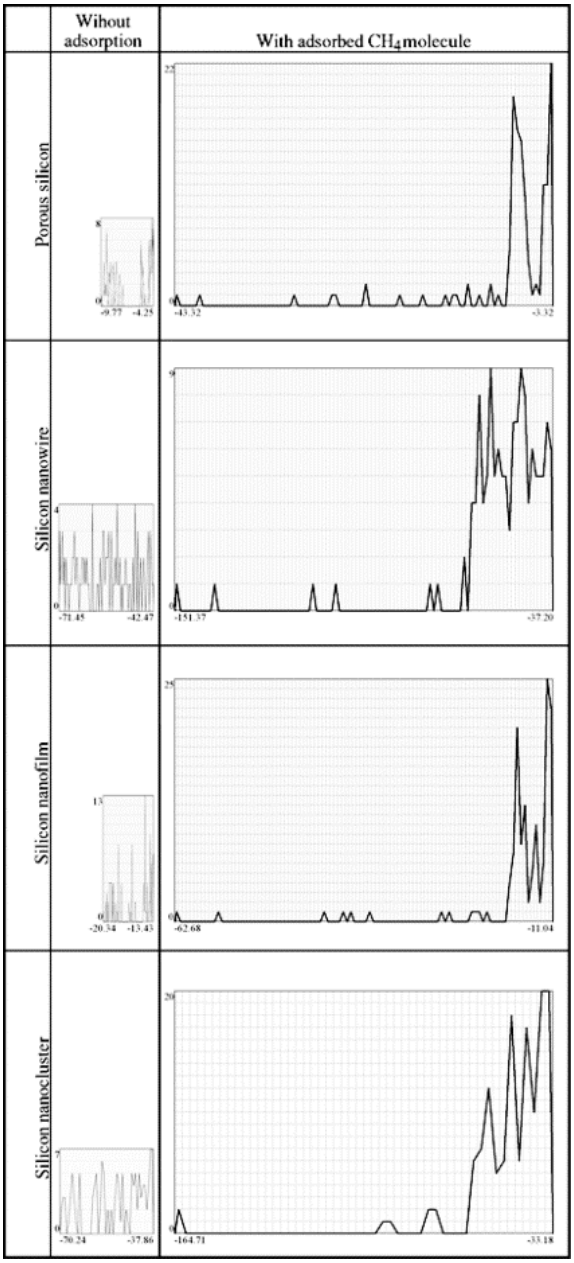

Fig. 2. Density of states for Γ-point of Brillouin zone for different examined nanostructures. The x-axis shows energy in atomic units. The y-axis shows number of states.

A similar internal reorganization of the electronic density is observed for nanowires.

The valence-electrons' density of allowed states in the energy range is shown in Fig. 2. The low-populated states (states occupied by one electron) at the bottom of the energy range are states of the molecule CH_4, and the states in the upper part of the range belong to the silicon nanostructures. The analysis of these distributions shows that, with such graph resolution, it is difficult to determine the details of the changes in the part of the range, corresponding to silicon nanostructures. Nevertheless, it can be detected that the most of the spectrum is concentrated near the Fermi level (*i.e.*, the right boundary of the energy range of occupied states). Moreover, this effect is most emphasized for the porous silicon and silicon nanofilm.

The distribution of low-populated states in the lower part of energy range is different for different types of nanostructures. This may indicate that the adsorption of the molecule occurs either by physical or by chemical way. In addition, looking to the degree of changes in the electronic structure, we assume that the adsorption on silicon nanoclusters and nanowires is carried out by physical principles and on porous silicon—by chemical principles.

Therefore, nanoscale silicon film is most sensitive to the adsorption process: its electronic spectrum changes most significantly. The expansion of occupied-states' range and the emergence of local states at the top of the energy range of occupied states are observed. The changes of a similar nature, but less noticeable, are present in other examined nanostructures. The observed transformations of the electronic spectrum, leading to a conductivity-type changing of silicon nanostructures, may be used for the construction of gas sensors.

4. CONCLUSIONS

Ab initio calculations show that silicon nanostructures change their electronic properties because of gas molecules adsorption, which leads to change of the material conductivity. These changes are most intensive in silicon nanofilm compared to nanoclusters, nanowires and porous silicon. Thus, nanoscale silicon films may be used to construct CH_4 sensors. The still actual issue is studying the selectivity of this type of sensors.

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