ADSORPTION OF MOLECULAR OXYGEN ONTO $Si_{1-x}Ge_x$/Si(001) SURFACE

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PACS 68.43.BC
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On the basis of *ab initio* calculations, the adsorption of O_2 molecules onto a $Si_{1-x}Ge_x$/Si(001) surface has been considered at a qualitative level, and stable adsorption configurations of molecular oxygen have been determined. The O_2 molecule was found to be chemisorbed without dissociation onto the $Si_{1-x}Ge_x$/Si(001) surface. In the case where the $Si_{1-x}Ge_x$/Si(001) surface is presented by pure Si–Si or mixed Si–Ge addimers, the adsorption of O_2 molecules was found to be barrierless. In the case where the surface is presented by pure Ge–Ge addimers, the chemisorption barrier was found to be lower than 0.1 eV. The adsorption of O_2 molecule on the $Si_{1-x}Ge_x$/Si(001) surface is accompanied by a change of the spin state of the system from the triplet to the singlet one and by a reduction of the surface chemical reactivity.

1. Introduction

Nanostructures fabricated on the basis of $Si_{1-x}Ge_x$ alloys are used in modern micro- and nanoelectronics, while developing and creating integrated circuits, memory, optoelectronic, and high-speed devices. It is so, because the mobility of holes in a SiGe layer is higher than in pure Si used in MOS devices. In addition, to improve the characteristics of MOS devices, the process of thin oxide layer formation has to be made controllable as much as possible.

The formation of superthin oxide layers on a $Si_{1-x}Ge_x$/Si(001) substrate starts from molecular oxygen adsorption. As was shown in work [1], the sticking coefficient of O_2 molecule to the clean Si(001) surface is an order of magnitude higher than that to a surface with a coating of 0.9 ML Ge. The mixing of Ge atoms with substrate Si atoms also increases the coefficient of oxygen absorption by the $Si_{1-x}Ge_x$/Si(001) surface [1]. Hence, the mixing of Si and Ge atoms can change the process of O_2 molecule adsorption onto the $Si_{1-x}Ge_x$/Si(001) surface. In works [2–7], the molecular beam epitaxy was used to study the interaction between O_2 molecules and the Si(001) surface under various conditions. In particular, the presence of O_2 molecules physically adsorbed on the Si(001) surface at low temperatures (77 K) was demonstrated in [2]. The states formed due to the physical adsorption are related to the presence of a barrier for the chemisorption of O_2 molecules, which was indicated in monography [8]. After overcoming this barrier, the stable adsorption configurations of O_2 are formed on the Si(001) surface. Therefore, this work is aimed at the consideration of the adsorption of O_2 molecules on the $Si_{1-x}Ge_x$/Si(001) surface followed by the formation of their stable adsorption configurations. The dissociation of O_2 molecules is neglected.

2. Calculation Technique

Ab initio calculations were carried out in the framework of spin-restricted open-shell Hartree–Fock (ROHF) approximation, spin-unrestricted Hartree–Fock (UHF) approximation, and density functional theory (DFT). In DFT calculations, we used the B3LYP hybrid functional (Becke three-parameter hybrid functional combined with Lee–Yang–Parr correlation functional) [9] and the split-valence basis set N21-3** with two polarization functions [10].

The surface was simulated as a complex $O_2Ge_2Si_{10}H_4/O_2Ge_2Si_{32}H_{32}$ cluster (Fig. 1). Some part of this cluster was analyzed by quantum-mechanical calculations, and the whole cluster was calculated within molecular mechanics in the Surface Integrated Molecular Orbital Molecular Mechanics (SIMOMM) scheme [11] with the use of the GAMESS software package [12].

Stable adsorption configurations of O_2 molecules were determined within the DFT and UHF methods with a complete optimization of atomic coordinates in the cluster. The value of the squared spin operator $\langle S^2 \rangle = S(S+1)$ (spin contamination) was calculated in the framework of the UHF method. The deviation of $\langle S^2 \rangle$ from zero for singlet states evidences the presence of degenerate levels in the system and indicates the necessity to apply multiconfiguration wave functions [10]. In the case $\langle S^2 \rangle = 0$, single reference wave functions are enough for the description of the system. Therefore, while calculating structures with $\langle S^2 \rangle = 0$, we

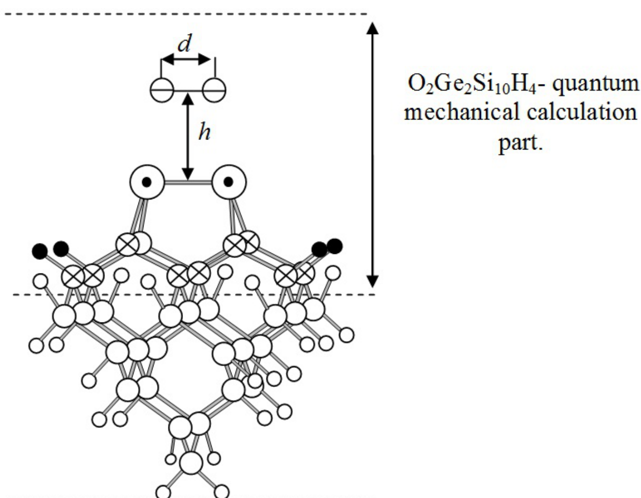

Fig. 1. Cluster that simulates the $Si_{1-x}Ge_x$/Si(001) surface and reaction coordinates d and h describing O_2 adsorption onto this surface. Designations for atoms calculated quantum-mechanically – Si (⊗), Ge (⊙), H (•), and O (⊖) – and for those calculated within molecular mechanics – Si (○) and H (○)

used the DFT method, which allowed the dynamic electron correlation [10] to be taken into consideration as well. The energies of O_2 molecule adsorption on the $Si_{1-x}Ge_x$/Si(001) surface, E_a, were determined by the formula $E_a = E_{S+O_2} - E_S - E_{O_2}$, where E_{S+O_2} and E_S are the energies of the system in the states with an adsorbed O_2 molecule or not, respectively, and E_{O_2} is the energy of O_2 molecule.

The result of the O_2 adsorption is known to depend on its kinetics, which is not taken into account by our model. Hence, we confine the consideration to the qualitative level by analyzing the equilibrium adsorption of O_2 molecules, which do not interact with one another and possess a low kinetic energy on the $Si_{1-x}Ge_x$/Si(001) surface, in the ROHF approximation, which allows the energy of the system to be determined with an error less than 1% [10]. To describe the adsorption of O_2 molecule, we used its two reaction coordinates, d and h (see Fig. 1), and completely optimized the coordinates of H, Si, and Ge atoms in the cluster under investigation. The positions of O atoms were optimized only along the coordinate d, and the corresponding dependence of the energy of the system on the coordinate h, $E(h)$, was obtained. With the help of the function $E(h)$, we determine approximately the saddle-point position and the adsorption barrier. More accurate values were calculated within the Quadratic Approximation (QA) method [10]. To verify that the obtained saddle point corresponded to the adsorption barrier for O_2 molecules, we calculated the path of O_2 adsorption, which was the most beneficial energetically, i.e. the dependence $E(Y)$ of the energy on Y, one of the characteristic reaction coordinates, and tested whether the saddle point and the points corresponding to the minima of the energy belong to this path. The fact that only one second derivative $d^2E(Y)/dY^2$ was negative confirmed that the analyzed point was really a saddle one. The dependence $E(Y)$ was determined using the fourth-order Runge–Kutta (RK4) method with adaptive step size [10]. The calculation of the most energetically beneficial adsorption path was carried out together with the optimization of all atomic coordinates in the cluster.

3. Results and Their Discussion

We considered the adsorption of O_2 molecules onto the cluster surface in two stages. First, the stable configurations of O_2 molecules in the adsorbed state on the surface were determined. Then, the corresponding qualitative analysis of the surface adsorption was carried out.

3.1. Stable adsorption configurations of O_2 molecules on the $Si_{1-x}Ge_x$/Si(001) surface

Addimers (dimers formed by adsorbed atoms) are chemically the most active part of the cluster surface, because every of them has two dangling bonds. Therefore, we confine the consideration to the adsorption of O_2 molecules on addimers of the $Si_{1-x}Ge_x$/Si(001) surface. In our previous work [11], the assumption was made that O_2 molecules more actively dissociate at those surface sites, where the occupation numbers for antibonding orbitals in the corresponding addimers are maximal. To test this assumption, we calculated the electron structures of O_2 molecule using the CASSCF(6;8)/N21-3** method and compared the natural orbital occupation numbers (NOONs) [14] at its bonding and antibonding orbitals (Fig. 2) with the corresponding occupation numbers for orbitals in addimers on the $Si_{1-x}Ge_x$/Si(001) surface, which were determined in our previous work [13].

For O_2 molecule to dissociate, it is known that the occupation numbers at its antibonding π^*, π^*, and σ^* orbitals should exceed the occupation numbers at its bonding π, π, and σ orbitals (Fig. 2,*e*). In the course of the adsorption of O_2 molecule on an addimer of the $Si_{1-x}Ge_x$/Si(001) surface as a result of their interaction, the antibonding π^*, π^*, and σ^* orbitals of the molecule become partially filled with electrons, which pass there from the antibonding π^* orbital of the addimer on the

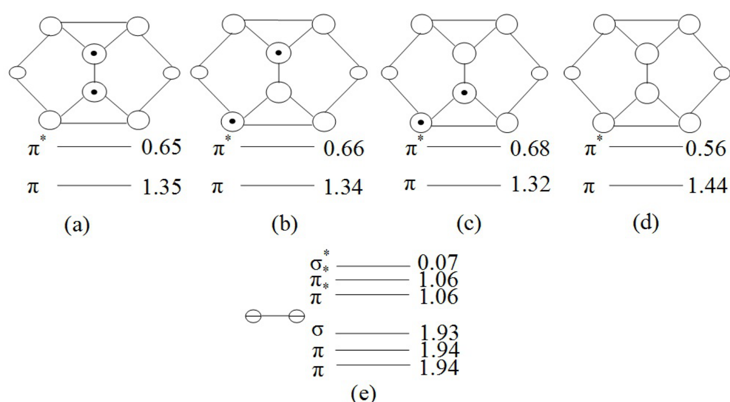

Fig. 2. Occupation numbers for bonding and antibonding orbitals of addimers on the $Si_{1-x}Ge_x$/Si(001) surface (panels a to d) and for a O_2 molecule (panel e). Designations for atoms: Si (○), Ge (⊙), and O (⊖)

substrate surface. The occupation numbers of the antibonding π^* orbitals of addimers amount to 0.65, 0.56, 0.68, and 0.66 for the cases of pure Ge–Ge (Fig. 2,a) and Si–Si (Fig. 2,d) and mixed Si–Ge (Figs. 2,c and b) addimers, respectively. Therefore, they are not high enough for the occupation numbers of antibonding π^*, π^*, and σ^* orbitals of O_2 molecule to become larger than the occupation numbers of its bonding π, π, and σ orbitals. Hence, one may assume that there exist the stable adsorption configurations of O_2 molecules on the studied surface. The existence of similar stable adsorption configurations of O_2 molecules on the Si(001) surface was demonstrated in work [8].

In work [15], on the basis of a detailed research of the adsorption of O_2 molecules on the Si(001) surface, three adsorption configurations were proposed (see Figs. 3,a to c). We made calculations for all of them in the cases of pure Ge–Ge (Figs. 3,a to c), pure Si–Si (Fig. 3,j to l), and mixed Si–Ge (Fig. 3,e to i) addimers to determine the structures with the minimal free energy of the system and, additionally, to test their stability taking advantage of vibrational analysis. Only the structures corresponding to panels a, d, g, and j in Fig. 3, which are in the singlet state with the spin contamination $\langle S^2 \rangle = 0$, turned out stable adsorption configurations of O_2 molecules on the $Si_{1-x}Ge_x$/Si(001) surface. This means that calculations in the framework of the DFT method are enough for the determination of the energy of those structures. It enabled us to obtain the energy differences ΔE, quoted in Fig. 3 for structures a and d, with respect to structure g with mixed Si–Ge addimers, which is energetically the most beneficial one.

Structure a with pure Ge–Ge addimers, for which $\Delta E = 0.54$ eV, is energetically the least beneficial one. Hence, the adsorption of O_2 molecules onto mixed Si–

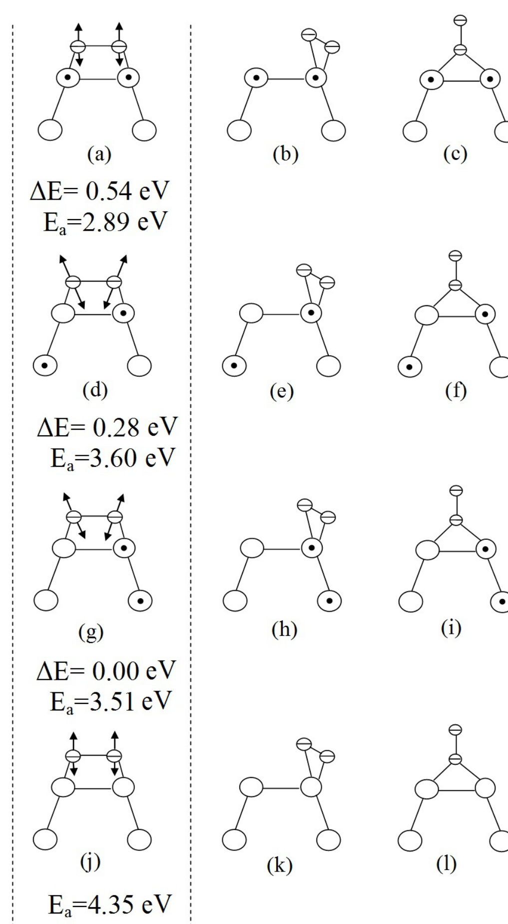

Fig. 3. Adsorption configurations of O_2 molecules on the $Si_{1-x}Ge_x$/Si(001) surface with various addimers: pure Ge–Ge (a to c), pure Si–Si (j to l), and mixed Si–Ge (d to f and g to i). ΔE is the energy with respect to that of structure g, E_a is the O_2 molecule adsorption energy. Designations for atoms: Si (○), Ge (⊙), and O (⊖)

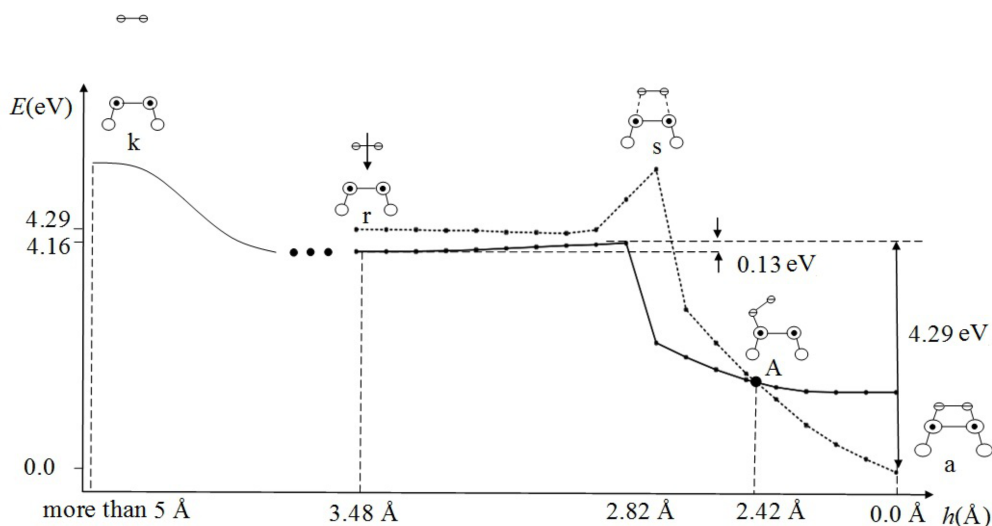

Fig. 4. Dependences $E(h)$ for the system with the optimized d-values on the Si(001) surface in its two states: triplet (solid curve) and singlet (dotted curve). Designations for atoms: Si (○), Ge (⊙), and O (⊖)

Ge addimers can be regarded as more probable than that onto pure Ge–Ge addimers.

In Fig. 3, the adsorption energies of O_2 molecules on the studied surface, which were determined by the DFT method, are also quoted. The highest value, $E_a =$ 4.35 eV, takes place for the adsorption of O_2 molecules on pure Si–Si addimers (Fig. 3,j) at the Si(001) surface, and the least one, $E_a = 2.89$ eV, for the adsorption on pure Ge–Ge addimers (Fig. 3,a) at the same surface. For mixed Si–Ge addimers g and d on the Si(001) surface, the energy E_a had intermediate values of 3.51 and 3.60 eV, respectively. These data correlate with experimental values of the sticking coefficient of O_2 molecules on the Ge/Si (001) surface reported in work [1], where the sticking coefficient of the Si(001) surface with pure Ge–Ge addimers was shown to be lower than that of the surface with mixed Si–Ge addimers.

Arrows in Fig. 3 mark the directions of the most intensive vibration modes of O_2 molecule in structures a, d, g, and j. One can see that, in the case of structures with pure Ge–Ge (Fig. 3,a) and Si–Si (Fig. 3,j) addimers, those modes are directed as if they favor the desorption of O_2 molecules, whereas, in the case of structures with mixed Si–Ge addimers (Figs. 3,d and g), they promote their dissociation. Hence, one may assume that the dissociation of O_2 molecule is more probable in the case of mixed Si–Ge addimers on the Si(001) surface (Figs. 3,g and h). For this assumption to be confirmed, it is necessary to determine the dissociation barriers for O_2 molecule at addimers on the $Si_{1-x}Ge_x$/Si(001) surface, which is the matter of the further research.

As was already mentioned, $\langle S_2 \rangle = 0$ for stable adsorption configurations of O_2 molecules on the examined surface, i.e. the structures depicted in Figs. 3,a, d, g, and j have no dangling bonds. Hence, the adsorbed O_2 molecule passivates the $Si_{1-x}Ge_x$/Si(001) surface; in other words, it reduces its chemical activity.

3.2. Adsorption of O_2 molecules on $Si_{1-x}Ge_x$/Si(001) surface

The ground state of O_2 molecule is the triplet one (the energy difference between the singlet and triplet O_2 states is 0.98 eV [16]), whereas structures a, b, c, and d (see Fig. 2) of the surface substrate are in the singlet state [13]. As was shown above, the ground states of structures a, d, g, and j with an adsorbed O_2 molecule (see Fig. 3) are singlets. Hence, in the course of the O_2 molecule adsorption, the system passes from the triplet state into the singlet one. Therefore, to describe this process, the surfaces of potential energy for both triplet and singlet system states have to be analyzed.

In Fig. 4, the dependences $E(h)$ for the system of pure Ge–Ge addimers with optimized d-values in the singlet and triplet states on the Si(001) surface are exhibited. They allowed us the analyze the dependence $E(h)$ rather than the dependence $E(h, d)$. One can see that there emerges a barrier of 0.13 eV for the adsorption of O_2 molecule in the triplet state. The barrier height was determined as a difference between the molecular energies at point r, where the energy of physically adsorbed O_2 molecule is minimal, and at saddle point s of the same

 ISSN 2071-0186. Ukr. J. Phys. 2012. Vol. 57, No. 3

system in the course of adsorption. However, the dependences $E(h)$ intersect at point A, where the system with O_2 molecule passes into the singlet state without energy losses. Then, it reduces its energy in the singlet state with respect to the state in the saddle point s by 4.29 eV, and this value may be taken as the desorption energy of O_2 molecule. Hence, a considerable energy of O_2 molecule desorption in comparison with the barrier height for its adsorption allows us to assert once more that there is a probability for a nondissociated O_2 molecule to be adsorbed onto the surface under investigation.

After determining the position of the saddle point and the magnitude of the adsorption barrier for O_2 molecule more accurately (the latter turned out lower than 0.1 eV) and finding the energetically most beneficial path of its adsorption onto the Ge–Ge addimer on the Si(001) surface, we got convinced that points a and s really belong to the dependence $E(h)$ (Fig. 4).

We also constructed similar dependences $E(d,h)$ for the cases of pure Si–Si and mixed Si–Ge addimers on the Si(001) surface and used them to determine the positions of corresponding saddle points. In both those cases, O_2 molecules turned out to be adsorbed without overcoming the barrier. The adsorption of O_2 molecules onto the $Si_{1-x}Ge_x$/Si(001) surface with pure Si–Si and mixed Si–Ge addimers, similarly to the case of pure Ge–Ge addimers, is accompanied by a change of the spin state of the system from the initial triplet one to the singlet state with a stable adsorption configuration of O_2 molecule (Figs. 3,a, d, j, and g).

4. Discussion

We qualitatively considered adsorption of O_2 molecules onto the $Si_{1-x}Ge_x$/Si(001) surface in the framework of selected model (see Section 2) and showed that there is no surface adsorption barrier, if the surface is presented by pure Si–Si and mixed Si–Ge addimers. For the surface with pure Ge–Ge addimers, the adsorption barrier does not exceed 0.1 eV. These conclusions agree with experimental data [8]. It is of interest that the adsorption of O_2 molecule is accompanied by the change of the spin state of the system from the singlet to the triplet one, which allows us to predict a possible influence of an external magnetic field on the process of O_2 molecule adsorption onto the $Si_{1-x}Ge_x$/Si(001) surface.

It has to be noted that our model does not take the kinetics of adsorption into consideration, which depends on the temperature, pressure, and presence of defects, steps, surface stresses, and so forth on the surface. The model deals with the adsorption of separate O_2 molecules not interacting with one another and possessing a very low kinetic energy. Nevertheless, it enabled us to detect a barrier of about 0.1 eV for the chemisorption of O_2 molecules onto pure Ge–Ge addimers on the $Si_{1-x}Ge_x$/Si(001) surface. The existence of a similar barrier to the O_2 chemisorption onto the pure Si(001) surface in the temperature interval $T = 77 - 100$ K was demonstrated in works [2–7], which confirms the adequacy of the model selected by us. It was also shown in work [2] that, if the molecule velocity in the beam is small (the beam energy of about 0.026–0.150 eV), and the substrate temperature is low ($T \approx 77$ K), the sticking coefficient does not depend on the angle, at which the beam falls on the surface. This testifies that the adsorption of O_2 molecule onto the Si(001) surface occurs in the same way. Taking the adequacy of the selected model into account, we may hope that the chemisorption of O_2 molecule onto the $Si_{1-x}Ge_x$/Si(001) surface at low temperatures ($T \approx 77$ K) and small velocities of O_2 molecules takes place, by passing through points r, s, A, and a in the dependence $E(h)$ and the corresponding structures, as is shown in Fig. 4.

A separate attention should be paid to the issue of stable adsorption configurations of O_2 molecules on the $Si_{1-x}Ge_x$/Si(001) surface, which were not studied earlier. Our calculations confirmed the existence of stable adsorption configurations of O_2 on the $Si_{1-x}Ge_x$/Si(001) surface. The dissociation of an adsorbed O_2 molecule on the Si(001) surface leads to the formation of a thin oxide layer on the $Si_{1-x}Ge_x$/Si(001) surface.

Another factor, which was not taken into account in our model, includes surface stresses that enhance the O_2 absorption [17] and can affect the interaction between O_2 molecules and the surface. The influence of surface stresses on the oxidation of the $Si_{1-x}Ge_x$/Si(001) interface will be analyzed elsewhere.

5. Conclusions

Stable adsorption configurations of O_2 molecules on the $Si_{1-x}Ge_x$/Si(001) surface and the corresponding adsorption energies have been determined. If the surface is presented by pure Si–Si or mixed Si–Ge addimers, O_2 molecules are adsorbed on the $Si_{1-x}Ge_x$/Si(001) surface without overcoming a barrier. In the case where the surface is presented by pure Ge–Ge addimers, an adsorption barrier less than 0.1 eV emerges. The adsorption of O_2 molecules onto the $Si_{1-x}Ge_x$/Si(001) surface is accompanied by the change of the spin state of the system from the triplet into the singlet one. The formation of sta-

ble adsorptive O_2 configurations on this surface reduces (passivates) its chemical activity.

The work was supported by the Ministry of Education and Science of Ukraine (grant M/90-2010). The authors are grateful for the opportunity to use a computer cluster at the Information and Computer Center of the Taras Shevchenko National University of Kyiv.

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Received 03.06.11.
Translated from Ukrainian by O.I. Voitenko

АДСОРБЦІЯ МОЛЕКУЛЯРНОГО КИСНЮ НА ПОВЕРХНЮ $Si_{1-x}Ge_x$/Si(001)

О.А. Гринчук, Т.В. Афанас'єва, І.П. Коваль, М.Г. Находкін

Р е з ю м е

За допомогою розрахунків із перших принципів якісно розглянуто адсорбцію молекули O_2 на поверхню $Si_{1-x}Ge_x$/Si(001) та визначено стабільні адсорбційні конфігурації молекулярного кисню. O_2 недисоціативно хемадсорбуються на поверхню $Si_{1-x}Ge_x$/Si(001). У випадку, коли поверхня $Si_{1-x}Ge_x$/Si(001) подана чистими Si–Si та змішаними Si–Ge аддимерами, адсорбція молекул O_2 проходить без подолання бар'єра. У випадку, коли поверхня подана чистими Ge–Ge аддимерами, бар'єр для адсорбції не перевищує 0,1 еВ. Адсорбція молекули O_2 супроводжується зміною спінового стану системи з триплетного на синглетний та зменшенням хімічної активності поверхні.