

## DIFFUSION OF OXYGEN ATOM INTO SUBSURFACE LAYERS OF $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$ INTERFACE

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*Ab initio* calculations have been carried out to verify a possibility for an oxygen atom to transit from the bridge bond between the addimer atoms and atoms in the second subsurface layer to the bond between atoms belonging to the second and third subsurface layers of the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  interface in the cases where one to three oxygen atoms are adsorbed. Such a transition was found to be unfavorable in the case where pure, Si–Si, and mixed, Si–Ge, addimers are present at the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  interface. If only pure Ge–Ge addimers are present at this interface, the diffusion of a single oxygen atom is possible, with the corresponding diffusion barrier being 2.09 eV. Pure Ge–Ge addimers at the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  interface favor the oxygen diffusion into the bulk to a greater extent than pure Si–Si and mixed Si–Ge addimers do.

### 1. Introduction

Nanostructures fabricated on the basis of Ge/Si heterostructures are used in modern micro- and nanoelectronics to develop and create integrated circuits, as well as storage, optoelectronic, and high-speed devices. The technology of their manufacturing includes the application of thin  $\text{SiO}_2$  layers, the formation of which on heterostructures is much more complicated in comparison with that on pure silicon substrates. In particular, as was pointed out in works [1–3], the diffusion of Ge and Si atoms, as well as the passivation of the substrate surface by Ge atoms that appear on it [1, 4, 5], must be taken into consideration, while analyzing oxidation processes.

In the previous works carried out at our laboratory [5, 6], the adsorption of oxygen atoms was shown to be accompanied by a shift of the core levels of Si atoms in the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  substrate, which are located at a distance of 4 Å from the oxygen. A considerable shift of electron levels of about 1 eV allows a conclusion to be made that the diffusion conditions for both substrate atoms and adsorbed oxygen atoms must substantially change at that. Hence, this system is characterized by a non-locality of the interaction between oxygen atoms and the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  heterostructure surface, which is to be taken into account when constructing a model of oxidation with regard for the diffusion.

In our previous work [6], by simulating the process of oxygen atom adsorption onto the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  heterostructure surface, we found the sites of most probable adsorption for one, two, and three oxygen atoms. It turned out that the most probable event is the formation of bridge bonds Si–O–Si between dimer atoms and atoms in the second subsurface layer, and that the formation of such bonds may be accompanied by the mixing of Ge and Si atoms. A hypothesis was put forward that the oxidation of  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  heterostructures is a complicated phenomenon, in which several near-surface layers of the substrate can be engaged. However, there was lack of information concerning the oxygen diffusion at the initial stages of oxidation at depths of the second and third layers of the substrate. Therefore, the aim of this work was to determine the energy barriers for oxygen atom diffusion into the subsurface layer located between the atoms of the second and third layers of the interface. The relevant information is needed to verify whether such diffusion of oxygen atoms is possible at the initial stages of  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  heterostructure oxidation.

### 2. Calculation Technique

In order to find diffusion barriers, we analyzed the calculation dependences of the energy of the system on the coordinates of an oxygen atom. The magnitudes of diffusion barriers and the energies of structures were calculated from the first principles using the density functional theory (DFT). We used the B3LYP (Becke, three-parameter, Lee–Yang–Parr) hybrid functional [7]. The basis set N21-3\*\* was used for all atoms (Si, H, Ge, and O). Calculations were carried out with the help of the GAMESS computer code [8].

The  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface was simulated – analogously to what was done in work [6] – in the form of a  $\text{Si}_{15}\text{H}_{14}\text{Ge}_2$  cluster (Fig. 1). The dangling bonds at the cluster boundaries were saturated with hydrogen atoms.

In the initial approximation, the lengths of all Si–Si bonds were assumed to equal 2.35 Å (as they are in the

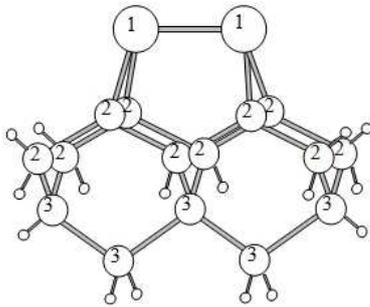


Fig. 1. Cluster  $\text{Si}_{15}\text{H}_{14}\text{Ge}_2$  used to simulate the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface: (1) addimer Si or Ge atoms, the positions of which were optimized; (2) Si atoms, the positions of which were optimized; (3) Si atoms, the positions of which were not optimized; unmarked atoms stand for H ones

bulk of crystalline silicon), and the lengths of Si–H bonds to equal 1.48 Å. During the diffusion, the variation of the oxygen atom position induces the variations in the positions of neighbor atoms. Since we examine the transition of an oxygen atom from the bridge bond between the addimer atoms and the atoms in the second subsurface layer to the bond between the atoms in the second and third subsurface layers, it is expedient to optimize the positions of addimer atoms in the second and third subsurface layers (Fig. 1). In our previous work [6], the adsorption of the second oxygen atom was shown to result in a variation of positions of those atoms which are located at a distance of 4 Å from the oxygen. Therefore, while calculating the stable adsorption configurations with two or three adsorbed O atoms, it is expedient to make a complete optimization of atomic coordinates in the cluster.

A diffusion event was regarded as a variation of the angular coordinates  $\theta_{\text{O}}$  and  $\theta_{\text{Si}}$  (Fig. 2) at the transition of the oxygen atom from the its initial state – when the oxygen is bound with the atoms belonging to the addimer and the second subsurface layer (Fig. 2,b) – into the final one – when the O atom is included into the bond in between the atoms belonging to the second and third subsurface layers (Fig. 2,c).

In the course of calculations, the distances  $r_{\text{O}}$  and  $r_{\text{Si}}$  were kept constant, and only the angles  $\theta_{\text{O}}$  and  $\theta_{\text{Si}}$  were varied. The expediency of the usage of such angular coordinates for the description of the diffusion was demonstrated in work [9]. The initial states were determined as early as in our work [6]. In this work, we calculated the dependences  $E(r_{\text{O}}, r_{\text{Si}}, \theta_{\text{O}}, \theta_{\text{Si}})$  of the cluster energy on the reaction coordinates at the transition of an oxygen atom from the initial state (Fig. 2,b) into the final one (Fig. 2,c). The dependences  $E(r_{\text{O}}, r_{\text{Si}}, \theta_{\text{O}}, \theta_{\text{Si}})$  al-

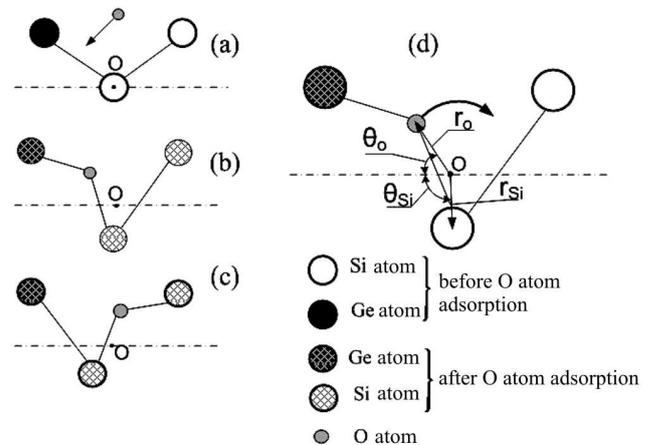


Fig. 2. Positions of atoms in the cluster: (a) before the adsorption of O atoms, (b) after the adsorption of an O atom (the initial state), (c) after the diffusion event (the final state), (d) coordinates used to describe the diffusion of an oxygen atom from the initial into the final state

lowed the position of the saddle point, at which there exists only one negative second derivative of the system energy with respect to either of the coordinates, to be roughly determined. A more exact position of the saddle point was determined with the use of the quadratic approximation (QA) method [10]. The vibrational analysis at the obtained saddle point revealed only one negative second derivative of the energy of the system with respect to the coordinate, which confirms that this point is really a saddle one. A complete description of the diffusion cannot be carried out by means of two reaction coordinates, because a perturbation that arises owing to a variation of the diffusing atom position affects the positions of neighbor atoms. In their turn, the latter also affect the behavior of the diffusing atom. Therefore, for the description of the diffusion to be correct, it is necessary to analyze the dependence of the energy of the system on the coordinates and the masses of all atoms in the cluster. The variation of coordinates of all atoms in the cluster in the course of the diffusion with regard for their masses is described by the intrinsic reaction coordinate  $y$ , which is defined as  $y = \sqrt{\frac{m}{M}} \Delta q$  ( $m$  is the mass of an atom that shifts by  $\Delta q$ , and  $M$  is the mass of a carbon atom) and is measured in Angströms [10]. Therefore, for the description of the diffusion to be complete, it is enough to derive the dependence of the energy of the system on the intrinsic reaction coordinate or the diffusion path which is the most favorable energetically. The latter was determined using the fourth-order Runge–Kutta method

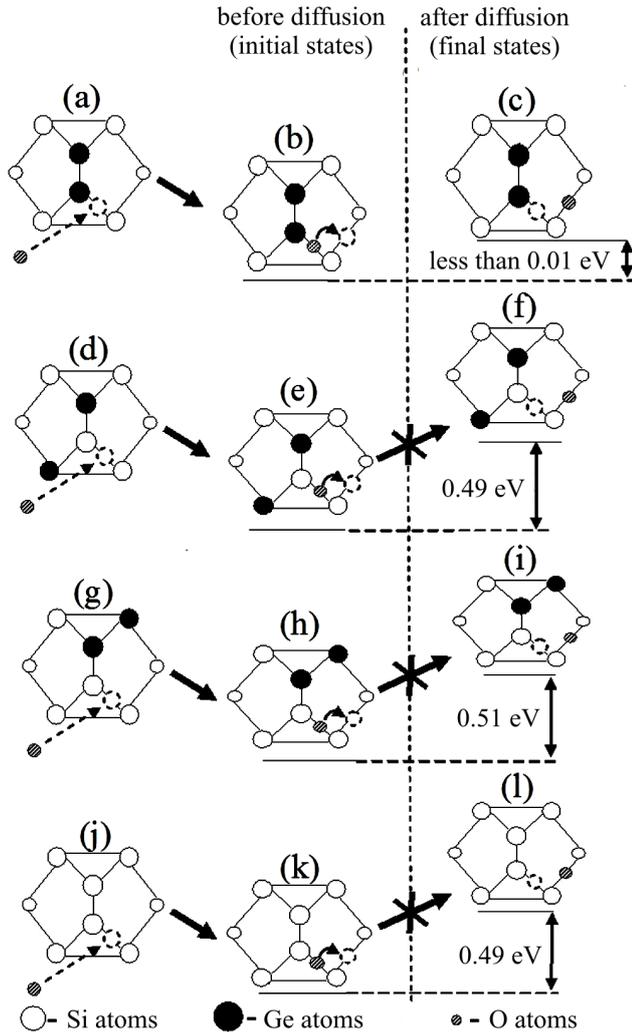


Fig. 3. (a), (d), (g) The most probable positions of Ge atoms on the Si (001) surface; (j) clean Si(001) surface with Si-Si addimers; (b), (e), (h) the initial states (the sites of O atom adsorption on the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface; (k) the initial state for O adsorption on the Si-Si/Si(001) surface [11]; (c), (f), (i) the final states of O atom diffusion on the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface; (l) the final state of O atom diffusion on the Si-Si/Si(001) surface. Small arrows in panels d, e, h, and k indicate the diffusion directions for the O atom

(RK4) with adaptive step size [10]. In the course of calculations of the most energetically favorable diffusion path, the coordinates of all atoms in the cluster were optimized. Afterwards, the points that correspond to the minima of the energy of the system and the saddle point were checked on whether they belonged to it or not.

### 3. Results of Calculations

While considering the diffusion, it is necessary, first of all, to compare the energies of the initial (when the O atom is located in the bond between the addimer atoms and the atoms of the second subsurface layer) and final states (when the O atom is located in the bond between the atoms of the second and the third layer). Such a comparison was fulfilled for three cases, namely, when the diffusion into the subsurface layer between the atoms of the second and third layers started from the initial state formed after one (3.1), two (3.2), or three (3.3) oxygen atoms had been adsorbed on the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface. The diffusion barriers were determined for those cases where the diffusion of an O atom into final states was energetically favorable.

#### 3.1. Diffusion of oxygen atom into the subsurface layer between the atoms of the second and third layers of the $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$ interface

In our previous work [6], the sites, which are the most favorable energetically for the adsorption of one oxygen atom on the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface, were determined. We chose them as the initial states for oxygen atom diffusion (Figs. 3,a, d, and g). As the final diffusion states, we selected structures, where the O atom is located in the bond between atoms of the second and third subsurface layers (Figs. 3,c, f, and i). The diffusion direction is indicated by arrows in Figs. 3,b, e, h, and k. We calculated the energies of the initial (Figs. 3,b, e, h, and k) and final (Figs. 3,c, f, i, and l) states of oxygen atom diffusion. The initial states turned out more favorable energetically than the final ones by 0.49 eV for structures with pure Si-Si addimers (Fig. 3,k) and by 0.49 and 0.51 eV for structures with mixed Si-Ge addimers (Figs. 3,e and h, respectively). Hence, the transition of an O atom from the bridge bond between the addimer atoms and atoms of the second layer to the bonds between atoms of the second and third subsurface layers turns out energetically unfavorable, if there exist pure Si-Si and mixed Si-Ge addimers on the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface.

In the case of pure Ge-Ge dimers on the Si(001) surface (Fig. 3,a), the energy difference between the initial and final diffusion states does not exceed 0.01 eV (Figs. 3,b and c). Hence, the diffusion of a single oxygen atom into the subsurface layer between atoms of the second and third subsurface layers of the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$

interface is possible, if the surface is represented by pure Ge–Ge addimers.

### 3.2. Diffusion of an oxygen atom into the subsurface layer between atoms of the second and third layers of the $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$ interface in the case of two adsorbed oxygen atoms

In work [6], it was shown that the adsorption of an oxygen atom is accompanied by a shift of the core levels in the atoms that are located at a distance of 4 Å from it. This can change the conditions for O atom diffusion into the subsurface layers of the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  interface. Therefore, we considered an opportunity for the O atom to transit from the bridge bond between the addimer atoms and the atoms of the second surface layer (the initial state) into the bridge bonds between atoms in the second and third subsurface layers (the final state), provided that there is a second oxygen atom in the neighbor bridge bonds, as is depicted in Figs. 4, *a*, *c*, *e*, and *g*. The most probable adsorption sites for two oxygen atoms on the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface, which were found in work [6], were selected as the initial states for the oxygen atom diffusion (Figs. 4, *a*, *c*, and *e*). The diffusion direction is indicated in Figs. 4, *a*, *c*, *e*, and *g* by arrows. The calculation of diffusion process from the initial (Figs. 4, *a*, *c*, *e*, and *g*) into final (Figs. 4, *b*, *d*, *f*, and *h*) states allowed the energies of those structures to be compared.

A comparison between the energies in the initial (Figs. 4, *a*, *c*, *e*, and *g*) and final (Figs. 4, *b*, *d*, *f*, and *h*) diffusion states of an oxygen atom showed that the former states are energetically more favorable than the latter ones by 0.12 eV for structures with pure Ge–Ge addimers (Fig. 4, *a*), by 0.86 eV for structures with pure Si–Si addimers (Fig. 4, *g*), and by 0.89 eV for structures with mixed Si–Ge addimers (Figs. 4, *c* and *e*). This allows us to assert that the diffusion of an oxygen atom into the subsurface layer between atoms of the second and third layers of the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  interface is energetically unfavorable in the presence of an oxygen atom in the neighbor bridge bond. This result is related to the fact that the existence of the (2+)-coordinated Si or Ge oxide is energetically more favorable than the existence of (1+)-coordinated Si or Ge oxide on the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface [6].

Note that the energy differences between the initial (Figs. 4, *a*, *c*, *e*, and *g*) and final (Figs. 4, *b*, *d*, *f*, and *h*) states of oxygen atom diffusion increased in comparison with the case of one oxygen atom (Fig. 3).

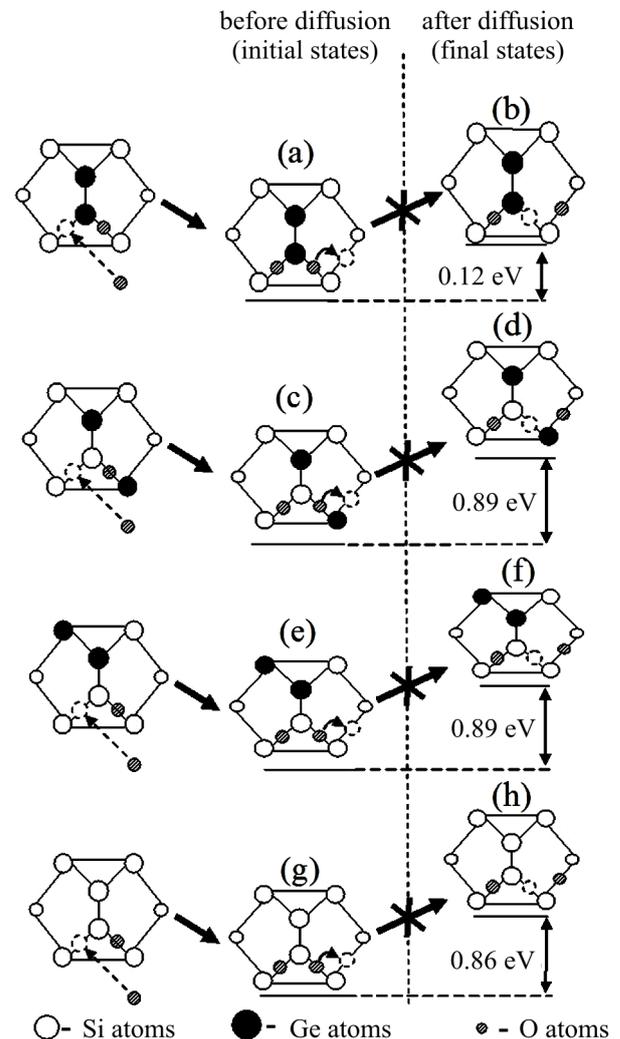


Fig. 4. (*a*), (*c*), (*e*) The initial states which correspond to the energetically favorable sites for the adsorption of two oxygen atoms on the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface; (*g*) the initial state of adsorption of two oxygen atoms on the Si–Si/Si(001) surface [11]. Small arrows in panels *a*, *c*, *e*, and *g* indicate the directions of O atom diffusion from the bridge bond between the addimer atoms and the atoms of the second surface layer into the bridge bonds between atoms of the second and third layers in the presence of another O atom in the neighbor bridge bond; (*b*), (*d*), (*f*), (*h*) the final states of O atom diffusion

### 3.3. Diffusion of an oxygen atom into the subsurface layer between atoms of the second and third layers of the $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$ interface in the case of three adsorbed oxygen atoms

We also verified an opportunity for the oxygen atom to diffuse into the subsurface layer between atoms of the

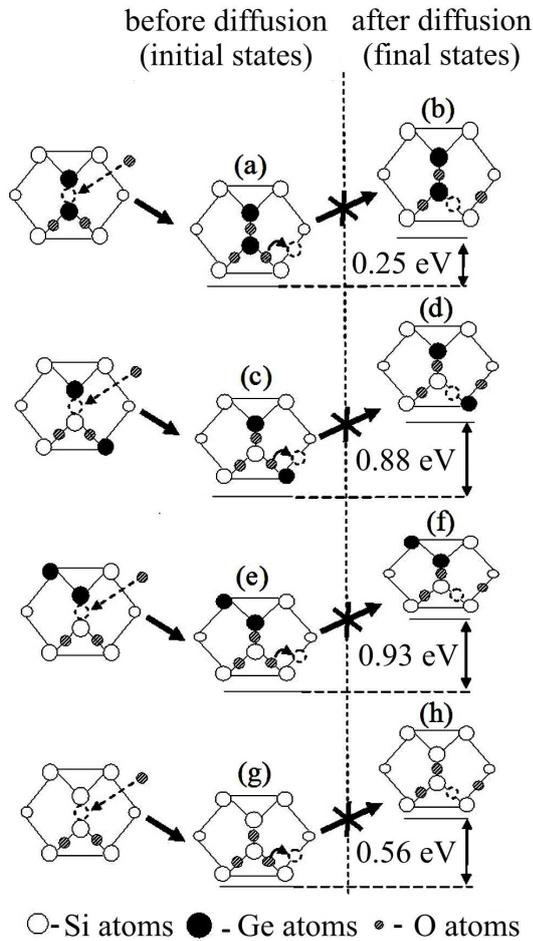


Fig. 5. (a), (c), (e) The initial states, which correspond to the energetically favorable sites for the adsorption of three oxygen atoms on the  $Ge_xSi_{1-x}/Si(001)$  surface; (g) the initial states, the adsorption sites of three oxygen atoms on the Si-Si/ $Si(001)$  surface [10]. Small arrows in panels a, c, e, and g indicate the diffusion directions of the O atom from the initial into the final state (the bridge bonds between atoms of the second and third layers) in the presence of two more O atoms in the neighbor bridge bonds; (b), (d), (f), (h) the final states of O atom diffusion

second and third layers of the  $Ge_xSi_{1-x}/Si(001)$  interface, provided that three oxygen atoms are adsorbed. The sites, which were found in work [6] to be the most favorable energetically for the adsorption of three oxygens on the  $Ge_xSi_{1-x}/Si(001)$  surface, were selected as the initial states of oxygen atom diffusion. The structures that appear after the diffusion event (Figs. 5,b, d, f, and h) – the diffusion direction is indicated in Figs. 5,a, c, e, and g by arrows – were selected as the final ones. The calculation of energies in the initial (Figs. 5,a, c, e, and g) and final (Figs. 5,b, d, f, and h) states of oxygen

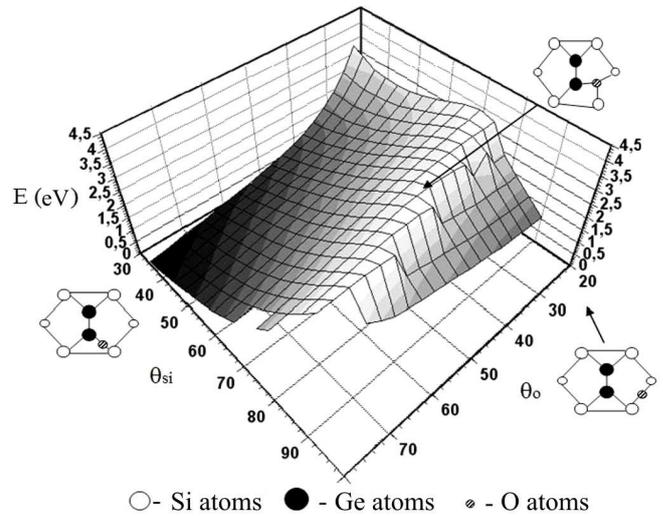


Fig. 6. Dependence of the energy of the system on the reaction coordinates for the structure shown in Fig. 4,a

atom diffusion showed that the former are energetically more favorable than the latter by 0.25, 0.88, 0.93, and 0.56 eV, respectively. This testifies that the diffusion of an oxygen atom into the subsurface layer between atoms of the second and third layers of the  $Ge_xSi_{1-x}/Si(001)$  interface is energetically unfavorable in the presence of two oxygens in the neighbor bridge bonds.

### 3.4. Oxygen diffusion into the subsurface layers of $Ge_xSi_{1-x}/Si(001)$ surface

As was shown above, the diffusion of a single oxygen atom into the subsurface layers of  $Ge_xSi_{1-x}/Si(001)$  interface is possible only if there are pure Ge-Ge addimers on the surface. It is expedient to determine a barrier for such diffusion (Fig. 3,b). For the structure depicted in Fig. 3,b, we obtained a dependence of the energy of the system on the reaction coordinates  $\theta_O$  and  $\theta_{Si}$  (Fig. 2), which is exhibited in Fig. 6. On the basis of this dependence, we roughly determined the position of the saddle point and the magnitude of oxygen diffusion barrier for the case depicted in Fig. 3,b. Afterwards, the data obtained were determined more exactly. After the complete optimization of atomic coordinates in the cluster, the magnitude of oxygen diffusion barrier for the structure with a pure Ge-Ge addimer (Fig. 4,a) was found to be 2.09 eV.

Then, we determined the most energetically favorable path for the transition of an O atom from the bridge bond between the addimer atoms and the atoms of the second subsurface layer into the bond between atoms of the second and third subsurface layers. The dependence

of the energy  $E$  of the of the system on the intrinsic reaction coordinate  $y$  reckoned along this path is given in Fig. 7. The dependence  $E(y)$  confirmed that a diffusion barrier of 2.09 eV really corresponds to the transition of an oxygen atom from the bridge bond between the addimer atoms and the atoms of the second layer into the bond between atoms of the second and third layers of the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface.

#### 4. Discussion

At the initial stages of oxidation (the case where one to three oxygen atoms are adsorbed) of the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface with pure Si-Si (Fig. 3,d) and mixed Si-Ge (Figs. 3,b and c) addimers, the diffusion of an O atom into the subsurface layer between the atoms of the second and the third layer of  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  interface is energetically unfavorable. If pure Ge-Ge addimers are formed on the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface (Fig. 3,a), the diffusion of oxygen atom into the subsurface layer between atoms of the second and third layers of  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  interface is possible only if a single O atom is adsorbed. After a second and a third oxygen atom have been adsorbed on the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface with pure Ge-Ge addimers (Fig. 3,a), the diffusion into the subsurface layer between atoms of the second and third layers of the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  interface becomes energetically unfavorable. Hence, at the initial stages of  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface oxidation, the oxygen atom interacts with two subsurface layers (with the layer composed of addimers and the second subsurface layer).

In work [12], it was found that the energies of interaction between an oxygen atom and either a pure Ge(001) surface or a Si(001) surface covered with 2 ML of Ge atoms are identical. This testifies to the fact that an oxygen atom interacts with two subsurface layers. This conclusion coincides with those drawn in work [12].

The differences between the initial and final state energies in the case of the single O atom diffusion ( $\Delta_1$ ) and

**Energy differences (in terms of electron-volts) between the initial and final states of O atom diffusion in the cases of one ( $\Delta_1$ ), two ( $\Delta_2$ ), and three ( $\Delta_3$ ) oxygen atoms on the surface SiGe for the structures exhibited in Figs. 3,a,d,g,j**

	Si-Si Fig. 3,d	Ge-Ge Fig. 3,a	Ge-Si Fig. 3,b	Ge-Si Fig. 3,c
$\Delta_1$	0.49	0.01	0.49	0.51
$\Delta_2$	0.86	0.12	0.89	0.89
$\Delta_3$	0.56	0.25	0.88	0.93

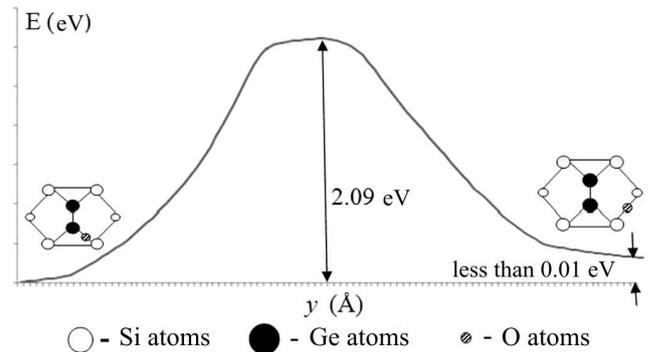


Fig. 7. Dependence of the energy of the system on the intrinsic reaction coordinate  $y = \sqrt{\frac{m}{M}} \Delta q$  ( $m$  is the mass of an atom that shifts by  $\Delta q$ , and  $M$  is the mass of a carbon atom) at the transition of an oxygen atom from the bridge bond between the addimer atoms and the atoms of the second subsurface layer into the bond between atoms of the second and third subsurface layers of the  $\text{Ge-Ge}/\text{Si}(001)$  surface (Fig. 4,a)

in the presence of one ( $\Delta_2$ ) or two ( $\Delta_3$ ) oxygen atoms in the neighbor bridge bonds are quoted in Table. One can see that, in the case of pure Ge-Ge addimers, the energy difference between the initial and final states of oxygen atom diffusion increases with the growth of the number of adsorbed O atoms. Therefore, the adsorption of every next oxygen atom reduces the probability of oxygen diffusion into the depth, when Ge-Ge addimers appear on the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface. The minimal difference between the energies of the initial and final states of oxygen atom diffusion was found for pure Ge-Ge addimers on the Si (001) surface (see Table). This difference is minimal for the diffusion of both a single O atom ( $\Delta_1$ ) and in the presence of one ( $\Delta_2$ ) and two ( $\Delta_3$ ) oxygen atoms in the neighbor bridge bonds. Hence, the presence of pure Ge-Ge addimers on the Si (001) surface facilitates the diffusion of oxygen atoms into the depth stronger than the presence of pure Si-Si or mixed Si-Ge addimers.

In the case of mixed Si-Ge addimers (Fig. 3,c), the energy difference between the initial and final states also increased with the adsorption of every next oxygen atom (see Table), as it took place in the case of pure Ge-Ge addimers. This fact also allows us to assert that the probability of the oxygen diffusion into the depth decreases with an increase of the number of adsorbed oxygen atoms, when mixed Si-Ge and pure Ge-Ge addimers appear on the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface. In work [5], a hypothesis was the put forward that surface stresses play a key role in the change of the oxidation character for the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface. Unfortunately, ow-

ing to small dimensions of a cluster used to simulate the surface, our model cannot describe the presence of such surface stresses in the system correctly, although they may play an important role in the oxidation of the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface at initial stages. The analysis of surface stresses that are inherent to  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surfaces and those that arise when one, two, or three oxygen atoms are adsorbed on such a surface will be carried out in our following works.

As was demonstrated above, the diffusion of an oxygen atom into the subsurface layers of the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  interface is possible only if a single oxygen atom diffuses and the surface is represented by pure Ge–Ge addimers. We recall that the enhanced formation of oxides was observed on the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface grown up at  $T = 600^\circ\text{C}$  [3], which assumes that the surface was covered with a mixed film. Therefore, we may suppose that such stimulated oxidation originates from the features of the interaction between an oxygen molecule and the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface; namely, the molecular adsorption on and dissociation at surface addimers. To confirm this assumption, it is necessary to determine the energies of oxygen molecule adsorption on and dissociation at pure and mixed (Si,Ge) addimers of the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface. This task will be the aim of our next research.

## 5. Conclusions

1. Diffusion of oxygen into the subsurface layer between atoms of the second and third layers of the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  interface is energetically unfavorable, if the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface is represented by pure Si–Si and mixed Si–Ge addimers. If pure Ge–Ge addimers prevail on the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface, such diffusion is possible only for a single oxygen atom. The diffusion barrier in this case is equal to 2.09 eV.

2. The presence of only Ge–Ge addimers on the  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  surface facilitates the diffusion of an oxygen atom into the depth more effectively than the presence of pure Si–Si or mixed Si–Ge addimers.

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## ДИФУЗІЯ АТОМА КИСНЮ У ПРИПОВЕРХНЕВІ ШАРИ ІНТЕРФЕЙСУ $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$

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### Резюме

За допомогою розрахунків з перших принципів перевірено можливість переходу одного атома кисню з місткового зв'язку між атомами аддимера та атомами другого приповерхневого шару в зв'язок між атомами другого та третього шарів поверхні  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  у випадку адсорбції одного, двох та трьох атомів кисню. Перехід кисню з місткового зв'язку між атомами аддимера та атомами другого приповерхневого шару у зв'язок між атомами другого та третього приповерхневого шарів енергетично не вигідний, коли на поверхні  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  присутні чисті Si та змішані Si–Ge аддимери. У випадку, коли на поверхні  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  присутні чисті аддимери Ge, то можлива лише дифузія поодинокого атома кисню. Бар'єр для такої дифузії становить 2,09 еВ. Присутність чистих аддимерів Ge на поверхні  $\text{Ge}_x\text{Si}_{1-x}/\text{Si}(001)$  полегшує дифузію атома кисню в глибину більше, ніж присутність чистих Si або змішаних Si–Ge аддимерів.