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Anisotropic atom diffusion on Si(553)-Au surface

M. Krawiec[*] and M. Jałochowski
Institute of Physics, M. Curie-Skłodowska University, Pl. M. Curie-Skłodowskiej 1, 20-031 Lublin, Poland

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Using density functional theory, we study atomic diffusion on the Si(553)-Au surface. We have calculated the potential energy surfaces for atoms of different chemical elements (Ag, Au, Mg, In, and Si). By tracing the adatom positions and the energetics of a fully relaxed surface, we have calculated energy barriers, diffusion paths, and hopping rates along and across the steps. The results show that in most cases, the surface diffusion is strongly anisotropic, while the energy barriers and hopping rates have a strong dependency on the chemical species of the adatom. In the case of Au, Ag, and Mg atoms, the diffusion can be realized in two separate one-dimensional channels, featuring different mechanisms of the diffusion.

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I. INTRODUCTION

Many fundamental processes on surfaces, like epitaxial growth of atomic layers, formation of islands, chains, and other nanostructures or chemical reactions, are governed by atom diffusion.[1–6] Movement of atoms on surfaces may proceed in many ways, including, for example, thermally activated hopping, exchange of atoms, and quantum-mechanical tunneling. At low surface coverage of adsorbates, we typically deal with uncorrelated hopping of independent atoms, while at higher coverage, the hopping may become correlated due to interatomic interactions, making the situation very complex.

Usually, the atom diffusion on flat surfaces is two-dimensional and rather isotropic. This is best illustrated in the case of silicon surfaces, where the diffusion of atoms, like Si, Pb, Au, Ag, H, Y, or Sr, was observed on the Si(111) surface reconstructed according to 7×7 and $\sqrt{3} \times \sqrt{3}$-Pb reconstructions.[7–22] On the other hand, the movement of atoms can become anisotropic or even quasi-one-dimensional by using specific reconstructions or vicinal (stepped) surfaces. Indeed, quasi-one-dimensional diffusion was observed in the case of Si adatoms on the Si(111)5×2-Au surface,[23,24] In atoms on the Si(110) surface[25–27] as well as In and Pb atoms on the Si(553)-Au surface.[28,29]

The Si(553)-Au surface consists of $4\frac{1}{3} \times a_{[11\bar{2}]} = 1.48$ nm wide Si(111) terraces separated by single atomic steps. The surface normal is tilted from [111] direction toward $[11\bar{2}]$ by 12.5°.[30] A well ordered Si(553)-Au surface is observed at gold coverage of 0.48 ML.[31] The topography of the surface measured by scanning tunneling microscope (STM) reveals arrays of single atomic chains, identified as step-edge Si atoms.[30,32–40] The photoemission spectra acquired in the direction parallel to the steps is dominated by two 1D bands with one of the bands substantially influenced by the Rashba spin-orbit interaction.[30,32,34,41] Although the atomic structure of the Si(553)-Au surface has been extensively studied both experimentally[42–44] and theoretically,[30,45–47] only recently the correct structural model has been proposed.[48] The model proposed in Ref. 48 consists of a double Au-chain with dimerized Au atoms in the middle of terrace and a honeycomb chain at the step edge. The validity of this model has been confirmed later by x-ray diffraction experiment[49] and independent DFT calculations.[50]

Due to its regular morphology, the Si(553)-Au surface can serve as a prepatterned template to grow 1D structures composed of atoms of various chemical elements. Indeed, first attempts utilizing In and Pb atoms have already been reported.[28,51] Furthermore, owing to its morphology of equally spaced troughs at the step edges, which can serve as diffusion channels, the Si(553)-Au surface suits perfectly for studying the one-dimensional (1D) diffusion of atoms. Not without significance is the fact that this surface contains a small number of defects, making the diffusion channels as long as several dozens nanometers or even longer; the recently observed diffusion of Pb atoms at temperatures above 110 K[29] supports this idea. Pb atoms move in a trough along the step edge confined by energy barriers as high as 1 eV, which makes the diffusion quasi-one-dimensional. Moreover, according to DFT calculations, the diffusion channel is composed of shallow energy barrier series equal to 0.18, 0.37, and 0.42 eV. On the other hand, when scanning the surface with different STM speeds, one can measure the hopping frequency, which at $T = 220$ K was equal to 1.31×10^3 Hz. Furthermore, combining STM measurements with DFT calculations of the Pb potential energy surface (PES), it was possible to determine the preexponential factor ν_0 in the Arrhenius equation for thermally activated atom motion. This yields 5.79×10^{12} Hz and agrees well with the ν_0 for Pb atoms on Si(111)7×7 surface, equal to $10^{12.2\pm1}$ and $10^{11.7\pm1.3}$ Hz for faulted and unfaulted parts of the 7×7 unit cell.[13] The diffusion of In atoms on the Si(553)-Au surface has also been reported,[28] however, no detailed analysis of the experimental data has been performed. Furthermore, the energy barriers have been calculated in this case, but with the structural model of the surface containing only single Au chain, thus not meeting the experimental conditions.

The aim of the present work is to determine the diffusion quantities characteristic of atoms of different chemical elements. We have chosen Ag, Au, Mg, In, and Si, to have atoms with different chemical properties (atomic mass, electron valency, etc.). To tackle the problem, we have used density functional theory. The obtained results (potential energy surfaces, energy barriers, and diffusion paths) show that, except of the Si atoms, the atomic diffusion is strongly anisotropic. In the case of Au, Ag, and Mg atoms, the diffusion can be realized in two separate 1D channels, featuring different mechanisms of the diffusion: the single atom hopping and the atom exchange. The rest of the paper is organized as follows. In Sec. II, details of calculations are described. The results of the calculations are presented and discussed in Sec. III. Finally, some conclusions are given in Sec. IV.

II. DETAILS OF CALCULATIONS

The calculations were performed within local density approximation (LDA) to density functional theory,[52] as implemented in SIESTA code.[53–57] Troullier-Martins norm-conserving pseudopotentials were used.[58] In the case of Au, Ag, and In, the semicore states (Au 5*d*, Ag 4*d*, and In 4*d*) and scalar relativistic corrections were included. A double-ζ polarized (DZP) basis set was used for all the atomic species.[54,55] The radii of the orbitals for different species were the following (in a.u.): Au 7.20 (5*d*), 6.50 (6*s*), and 5.85 (6*p*); Ag 5.75 (4*d*), 4.71 (5*s*), and 6.20 (5*p*); In 8.66 (4*d*), 8.87 (5*s*), 8.66 (5*p*), and 9.57 (5*d*); Mg 5.70 (3*s*), 7.32 (3*p*), and 5.03 (3*d*); Si 7.96 (3*s*), 7.98 (3*p*), and 4.49 (3*d*); H 7.55 (1*s*) and 2.94 (2*p*). Six nonequivalent *k* points for Brillouin zone sampling and a real-space grid equivalent to a plane-wave cutoff 100 Ry (up to 75 *k* points and 225 Ry in convergence tests) were employed.

The Si(553)-Au slab has been modeled by four silicon double layers and a vacuum region of 19 Å. Details of the atomic structure can be found in Ref. 48. A potential energy surface was calculated on a 0.45 Å × 0.45 Å grid. In the calculations of PES, each atom (Ag, Au, Mg, In, and Si) was placed at every grid point and allowed to move only in the *z* direction, i.e., perpendicular to the surface. The grid used for different atoms was adjusted accordingly to account for the lowest energy adsorption site of a given chemical element atom. The rest of the slab was fully relaxed until the maximum force in any direction was less than 0.01 eV/Å, except for the bottom layer. The Si atoms in the bottom layer were fixed at their bulk ideal positions and saturated with hydrogen. The lattice constant of Si was fixed at the calculated value, 5.39 Å. The diffusion paths have been obtained by choosing the lowest energy points of the PES in a given direction. A similar procedure of calculating PES and diffusion paths for Pb atoms on Si(553)-Au surface was used in Ref. 29.

III. RESULTS AND DISCUSSION

Due to its specific geometry and small number of defects, the Si(553)-Au surface is suitable to study the anisotropic atomic diffusion. The structural model of the Si(553)-Au surface,[48] consisted of (111) terraces, and single atomic steps, is shown in Fig. 1. The main building blocks of the surface structure are the honeycomb chain (HC) and the double Au chain with dimerized atoms. A diffusion channel, in which the atoms are expected to move freely in one direction, can be conceivable as a trench between the double Au chain and the step edge Si atoms ($\mathrm{Si}_{\mathrm{step}}$) of neighboring terrace. Indeed, in the case of Pb atoms, the validity of this assumption was demonstrated both experimentally and theoretically.[29] According to the DFT calculations of Ref. 29, the Pb atoms diffuse along the step edges encountering series of energy barriers $E_{\parallel}^{\mathrm{Pb}}$ equal to 0.179, 0.368, and 0.421 eV. Furthermore, the moving atoms are confined from both sides of the trench by energy barriers $E_{\perp}^{\mathrm{Pb}}$ higher than 1.0 eV, that results in a formation of quasi-one-dimensional diffusion channel. To be clear, we do not exclude the hopping events between different 1D diffusion channels at all. However, the probability of such events will be much lower than in the case of the in-channel diffusion. For example, the room-temperature (RT) hopping frequency of the Pb atoms along the step edges will be almost 20 orders of magnitude higher than in the direction perpendicular to the steps. Due to such huge asymmetry in the hopping frequencies, one can consider the diffusion to be quasi-one-dimensional.

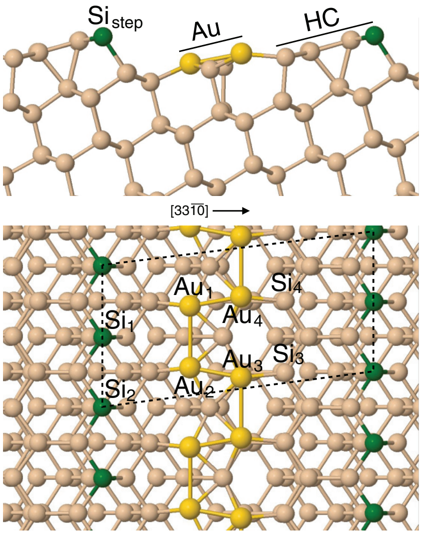

FIG. 1. (Color online) Side view (top) and top view (bottom) of the atomic structure of the Si(553)-Au surface, according to the model of Ref. 48. Silicon and gold atoms are marked by light green and orange balls, respectively. The main building blocks of the surface structure, i.e., a honeycomb chain (HC) and double Au chain together with the surface unit cell are also indicated. Note that atoms forming the Au chain are dimerized.

Since the step edge is considered as the most chemically active part of the Si(553)-Au surface, we also expect the diffusion of other chemical elements atoms to be possible in this channel. Some predictions can be obtained by comparing the density of states of various parts of the surface with the states of isolated foreign atoms expected to adsorb and eventually diffuse on this surface. It is well known that the adsorption can be possible due to energy gained by the hybridization of overlapping states of the adsorbate and the surface. Thus, at least, it should be possible to predict where the foreign atoms will adsorb. Of course, this cannot entirely explain the diffusion itself since the diffusion processes depend on high energy atomic configurations as well. These configurations are responsible for the heights of diffusion barriers. Nevertheless, some conclusions can be drawn. Thus, to determine the expected adsorption sites and bonding of adsorbate atoms, we focus on the corresponding densities of states. To fully understand the bonding mechanism, one must consider a hybridization of the adatom states with neighboring surface atoms. However, the most chemically active parts of the Si(553)-Au surface are the step edge, HC, and Au chain. Thus we restrict our study to these structures.

Figure 2 shows the projected density of states (PDOS) of the step-edge (Si_1, Si_2), Au chain (Au_1-Au_4), and HC (Si_3, Si_4) atoms of the Si(553)-Au surface (two top panels) together

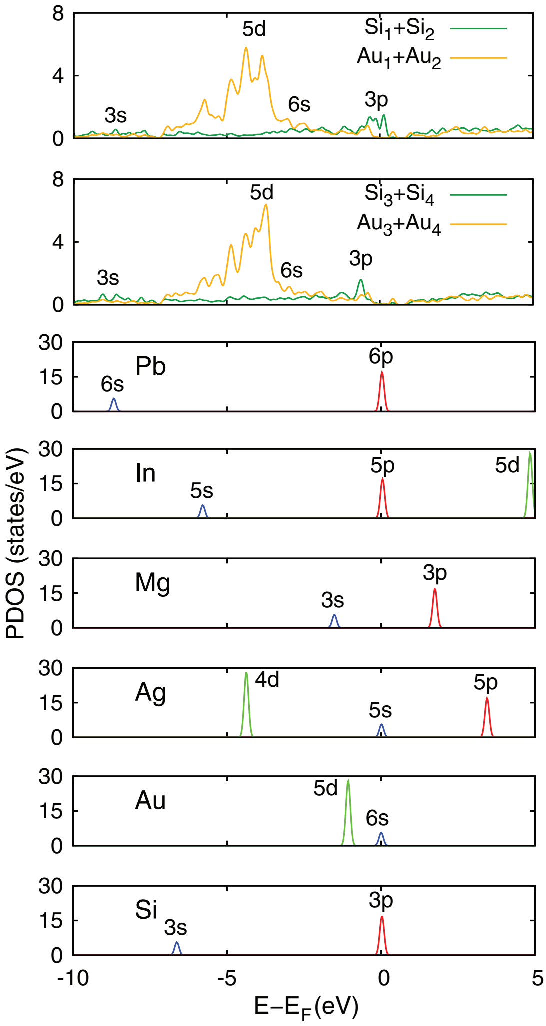

FIG. 2. (Color online) The projected density of states (PDOS) of the step-edge Si atoms (Si$_1$ and Si$_2$) and part of the double-Au chain (Au$_1$ and Au$_2$), the HC Si atoms (Si$_3$ and Si$_4$), and the other part of the Au chain (Au$_3$ and Au$_4$), and isolated Pb, In, Mg, Ag, Au, Si atoms.

with the densities of states of isolated atoms (Pb, In, Mg, Ag, Au, and Si). The main character of the states is indicated in each panel. As we mentioned already, due to unsaturated Si bonds, the most chemically active part of the surface is located at the step edge. Their associated ($3p$) electronic states are at the Fermi energy E_F, as is evident in the top panel of Fig. 2. On the other hand, the $3p$ states associated with the Si$_3$ and Si$_4$ atoms of the HC (terrace channel) are shifted below the Fermi energy (second panel from the top). There is no such difference between atoms of the Au chain. The PDOS of all the atoms of the Au chain features the $5d$ states around $E = -4$ eV and $6s$ states close to the E_F. Thus we could conclude that foreign atoms should preferably adsorb in the step-edge channel. Indeed, this is expected for almost all the atoms, with their s or p states located at the E_F. The only exception is expected for Mg atoms. The energies of their $3s$ and $3p$ states do not coincide with the Fermi level. However, in this case, one can notice the overlap of their $3s$ states with the $6s$ states of the Au chain. Thus Mg atoms can adsorb on both sides of the Au chain, i.e., near the step edge as well as in the middle of terrace. This is a clue that two-channel diffusion might be possible in the case of Mg atoms. Similar, two-channel diffusion is expected for Ag and Au atoms. In the case of Ag atoms, besides the hybridization of their $5s$ states with the $3p$ states of the step-edge Si atoms, there is also strong overlapping of their $4d$ states with the $5d$ states of the Au chain. Therefore Ag atoms can adsorb also on both sides of the Au chain. A slightly different situation is observed for Au adsorbates, where their $5d$ states can hybridize with the $6s$ states of the Au chain, thus allowing for adsorption on both sides of the Au chain. However, the $5d$ states of Au overlap also with the $3p$ states of both, the step edge and HC chains. This difference between Ag and Au atoms will be reflected in their arrangement with respect to the step edge and Au chains. On the other hand, in the case of Pb and In adsorbates, there is no such strong hybridization of their states with the states of the other characteristic parts of the surface. Thus the Pb and In atoms are expected to bind easily to the Si$_1$ and Si$_2$ atoms, and diffuse in the step-edge channel. We should expect also the Si adatoms to adsorb only at the step edges due to similar density of states of isolated Si and In or Pb atoms. However, the situation is more complicated in this case. Namely, the Si adatoms interact mainly not only with the step-edge, HC, and Au chain but also with other surface Si atoms. Thus we could expect a more isotropic diffusion of Si atoms on the Si(553)-Au surface. To summarize, we expect the single-channel diffusion for In and Pb atoms, two-channel diffusion for Mg, Ag, and Mg atoms, and rather isotropic diffusion for Si atoms. In the following, we shall discuss how the diffusion on the Si(553)-Au surface performs and illustrate this by some representative examples.

While the diffusion of In atoms along the step edges of the Si(553)-Au surface has already been reported,[28] the theoretical values of diffusion barriers have been obtained for the structural model of the surface featuring a single Au chain only. As a result, this model does not describe properly the situation in the experiment. Therefore we have recalculated corresponding quantities for the structural model of Ref. 48. The potential energy surface of an In atom on the Si(553)-Au surface is shown in the left panel of Fig. 3. The potential landscape of In atoms is similar to that of Pb atoms (compare Fig. 4 of Ref. 29). A similar diffusion channel is observed between the step edge and double Au chain. Note that the positions of the step-edge Si atoms in Figs. 3 and 4 coincide with the vertices of the parallelogram defining the surface unit cell (compare Fig. 1). The diffusion trajectory in the step-edge channel is highlighted by black line (A) passing through the lowest energy adsorption sites visible as deep minima of the PES. A corresponding profile of the PES along the path A, shown in the right panel, is composed of shallow minima with the highest energy barrier equal to 0.193 eV, a value twice as small as in the case of the Pb atoms. At the same time, movement of In atoms in the perpendicular direction is now confined by lower energy barriers than for Pb atoms, i.e., $E_\perp^{\mathrm{In}} = 1.179$ eV, to be compared with $E_\perp^{\mathrm{Pb}} = 1.579$ eV. The corresponding trajectories across the steps (C and D) are also shown in Fig. 3. Note that the present values of the energy barriers differ from those of Ref. 28, which suggests that an additional row of Au atoms lowers the $E_\parallel^{\mathrm{In}}$ by

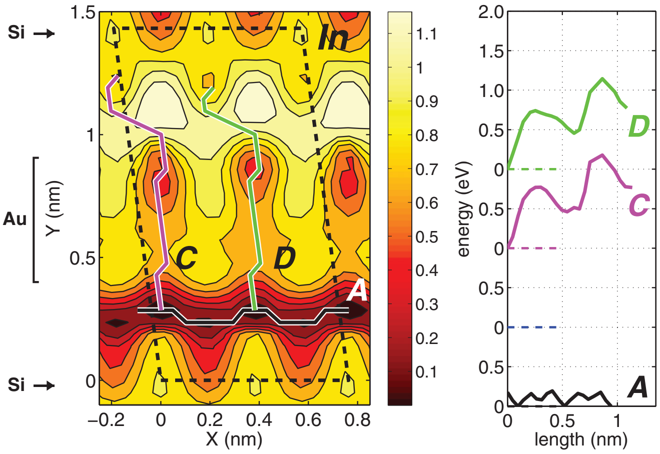

FIG. 3. (Color online) Potential energy surface of an In atom on the Si(553)-Au surface (left) and the energy barriers (right) along the diffusion trajectories highlighted on the PES landscape. Labels Au and Si on the left side of the left panel indicate the positions of the double-Au chain and the step-edge Si atoms, respectively. The diffusion path marked by A passes through the lowest energy adsorption sites, shown as deep minima of PES. The parallelogram shows the unit cell of the surface with its vertices indicating positions of the step-edge Si atoms (compare Fig. 1). Note the differences in the abscissas of the left and right panels. The label X in the left panel describes the position in the direction parallel to the steps, while the length shown in the right panel is measured along the diffusion paths.

0.1 eV and increases $E_{\perp}^{\mathrm{In}}$ by 0.3 eV, thus substantially improving conditions for 1D movement of In atoms.

Basically, in the case of all the atoms studied here, the heights of the diffusion barriers along the steps in the step-edge channel do not excess 1 eV and are much lower than in the direction perpendicular to the steps (see Table I). Again, Si atoms make an exception, as the corresponding $E_{\parallel}^{\mathrm{Si}}$ and $E_{\perp}^{\mathrm{Si}}$ values are similar to each other, with the $E_{\parallel}^{\mathrm{Si}}$ slightly higher. Thus, indeed, the diffusion of Si atoms should be isotropic.

The shape of the diffusion paths for other chemical element atoms in the step-edge channel look similar to the path A of the In atom. A slightly more waved shape is predicted for Au and Si atoms. As it has already been mentioned, the electronic states of the Au atom strongly hybridize with the $3p$ states of the Si atoms, and prefer to bond to the step-edge Si or to other surface Si atoms rather than to the Au chain. Therefore one can say that the diffusing Au atom is looking for the Si atoms on its way. A similar situation is observed in the case of the diffusing Si atoms. However, in this case, the substrate Si atoms play a more significant role.

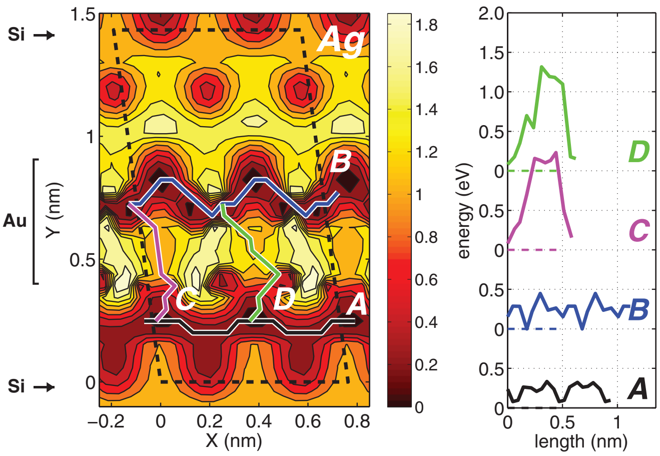

FIG. 4. (Color online) The same as in Fig. 3 for Ag atom.

TABLE I. The calculated energy barriers and the RT hopping frequencies along and across the step edges for atoms of different chemical elements.

Element	$E_{\parallel}$(eV)	$E_{\perp}$(eV)	$\nu_{\parallel}$(Hz)	$\nu_{\perp}$(Hz)	$\nu_{\parallel}/\nu_{\perp}$
In	0.193	1.179	2.77×10^{9}	3.05×10^{-8}	9.10×10^{16}
Mg[a]	0.642	1.655	5.25×10^{1}	1.97×10^{-16}	2.66×10^{17}
Mg[b]	0.427	1.655	2.62×10^{5}	1.97×10^{-16}	1.33×10^{21}
Au[a]	0.383	1.862	1.49×10^{6}	5.45×10^{-20}	2.74×10^{25}
Au[b]	0.267	1.862	1.48×10^{8}	5.45×10^{-20}	2.71×10^{27}
Ag[a]	0.255	1.230	2.38×10^{8}	4.03×10^{-9}	5.91×10^{16}
Ag[b]	0.447	1.230	1.18×10^{5}	4.03×10^{-9}	2.93×10^{13}
Si[a]	0.923	0.786	7.69×10^{-4}	1.75×10^{-1}	4.39×10^{-3}
Si[b]	0.934	0.786	4.97×10^{-4}	1.75×10^{-1}	2.84×10^{-3}
Pb[c]	0.421	1.579	3.32×10^{5}	4.02×10^{-15}	8.27×10^{19}

[a] In the step-edge channel (along trajectory A).

[b] In the middle-terrace channel (along trajectory B).

[c] Reference 29.

Since Ag, Au, and Mg atoms can adsorb on both sides of the Au chain, a two-channel diffusion is expected in this case. Besides the step-edge channel, an additional channel exists in the middle of terrace. This is illustrated in Fig. 4, where the potential energy surface of an Ag atom together with the diffusion trajectories are shown. Assuming that adsorption of the Ag atom in one of the channels does not influence substantially the properties of another Ag atom in the other channel, we expect diffusion to be possible in both channels at the same time. However, the energy barriers in the step-edge channel (A) are lower than in the middle-terrace channel (B). Thus it is natural to expect the diffusion in the step-edge channel to be observable first. Also in the case of Mg atoms, the diffusion should start first in the step-edge channel. An opposite behavior is expected in the case of Au atoms. Since the adsorption of Au atoms in the middle terrace is energetically more favorable than at the step edge, and due to the lower energy barriers in this channel, the diffusion is expected to start first in the middle of terrace.

Again, a completely different situation is expected in the case of Si atoms. Even as the Si adsorption sites exist on both sides of the Au chain, no 1D diffusion channel in the middle of terrace is present. Instead of that, a two-dimensional diffusion is expected, with a slightly higher frequency in the direction perpendicular to the steps. Of course, the much higher diffusion barriers associated with the step edges confine the movement of Si atoms to a single terrace. Furthermore, since all the Si adsorption sites are separated by thick energy barriers, comparable to or higher than 0.8 eV in any direction, the room temperature diffusion should be very slow.

The energy barriers along ($E_{\parallel}$) and across the step edges ($E_{\perp}$) of different chemical element atoms at the room temperature are summarized in Table I. We can see, that the reasonably low energy barriers for a movement of atoms along the steps are found in the case of In, Au, Ag, Pb and, perhaps, Mg atoms. The trajectories of all the above atoms are delimited by much higher barriers across the steps that make the diffusion of atoms quasi-one-dimensional. In the case of Si atoms, the barriers in both directions are comparable to each other and are among the highest observed.

Having found the energy barriers, we can determine the hopping frequencies ν for a thermally activated atom motion according to the Arrhenius equation: $\nu = \nu_0 \exp(-E/kT)$. In the above equation, the preexponential factor ν_0, taken from Ref. 29, is equal to 5.79×10^{12} Hz. The RT hopping frequencies along the step edges $\nu_\parallel$ and in the direction perpendicular to the step edges $\nu_\perp$, as well as their ratio $\nu_\parallel/\nu_\perp$, are listed in Table I. Note that $\nu_\perp$ corresponds to a movement of atoms between adsorption sites on paths A and B on the same terrace of the surface, not through the step edges. Clearly, the best conditions for 1D diffusion on the Si(553)-Au surface fulfill Pb, In, Ag, Au, and Mg atoms. Note that the Mg, Ag, and Au atoms can move in two separate 1D channels. The highest asymmetry ratio $\nu_\parallel/\nu_\perp$ is predicted for Au atoms. On the other hand, the RT movement of Si atoms is expected to be extremely slow in comparison to the other studied elements. Of course, faster diffusion is expected at higher temperatures, but it will be rather isotropic. At this point, we would like to mention that the calculated hopping frequencies for Mg, Au, and Ag atoms moving in the middle-terrace channel should be taken with care, since the Arrhenius formula applies for uncorrelated hopping of independent atoms, and as it will be shown later on, the mechanism of diffusion in this channel is different.

As it was mentioned in Sec. I, the diffusion of atoms on the Si(111) surface has been intensively studied. A rather isotropic, i.e., 2D, diffusion has been observed. It would be interesting to make a short comparison of the present results to the diffusion of atoms on other Si surfaces.

In most cases, the diffusion barriers of a given chemical element atom on various Si surfaces are comparable to the present values. For example, in the case of Pb, these values range from 0.29 to 0.64 eV, depending on the surface reconstruction.[12,13,22] The barriers for Mg atoms on the Si(111) surface are equal to 0.60–0.66 eV,[60] while for Ag they vary between 0.24 eV on the Si(111)7×7 and 1.23 eV on Si(111)$\sqrt{3} \times \sqrt{3}$.[15,16,61] A similar barrier of 1.17 eV on the Si(111)$\sqrt{3} \times \sqrt{3}$ surface has been found for Au atoms.[61] Note that the diffusion barriers on the last surface are much higher in comparison to the present values. Various 2D reconstructed surfaces have also been used to study the diffusion of Si atoms.[8–11,60] In these cases the diffusion barriers range from 0.3 to 1.21 eV. From the results discussed above one can conclude that the barrier heights for a diffusion of atoms on the Si(553)-Au surface are comparable to the values on other Si(111) surfaces, except the $\sqrt{3} \times \sqrt{3}$ reconstruction.

From the point of view of the present study, the diffusion on anisotropic Si surfaces seem to be more interesting. For example, the diffusion of In atoms has been studied on the Si(100) and Si(553)-Au surfaces.[25–28] In the case of the former surface, the diffusion barriers vary between 0.26 and 0.64 eV, while for the Si(553)-Au surface the barrier was determined to be 0.29 eV. However, as it was already mentioned before, this value has been obtained by the DFT calculations for an inappropriate structural model. In view of these results, the presence of an additional Au chain substantially lowers the diffusion barriers along the step edges of the Si(553)-Au surface.

Another example is the Si(111)5×2-Au surface.[63] Similar as in the case of Si(553)-Au, the honeycomb and dimerized double-Au chains constitute the main building blocks of structural models of the surfaces.[48,63] In the case of Si(111)5×2-Au surface, the diffusion of Si adatoms has been observed at elevated temperatures, and determined energy barrier yields 1.24 ± 0.08 eV.[24] Slightly lower barriers have been predicted for the Si(110) surface.[62]

All the above shows that various Si surfaces, even those featuring different atomic structures, share many characteristic features of the atomic diffusion. In many cases, the diffusion barriers for atoms of a given chemical element seem to be comparable. Of course, details of the diffusion processes may be very different, since they are sensitive to a local arrangement of the surface atoms.

So far, we have discussed the possibility of diffusion on the Si(553)-Au surface. Now the following questions arise: how does the diffusion occur and what are the underlying mechanisms of the diffusion? To answer these questions, we shall discuss the structural properties of the adsorbate atoms on the Si(553)-Au surface.

Adsorbate atoms in the diffusion channel near the step edge prefer to bond to the step-edge Si atoms and to the double-Au chain atoms. The arrangements of adsorbate atoms in their energy minima are symmetric, which results in almost equal bond lengths between a given adsorbate and the step-edge and Au-chain atoms. The remaining points of the step-edge diffusion trajectory feature a less symmetric arrangement of the atoms, resulting in different bond lengths or even broken bonds. Of course, for breaking the bonds we must pay an extra energy, which is related to the height of the diffusion barrier. In this channel, the diffusion of atoms happens via thermally activated hopping processes.

For example, the lowest energy structural configurations of In atoms along the step-edge diffusion channel are presented in Fig. 5. As we can see, the In atoms prefer to bond either to two Au atoms and single step-edge Si atom [Figs. 5(a) and 5(c)] or to a single Au atom and two step-edge Si atoms [Figs. 5(b) and 5(d)]. The lowest energy structures, according to which each In atom forms bonds with two Au atoms of the same dimer, are shown in Figs. 5(a) and 5(c). The structure of Fig. 5(c) is related to the structure of Fig. 5(a) via reversal of the phase of the dimerized Au chain. Both structures are energetically degenerate. Thus the In atoms prefer to bind more strongly to the atoms of the same Au dimer rather than to the atoms of different Au dimers. As a results, it is more easy to reverse the phase of the whole Au chain than to bind the In atoms to different Au dimers. Whether this scenario is realized in experiment is not clear at the moment, since the present calculations have been done in ×2 unit cell along $[1\bar{1}0]$ direction, so the distance between In atoms is equal to $2 \times a_{[1\bar{1}0]} = 7.68$ Å. In reality, at very low In coverage, this distance is expected to be much longer, so the energy required to reverse the phase of the Au chain may exceed the binding energy of the In atoms to two neighboring dimers. This needs further calculations in much larger unit cells.

Basically, such a behavior is observed in the case of all the adsorbates studied here. The lowest energy configurations of

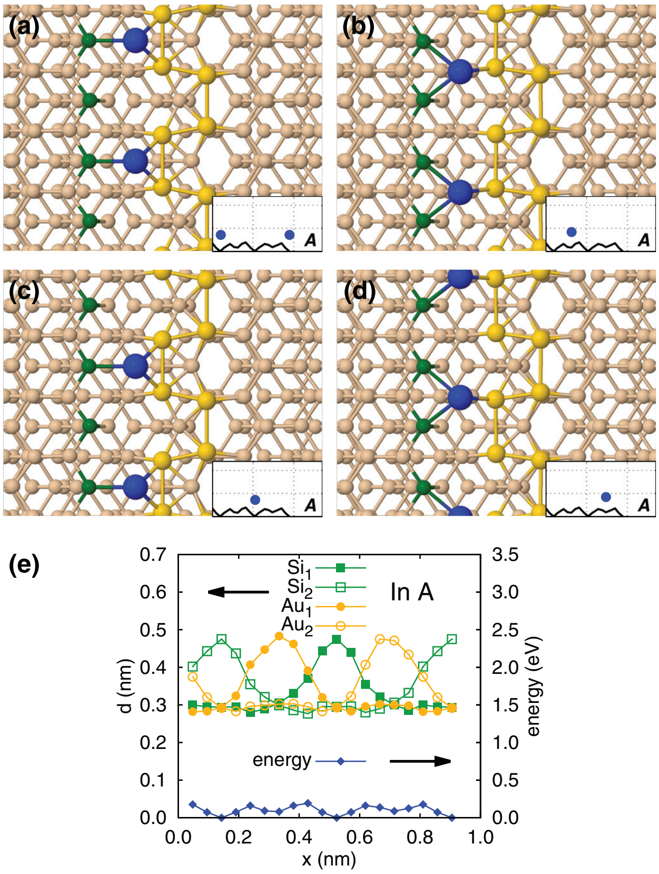

FIG. 5. (Color online) The lowest energy structural configurations of In atoms in the step-edge diffusion channel [(a)–(d)]. (e) Distances of the Pb atom to the Si$_1$, Si$_2$, Au$_1$, and Au$_2$, indicated in Fig. 1, together with the energy barriers (curve A in Fig. 3) vs the position of the In atom in the [$\bar{1}$10] direction (not along the diffusion path). Insets show the positions of the In atom on this energy barrier landscape.

all the atoms feature the bonding of a given adsorbate atom to a single step-edge Si atom and to two Au atoms of the same dimer. However, only the Au adatoms make an exception, as they prefer to bind to two step-edge Si atoms rather than to two Au-chain atoms. In fact, we expected such a behavior from the analysis of the overlapping electronic states, as was mentioned before. Another difference regards the reversing of the dimerized Au-chain phase. We do not observe this effect in the case of Pb, Mg, and Si atoms; the Au chain remains intact in the diffusion processes.

All the structures shown in Figs. 5(a)–5(d) feature a symmetric arrangement of the bonds between the In atom and neighboring atoms. Furthermore, in each of these configurations, the distance between the In atom and the step edge (Si$_1$ or Si$_2$) is the same as between the In atom and the Au chain (Au$_1$ or Au$_2$). This is clearly illustrated in Fig 5(e). In the energy minima three out of four distances (In to Si$_1$, Si$_2$, Au$_1$, and to Au$_2$) are equal to each other. Again, such a behavior is observed for other adsorbate atoms. However, in the case of the Si adatoms in their higher energy minima, only two these distances (Si adatom to Si$_1$ and to Si$_2$) are equal, i.e., the Si adatoms make bonds with the step-edge Si atoms. In the lowest energy configuration, the Si adatoms show a similar behavior to the remaining adsorbates.

The mechanism of diffusion in the middle-terrace channel is substantially different than the thermally activated single atom hopping discussed above. Namely, the diffusion is facilitated by atomic exchange. In this regard, only silicon makes an exception, i.e., Si atoms should diffuse according to the single atomic hopping. Basically, the diffusion of the Si atoms performs in a similar fashion as in the step-edge channel. However, now the reversing of the Au-chain phase accompanies the diffusion of Si atoms. Note also that we do not expect any RT diffusion in the terrace channel in the case of Pb and In atoms.

An example of the lowest energy atomic configurations in the middle-terrace channel is shown in Fig. 6 for Ag

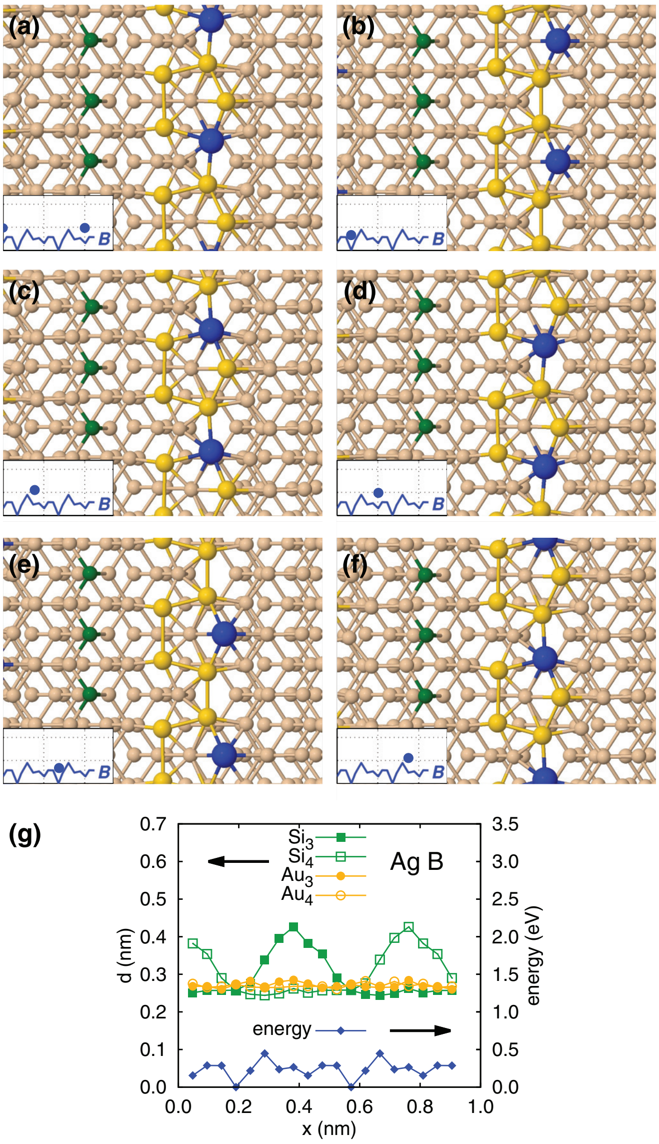

FIG. 6. (Color online) The lowest energy structural configurations of Ag atoms in the middle-terrace diffusion channel [(a)–(f)]. (g) Distances of the Ag atom to the Si$_3$, Si$_4$, Au$_3$, and Au$_4$, indicated in Fig. 1, together with the energy barriers vs the position of Ag atom in the [$\bar{1}$10] direction. Insets (a)–(f) show the positions of the Ag atoms on this energy barrier landscape.

adatoms. Comparing the arrangement of the atoms shown in different panels, Figs. 6(a)–6(f), one can learn that, indeed, the mechanism of the diffusion is related to the atomic exchange. The atoms of the Au chain are substituted by Ag atoms, forming a set of connected pentagons comprising of a single Ag and four Au atoms. Note that the Ag atom can be located in one of three available positions, shown in Figs. 6(a)–6(c), which are energetically degenerate with structures in Figs. 6(d)–6(f), respectively. Both sets of the structures are related to each other by reversing the phase of the Au chain. Comparing the adsorption energies of Ag atoms on the surface, one can notice that the Ag atoms prefer to adsorb and attach to the Au chain [Figs. 6(b) and 6(e)] rather than to substitute the Au-chain atoms [Figs. 6(a), 6(c), 6(d), and 6(f)]. A similar behavior is observed in the case of Au and Mg adatoms. However, in the case of Mg, the substitution of Au-chain atoms by Mg adatoms is preferable. Note also that in the case of the Au diffusion, the corresponding atomic structures, shown in Figs. 6(a)–6(f), should be all equivalent and consequently energetically degenerate.

Similar as in the case of diffusion in the step-edge channel, the adsorbate atoms in their lowest energy minima are arranged symmetrically with respect to the neighboring atoms of the Au-chain (Au_3 and Au_4) and honeycomb chain (Si_3 and Si_4). This, for Ag adatoms, is shown in Fig. 6(g). Note that when the Ag atom moves, three out of four distances to neighboring atoms remain almost the same. This is also observed for other atoms diffusing according to the atomic exchange in the middle-terrace channel.

The diffusion process discussed above requires the reversing of the Au chain, which in the present case seems to be acceptable because of the low barriers between different energy minima. However, as it was discussed previously, at very low adsorbate coverage, this mechanism may be more demanding energetically. Breaking of the Au chain and formation of domains with reversed Au chains must also be taken into account. Nevertheless, the mechanism of the atomic exchange seems to be a conceivable scenario of the middle-terrace diffusion.

IV. CONCLUSIONS

In conclusion, we have studied the atomic diffusion on the Si(553)-Au surface. The obtained results show that except of the Pb and In atoms it is also possible to observe 1D diffusion of Au, Ag, and Mg atoms at the room temperature. Moreover, the diffusion of these atoms can be realized in two separate 1D channels, featuring different mechanisms of the diffusion: the thermally activated hopping and the atomic exchange. Si atoms show a completely different behavior. Instead of 1D channels, we observe the potential minima separated by high-energy barriers, suppressing substantially the room-temperature diffusion of Si. All this makes the Si(553)-Au surface a promising candidate to study experimentally the diffusion phenomena in a reduced dimensionality.

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*mariusz.krawiec@umcs.pl

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