STRUCTURE OF PURE Si–Si, Ge–Ge, AND MIXED Si–Ge ADDIMERS ON Si(001) SURFACE

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The adsorption of Ge on the Si(001) surface has been studied using *ab initio* quantum chemical (QM) and combined quantum-chemical–molecular-mechanical (QM/MM) cluster calculations. Multiconfigurational self-consistent field calculations that took the configuration interaction into account were performed to examine the geometric and electronic structures of pure Si–Si, Ge–Ge, and mixed Si–Ge addimers on the Si(001) surface. All addimers were found to possess a biradical character, being not tilted with respect to the surface. The bond lengths in Si–Si, Ge–Ge, and Si–Ge addimers were determined to equal 2.35, 2.45, and 2.41 Å, respectively. The formation of pure Ge–Ge addimers on the Si(001) surface was found to be more beneficial energetically than that of mixed Si–Ge addimers. The natural orbital occupation numbers (NOONs) of antibonding orbitals in Si–Si, Ge–Ge, and mixed Si–Ge addimer structures on the Si(001) surface were calculated to be 0.56, 0.65, and 0.66, respectively. The NOONs of antibonding orbitals for surface dimers was found to be 0.35. The biradical character was more pronounced in the addimer case. The influence of a voltage applied to an STM tip on the NOONs of antibonding orbitals in pure Si–Si and mixed Si–Ge addimers on the Si(001) surface has been analyzed. Under the action of the tip voltage, the multiplicity of a pure Ge–Ge addimer was observed to change from the singlet to the triplet one.

1. Introduction

Since heterostructures of type $\mathrm{Ge}_x\mathrm{Si}_{1-x}$/Si(001) are used in micro- and nanoelectronics, information is required concerning the structure of dimer layers consisting of either pure (Ge–Ge) or mixed (Ge–Si) addimers. As was demonstrated in work [1], those addimers are formed on the surface of heterostructures concerned, provided submonolayer coverages of the Si(001) surface with Ge atoms.

The Si(001) surface is the most analyzed system in surface science. It is known that a reconstruction takes place on a clean Si (001) surface. The reconstruction is accompanied by the formation of surface dimers, which reduces the number of dangling bonds by a factor of two. The dimerized Si(001) surface remains chemically active owing to the remaining dangling bonds: one bond per every atom of surface dimers. However, the issue concerning the structure of surface dimers still remains the point of discussion. The variations of experimental conditions or the application of various theoretical research methods for studying the Si (001) surface structure bring about different results. Scanning tunnel microscopy (STM) researches [2] testified that Si-Si dimers on the Si(001) surface look like untilted ones at the temperature $T = 300$ K, owing to the rapid "switching over" between tilted states. As the temperature is lowered down to 110–120 K, tilted dimers can be observed in the STM images owing to the deceleration of atomic motion [3, 4]. However, a further reduction of the temperature to $T < 40$ K is accompanied by a transition of dimers from tilted to untilted state [4, 5]. There are discrepancies in explanations of the appearance of a $p(2 \times 1)$-reconstruction on the Si(001) surface at low temperatures ($T < 40$ K). In work [4], it was demonstrated that dimers on the surface are untilted at $T \approx 0$ K. In work [5], the $p(2 \times 1)$-reconstruction of the Si(001) surface with untilted dimers was shown to take place owing to the local interaction between dimers and an STM tip.

In theoretical researches, there are substantial mismatches between the results of single-determinant methods of calculation (Hartree–Fock, HF; density functional theory, DFT) and the methods that take the configuration interaction into account (complete active space self-consistent field, CASSCF). In calculations carried out using the single-determinant methods, tilted dimers turned out energetically more beneficial, whereas, in calculations that take the configuration interaction into account [6, 7], so were untilted ones. Such a difference between the calculation results is explained by the fact that the DFT and CASSCF methods make allowance for somewhat different components of electron correlation. The DFT methods involve a dynamic correlation related to the correlated motion of electrons. The quantum chemical approximations of CASSCF method describe a static correlation which arises, if the almost degenerate energy levels exist. A mismatch (a contradiction) between the simulation results for the dimer structure on the Si(001) surface obtained in the framework of DFT and MCSCF methods are connected with the difference between the correlation effects which are considered. There are a few techniques to determine whether the use of the multiconfiguration description of a wave function is necessary: by the NOON values [8] and by the value of spin contamination $\langle S^2 \rangle$ for wave functions in the spin-unrestricted Hartree-Fock (UHF) method [9]. Single-determinant wave functions are correct, if the NOON of the lowest unoccupied molecular orbital (NOON LUMO) equals 0, and the NOON of the highest occupied molecular orbital (NOON HOMO) equals 2.0. In work [8], it was also demonstrated that the single-determinant approximation is insufficient, if the NOON LUMO for a multiconfiguration wave function is higher than 0.1. The authors of work [6] found that a clean Si (001) surface has a biradical character, and its surface dimers have partially filled antibonding orbitals (the corresponding NOON LUMO amounts to 0.33).

Despite plenty of works devoted to the research of SiGe/Si(001) structures, no *ab initio* calculations have been carried out till now with the use of multiconfiguration wave functions for the description of structures that are formed at the initial stages of Ge adsorption on the Si(001) surface. This work aimed at analyzing the electron and geometric structures of both surface dimers (Si–Si and Si–Ge) and addimers (Si–Si, Ge–Si, and Ge–Ge) on the Si(001) surface, by using the multiconfiguration wave functions. We also considered the influence of an external electric field (the field created by an STM tip) on the electron structure of both pure and mixed addimers on the Si(001) surface.

2. Calculation Technique

Calculations were carried out from the first principles with the help of a completely quantum-mechanical (QM) approach and the combined Quantum Mechanics/Molecular Mechanics (QM/MM) method implemented in the GAMESS package [10]. In the work, we used single-determinant approximations of the spin-restricted (RHF) and spin-unrestricted (UHF) Hartree–Fock methods and multideterminant approximations CASSCF(2,2) and CASSCF(4,4). First, the calculations were carried out within the single-determinant RHF and UHF methods. Then, the verification was carried out, whether the single-determinant description of a wave function was sufficient or not. The magnitude of spin contamination, i.e. the expected value of the squared spin operator $\langle S^2 \rangle = S(S+1)$ for the Hartree–Fock wave function, was determined following the UHF method. For singlet states, the deviation of $\langle S^2 \rangle$-value from zero (the so-called spin contamination) testifies to the existence of a strong electron correlation and the multiradical character of the system [9]. The multiconfiguration CASSCF wave functions were constructed on the basis of RHF wave functions. In molecular-mechanical (MM) calculations, the empirical force field MM3 was used. For all Si, H, Ge, and O atoms, the basis sets N21-3** and N21-3 of wave functions were used.

The X-ray diffraction researches of the Si(001) surface showed that atoms in eight surface layers are shifted with respect to the corresponding positions in the crystal lattice of bulk Si [11]. On the one hand, the cluster model of the surface has to be large enough to describe the surface relaxation correctly. On the other hand, to carry out *ab initio* calculations, the model has to include a small number of atoms; it is the more so if the multiconfiguration wave functions are used, which requires large computation capacities, even if small systems are analyzed. Therefore, in this work, we used the Surface Integrated Molecular Orbital Molecular Mechanics (SIMOMM) method [12], which allows the bulk environment to be simulated correctly at acceptable computational costs.

Let us consider the application of this calculation scheme to the simulation of $\mathrm{Ge}_x\mathrm{Si}_{1-x}$/Si(001) surface. The cluster that simulates the surface is separated into two parts (Figs. 1,*a* and *b*). A small cluster $\mathrm{Ge_2Si_{10}H_{12}}$, which was calculated with the help of quantum mechanics (QM) (Fig. 1,*a*), is built into a large cluster $\mathrm{Ge_2Si_{32}H_{32}}$ (Fig. 1,*b*), which was calculated by the MM technique. The MM calculations consume much less calculation resources than the QM calculations do; therefore, such a separation would expectedly give rise to a substantial reduction of the calculation time. As was shown in work [12], quantum-mechanical calculations of $\mathrm{Si_{38}H_{36}}$ cluster (Fig. 2) took eight times as much time, as was required for the calculation of the same cluster in the framework of the SIMOMM $\mathrm{Si_6H_{12}}/\mathrm{Si_{38}H_{36}}$ (QM part /MM part) scheme, with the calculations being executed provided the same approximation conditions (the identical calculation method and basis set).

The QM and MM calculations were carried out separately. In order to explain the calculation scheme better, let us split the cluster into three regions (Fig. 1). Atoms belonging to the first region are taken into account in both QM and MM calculations. Their positions change under the action of QM/MM gradients in QM calculations, but remain fixed in MM ones. Atoms of region 2 saturate dangling bonds at the boundary of the active cluster part; they are present only in QM calculations

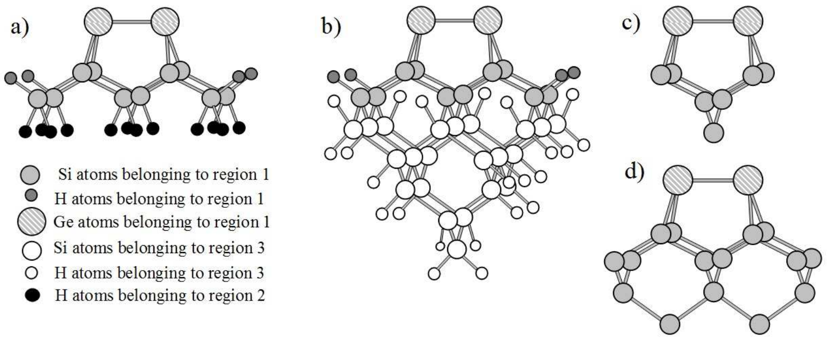

Fig. 1. (*a* and *b*) Model of calculations in the SIMOMM scheme: (*a*) cluster $Ge_2Si_{10}H_{12}$ calculated using the quantum mechanics and (*b*) cluster $Ge_2Si_{32}H_{32}$ calculated using the molecular dynamics methods. Clusters that simulate Si(001) surface (2×1): (*c*) $Ge_2Si_7H_{12}$ and (*d*) $Ge_2Si_{15}H_{16}$. Hydrogen atoms are not shown

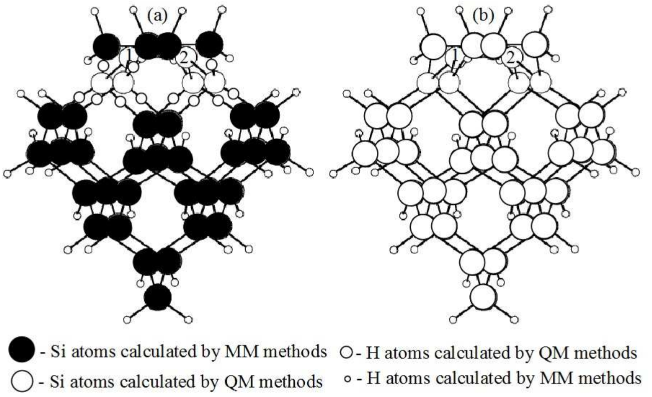

Fig. 2. (*a*) Cluster $Si_6H_{12}/Si_{38}H_{36}$ used in QM/MM calculations and (*b*) cluster $Si_{38}H_{36}$ used in QM calculations in work [12]

and change their positions under the influence of QM gradients. Atoms belonging to the third region are taken into account only in MM calculations, and their positions change under the influence of MM gradients. Such a calculation scheme allows both the calculation time to be reduced substantially and the boundary conditions to be improved. Calculations in the SIMOMM scheme were compared with QM calculations using small clusters Si_9H_{12} and $Ge_2Si_7H_{12}$ depicted in Figs. 1,*c* and *d*.

Note that, in the course of calculations, the optimization of atomic positions in region 1 is stimulated by QM and MM gradients. It is this fact that allowed the influence of atoms representing the bulk (atoms of region 3) on addimer atoms and atoms in two near-surface layers (atoms of region 1) to be taken into account. Such an approach allows not only the calculation time to be reduced, but also the results identical to those obtained in the quantum-mechanical calculation to be obtained. For instance, the difference between the interatomic bond lengths obtained in mere quantum-mechanical calculations of $Si_{38}H_{36}$ cluster (Fig. 2,*b*) and in calculations of $Si_6H_{12}/Si_{38}H_{36}$ cluster (Fig. 2,*a*) in the SIMOMM scheme was 0.03 Å (between atoms 1 and 2 in Fig. 2,*a* and *b*). At the same time, the differences between the corresponding dihedral angles and angles between atoms did not exceed 2° [12].

Hence, the combined QM/MM calculations allow the total calculation time to be reduced (due to a short time needed for MM calculations). Nevertheless, they provide a determination accuracy for geometrical parameters which is close to the accuracy obtained at fully quantum-mechanical calculations.

The following bond lengths were selected: 2.35 Å for Si–Si (as in the crystalline silicon bulk), 1.48 Å for Si-H, 2.41 Å for Si–Ge, and 2.44 Å for Ge–Ge. In calculations of the $Ge_2Si_7H_{12}$ cluster (Fig. 1,*c*), we optimized the coordinates of Ge adatoms. In calculations of the $Ge_2Si_{17}H_{14}$ cluster (Fig. 1,*d*), we optimized the coordinates of Si atoms in two upper near-surface layers and the coordinates of Ge adatoms. In calculations of clusters $Ge_2Si_{32}H_{32}$ and $Si_{34}H_{32}$ by the SIMOMM method, a complete coordinate optimization for Ge, Si, and H atoms was fulfilled.

To simulate the influence of the electric field produced by an STM tip, the $Ge_2Si_{32}H_{32}$ and $Si_{34}H_{32}$ clusters were imbedded into an external uniform electric field 2 V/Å in strength. Such an electric field gives rise to a considerable growth of energy gradients for the system in its ground state. Therefore, to find the stationary state of the system, the criteria of iteration procedure convergence at the solution of the Schrödinger equation have to be changed. Searching for the new criteria of iteration procedure convergence is a matter for a separate study, which would require substantial calculation expenses. Therefore, in this work, we calculated the electron struc-

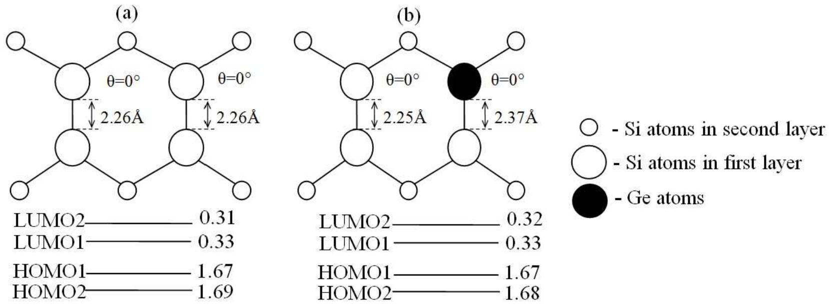

Fig. 3. Si(001) surface models: (*a*) clean and (*b*) with a mixed Si–Ge dimer. HOMO1, LUMO1, HOMO2, LUMO2 are the natural orbitals occupation numbers; θ is the tilt angle of dimers with respect to the surface

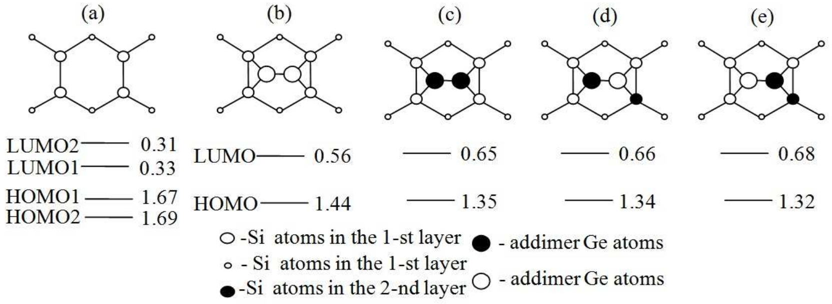

Fig. 4. Structures and occupation numbers of bonding (HOMO) and antibonding (LUMO) orbitals of surface dimers and addimers in the cases of clean Si(001) surface (*a*) and Si(001) surface with pure Si–Si (*b*), Ge–Ge (*c*) and mixed Si–Ge (*d* and *e*) addimers

ture of clusters (already optimized at $E = 0$ V/Å) in an applied external electric field, making no optimization of cluster atom coordinates.

3. Clean Si(001) Surface and Si(001) Surface with Mixed Si–Ge Dimers

The Si(001) surface was shown in work [6] to have a biradical character. Therefore, it is of importance to test whether it remains biradical being covered with a submonolayer coating of Ge atoms, when, besides pure (Ge–Ge) and mixed (Si–Ge) addimers, mixed Si–Ge dimers (Fig. 3) can be formed on the surface. For this purpose, we carried out *ab initio* calculations, taking the correlation interaction into account (the CASSCF(4;4)(N21-3**) method), for two Si(001) surfaces: a clean one with two Si dimers (Fig. 3,*a*) and a surface with one mixed Si-Ge dimer (Fig. 3,*b*). The active space in the CASSCF(4;4) method consisted of bonding (π,π) and antibonding (π^*,π^*) orbitals of two surface dimers.

Our calculation showed that the biradical character persists for both considered surface models, which are exhibited in Fig. 3. The obtained bond lengths for surface dimers agree well with experimental values of 2.26±0.1 Å [13]. The calculations of work [7] also demonstrated that untilted dimers with a bond length of 2.28 Å are energetically the most beneficial ones on the Si(001) surface. Hence, as is seen from Fig. 3, the occupation numbers of antibonding orbitals (LUMO1, LUMO2) in surface dimers do not change, if the Si atom is substituted by the Ge one. The bond length in a pure Si–Si dimer and its tilt angle with respect to the surface (see Fig. 3,*b*) also do not change, if the Ge atom, instead of the Si one, appears in the neighbor dimer.

4. Si(001) Surface with a Submonolayer Ge Coverage

The authors of work [1] noted that both pure (Si–Si, Ge–Ge) and mixed (Si–Ge) addimers are formed in submonolayer films of Ge atoms on the Si(001) surface. In our previous work [14], we demonstrated that the structures shown in Figs. 3,*c*–*e* are the most beneficial energetically. In this part of work, we compared the geometrical and electronic structures of surface dimers (Fig. 4,*a*) and Si–Si, Ge–Ge, and Si–Ge addimers (Figs. 4,*b*–*e*, respectively).

Table 1. Calculated and experimental parameters of surface addimers: the bond length d; the energy ΔE of mixed Si-Ge addimer (Fig. 4,*d* and *e*) formation with respect to the formation energy of a pure Ge-Ge addimer (Fig. 4,*c*), both being calculated with identical approximations; the occupation numbers of natural bonding (HOMO) and antibonding (LUMO) orbitals; the tilt angle of an addimer with respect to the surface θ; and the spin contamination $\langle S^2 \rangle$

	d, Å	ΔE, eV	HOMO	LUMO	θ	$\langle S^2 \rangle$
Ge–Ge/Si(001) (Fig. 4,*c*)						
$Ge_2Si_7H_{14}$(UHF(N21-3)	2.58	0	–	–	0°	1.0
$Ge_2Si_7H_{14}$(RHF(N21-3))	2.73	0	2	0	13.2°	0.0
$Si_{17}H_1 4Ge_2$(RHF(N21-3**)[14]	2.62	0	2	0	13.8°	–
$Ge_2Si_{32}H_{32}$(RHF(N21-3**))	2.54	0	2	0	11.5°	0.0
$Ge_2Si_{32}H_{32}$(CASSCF(2;2)(N21-3**))	2.45	0	1.35	0.65	0°	–
Exp.	2.51 Å ($\theta = 0°$) [15], 2.55 Å ($\theta = 12°$) [16]					
Ge–Si/Si(001) (Fig. 4,*d*)						
$Ge_2Si_7H_{14}$(UHF(N21-3))	2.52	0.95	–	–	0°	0.9
$Ge_2Si_7H_{14}$(RHF(N21-3))	2.65	0.31	2	0	12.5°	0
$Ge_2Si_{17}H_{14}$ (RHF(N21-3**)[14]	2.58	0.10	2	0	11.7°	–
$Ge_2Si_{32}H_{32}$(RHF(N21-3**))	2.51	0.35	2	0	15.2°	0.0
$Ge_2Si_{32}H_{32}$(CASSCF(2;2)(N21-3**))	2.41	0.41	1.34	0.66	0°	–
Ge–Si/Si(001) (Fig. 4,*e*)						
$Ge_2Si_7H_{14}$(UHF(N21-3))	2.51	0.15	–	–	0°	1.0
$Ge_2Si_7H_{14}$(RHF(N21-3))	2.58	0.44	2	0	9.7°	0
$Ge_2Si_1 7H_{14}$ (RHF(N21-3**)[14]	2.51	0.06	2	0	6.9°	–
$Ge_2Si_{32}H_{32}$(RHF(N21-3**))	2.46	0.34	2	0	14.2°	0.0
$Ge_2Si_{32}H_{32}$(CASSCF(2;2)(N21-3**))	2.41	0.13	1.32	0.68	0.0°	–
Si–Si/Si(001) (Fig. 4,*b*)						
Si_9H_{12}(UHF(N21-3))	2.33	–	–	–	0°	1.0
Si_9H_{12}(UHF(HW*))[7]	2.32	–	–	–	0°	0.9
Si_9H_{12}(RHF(N21-3))	2.55	–	2	0	13.0°	0.0
$Si_{34}H_{32}$(CASSCF(2;2)(N21-3**))	2.35	–	1.44	0.56	0°	–
Si(001)						
$Si_{32}H_{32}$(CASSCF(4;4)(N21-3**))	2.26	–	1.67	0.33	0.0°	–

To select the most correct method of calculation, the structures of Si–Si, Si–Ge, and Ge-Ge addimers–tilted and untilted with respect to the Si(001) surface–were calculated at first in the single-determinant approximation with the help of RHF and UHF methods, using the N21-3 basis set and small $Ge_2Si_7H_{14}$ and Si_9H_{14} clusters. The formation of pure Ge-Ge addimers on the Si(001) surface (Fig. 4,*c*) turned out energetically more beneficial than the formation of mixed Si-Ge addimers (Fig. 4,*d* and *e*), irrespective of the calculation method (RHF, UHF) applied. The formation energy ΔE of a mixed Si-Ge addimer with respect to that of a pure Ge-Ge addimer (Fig. 4,*c*) – the both were calculated adopting the same approximations, – and the bond lengths and the addimer-to-surface tilt angles are listed in Table 1.

The results of calculations in the framework of the RHF method showed that, irrespective of the cluster dimension, the formation of Ge–Ge, Si–Ge, and Si–Si addimers tilted with respect to the surface is energetically the most beneficial. No energy minima, which correspond to the formation of untilted Ge–Ge, Si–Ge, and Si–Si addimers were found. The bond lengths in Ge-Ge, Si–Ge, and Si–Si addimers were calculated making use of small cluster models ($Ge_2Si_7H_{14}$, $Si_{17}H_{14}Ge_2$) with a small number of atomic coordinates to be optimized; they turned out longer than the bond lengths of addimers measured experimentally [15, 15]. The experimental values of bond lengths in Ge-Ge addimers on the Si(001) surface were found to fall within the interval of 2.51–2.55 Å. An improvement of the N21-3 basis set taking advantage of *p*- and *d*-polarization functions, the enlargement of the cluster model, and the extension of the number of geometrical parameters to be optimized give rise to a reduction of the bond lengths in addimers, so that the values obtained are in agreement with experiment.

The UHF calculation method gave energy minima that correspond to the formation of untilted Si–Si, Si–Ge, and Ge–Ge addimers of the Si(001) surface. For all structures with untilted addimers, the values of $\langle S^2 \rangle$ obtained in the framework of this method were different from zero (Table 1). The discrepancy between of the results obtained in the framework of UHF and RHF calculation methods and a nonzero magnitude of the quantity $\langle S^2 \rangle$, which is inherent to the so-called spin contamination of the system, testifies that the correlation interaction has to be taken into account.

The calculations with the use of a multiconfiguration wave function were carried out by applying the CASSCF(2;2) method in the case where there was one bonding, π, and one antibonding, π^*, orbital of addimers in the active space. In calculations, when correlation interaction is taken into account, the wave function must be versatile enough [8]; therefore, the basis N21-3** was used. The results of calculations are presented in Table 1. The formation of pure Ge–Ge addimers on the Si(001) surface (Fig. 4,*c*) turned out energetically more beneficial than the formation of mixed Si–Ge addimers (Fig. 4,*d* and *e*) in all calculation techniques (RHF, UHF, CASSCF).

The calculations carried out by the CASSCF(2;2) method showed that Si–Si, Si–Ge, and Ge–Ge addimers are untilted and have a biradical character for all three structures depicted in Figs. 4,*b* to *e*. The occupation numbers of antibonding orbitals (LUMO) in Si-Si, Ge–Ge, and Si-Ge addimers on the Si(001) surface equal 0.56, 0.65, and 0.66, respectively, whereas this quantity for antibonding orbitals in surface dimers in the case of clean Si(001) surface is equal to 0.35. The occupation numbers for bonding and antibonding orbitals in surface dimers and addimers on the Si(001) surface (see Table 1 and Fig. 4) show that interatomic bonds are stronger in surface dimers than in Si–Si, Si–Ge, and Ge–Ge addimers. The Si(001) surface with adsorbed dimers is more active chemically than a clean Si(001) surface. The biradical character of Ge–Ge and Si–Ge addimers turned out more pronounced than that of Si–Si addimers. This means that a submonolayer Ge film enhances the activity of Si(001) surface.

Table 2. Occupation numbers of the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbital in an external uniform electric field 2 and −2 V/Å in strength and with no applied field (0 V/Å) and the multiplicity *S* of the system

	Ge–Ge/Si(001)			Si–Si/Si(001)		
E (B/Å)	0	–2	2	0	–2	2
S	0	1	0	0	0	0
NOONLUMO	0.65	0.94	0.57	0.56	0.64	0.41
NOONHOMO	1.35	1.06	1.43	1.44	1.36	1.59

The dissociation of an O_2 molecule is known to precede the oxidation process. The oxygen molecule dissociates after the antibonding orbital has been filled. Oxidation can be supposed to run more intensively on the Si(001) surface with Ge–Ge and Si–Ge addimers than on a clean Si(001) surface. This assumption should be verified, and the corresponding results will be published in our next work.

5. External Electric Field Effect on Electronic Structures of Si–Si, Ge–Ge, and Si–Ge Addimers on the Si(001) Surface

As was shown above, there are partially filled levels in the system. Under the action of an external electric field–e.g., created by an STM tip–the occupation numbers of partially filled levels (HOMO and LUMO) and the electron density distribution may change. Hence, it is expedient to study the influence of an external electric field on the distribution of the electron density created by Ge–Ge, Si–Si, and Si–Ge addimers on the Si(001) surface. To simulate the electric field around an STM tip, the clusters $Ge_2Si_{32}H_{32}$ and $Si_{34}H_{32}$ were embedded into an external uniform electric field 2 V/Å in strength. The electric field was applied perpendicularly to the surface. The positive value of electric field strength ($E = 2$ V/Å) meant that the field strength vector was directed toward the surface. This orientation corresponded to the regime of occupied states in the STM experiment. The negative value of electric field strength ($E = -2$ V/Å) corresponded to the regime of free states in the STM experiment. The results of calculations dealing with variations of the molecular orbital occupation number under the action of the electric field are quoted in Table 2.

Table 2 demonstrates that the occupation numbers of antibonding orbitals in Si–Si and Ge–Ge addimers decrease under the influence of the positive electric field $E = 2$ V/Å. This can result in an enhancement of the stability and a reduction of the bond length in addimers under the influence of the field created by an STM tip in the regime of occupied states. The occupation numbers of antibonding orbitals in Si–Si and Ge–Ge addimers increase under the influence of the negative electric field $E = -2$ V/Å. This means that the negative field of an STM tip can reduce the bond length between addimer atoms in the STM experiment executed in the regime of free states. Graphically, the variation of HOMO occu-

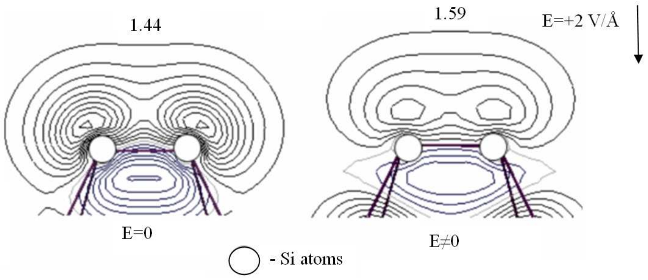

Fig. 5. Variation of the bonding-orbital occupation number in a Si–Si addimer on the Si(001) surface under the influence of the STM tip field (2 V/Å)

pation numbers can be well illustrated using the Si–Si addimer on the Si(001) surface as an example (Fig. 5).

In work [17], the applied tip field was found to be able to change the mechanism of Si–Si addimer diffusion along the chain of dimers. In particular, the addimer diffuses as a whole in a positive field, whereas the diffusion of the addimer in a negative field is accompanied by a break of its bond. This fact agrees well with the results presented above and in Table 2.

The data in Table 2 also evidence that the multiplicity of the system “the Ge–Ge addimer on the Si(001) surface” changes, if the tip field is negative. This circumstance testifies that the surface under examination can be in different states at different polarities of the STM tip voltage, which is to be taken into consideration, while interpreting STM images.

6. Conclusions

Calculations carried out in the framework of the multiconfiguration method (CASSCF (2;2)) showed that Si–Si, Si–Ge, and Ge–Ge addimers on the Si(001) surface are untilted with respect to it and have a biradical character. The formation of pure Ge–Ge addimers on the Si(001) surface is energetically more beneficial than that of mixed Si–Ge addimers. The bond lengths in Si–Si, Ge–Ge, and Si–Ge addimers on the Si(001) surface are equal to 2.35, 2.45, and 2.41 Å, respectively.

The occupation numbers of antibonding orbitals (LUMO) in Si–Si, Ge–Ge, and Si–Ge addimers on the Si(001) surface equal 0.56, 0.65, and 0.66, respectively. For the clean Si(001) surface, the occupation number of antibonding orbitals in surface dimers equals 0.35. The biradical character of Ge–Ge and Si–Ge addimers on the Si(001) surface was found to be more pronounced than that in Si–Si addimers. The Si(001) surface with adsorbed germanium dimers is more active chemically than the clean surface.

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СТРУКТУРА ЧИСТИХ Si–Si, Ge–Ge ТА ЗМІШАНИХ АДДИМЕРІВ Si–Ge НА ПОВЕРХНІ Si(001)

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Резюме

Використовуючи кластерні квантовохімічні та гібридні квантово-хімічні–молекулярно-механічні розрахунки з перших принципів (*ab initio*), досліджено адсорбцію Ge на поверхню Si(001). Розрахунки з врахуванням конфігураційної взаємодії використовувалися для визначення геометричної та електронної структури чистих Si–Si, Ge–Ge, та змішаних Si–Ge аддимерів на поверхні Si(001). Як чисті Si–Si, Ge–Ge, так і змішані Si–Ge аддимери – не нахилені до поверхні та носять бірадикальний характер. Довжини зв'язків чистих Si–Si та змішаних Si–Ge аддимерів становлять 2,35 Å, 2,45 Å та 2,41 Å відповідно. Утворення чистих Ge–Ge аддимерів на поверхні Si(001) є більш енергетично вигідним, ніж утворення змішаних аддимерів Si–Ge. Заселеності натуральних антизв'язуючих орбіталей чистих Si–Si, Ge–Ge та змішаних Si–Ge аддимерів становлять 0,56, 0,65 та 0,66 відповідно. Натуральні заселеності антизв'язуючих орбіталей для димерів поверхні становлять 0,35. Бірадикальний характер був більший у випадку аддимерів. Також розглянуто вплив прикладеної до вістря напруги на натуральні заселеності антизв'язуючих орбіталей чистих Si–Si та змішаних Si–Ge аддимерів поверхні Si(001). Під дією напруги вістря спостерігалася зміна плетності чистого аддимера Ge–Ge з синглету на триплет.