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Surface diffusion of Si, Ge and C adatoms on Si (001) substrate studied by the molecular dynamics simulation*

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Depositions of Si, Ge and C atoms onto a preliminary Si (001) substrate at different temperatures are investigated by using the molecular dynamics method. The mechanism of atomic self-assembling occurring locally on the flat terraces between steps is suggested. Diffusion and arrangement patterns of adatoms at different temperatures are observed. At 900 K, the deposited atoms are more likely to form dimers in the perpendicular [110] direction due to the more favourable movement along the perpendicular [110] direction. C adatoms are more likely to break or reconstruct the dimers on the substrate surface and have larger diffusion distances than Ge and Si adatoms. Exchange between C adatoms and substrate atoms are obvious and the epitaxial thickness is small. Total potential energies of adatoms and substrate atoms involved in the simulation cell are computed. When a newly arrived adatom reaches the stable position, the potential energy of the system will decrease and the curves turns into a ladder-like shape. It is found that C adatoms can lead to more reduction of the system energy and the potential energy of the system will increase as temperature increases.

Keywords: molecular dynamics simulations, Tersoff potential, surface diffusion, potential energy
PACC: 8715D, 6185, 6822

1. Introduction

SiGe and SiC are extremely important materials for needs of high speed optoelectronic devices, high power electronics and sensors. Developing the method of constructing nanostructures on surfaces is necessary for fabricating microelectromechanical systems (MEMS) and nanodevices. With the development of deposition methods such as molecular beam epitaxy（MBE）and chemical vapor deposition (CVD), the quality of thin films and nanostructures has been greatly improved. SiGe films were grown on patterned Si (001) substrates by MBE.[1]

Self-assembling on surfaces is important to the quality of the product, and surface diffusion plays a very important role in the formation of material structure. Therefore, the better knowledge of adatom diffusion over the terraces, as well as an understanding of the growth properties of the steps is necessary.

Theoretically, many calculation methods can provide accurate results for the epitaxial growth and cluster structures.[2−11] However, the Monte Carlo (MC) method considers only configuration space without detailed dynamics; first-principles method is computationally limited to very small models because of the necessity to include a large number of degrees of freedom in the electronic wave functions. Molecular dynamics (MD) simulation, in which the atoms are modelled as point-like particles in an empirical potential field, can tackle a much larger system than the first-principles calculation and show more dynamic details than the MC method. The MD simulation is useful to analyse the local behaviours of adatoms, and it has been applied to a wide variety of deposition phenomena.[12−16]

In the present paper, diffusion and arrangement patterns of different kinds of adatoms at different temperatures are observed by MD simulations; total potential energies of adatoms and substrate atoms in-

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volved in the simulation cell at different temperatures are investigated. It is revealed that diffusion length and direction of the adatoms, arrangement of the adatoms and total potential energy of the system are related to the temperature of substrate and the species of adatoms.

2. Potential function

Empirical potentials such as the Stillinger–Weber (SW) potential[17] and the Tersoff potential[18] are frequently used in MD simulation to study the growth of the semiconductor materials. Here, we use Tersoff potential to simulate the homoepitaxial growth of Si and the heteroepitaxial growth of Ge and C on Si substrate because of its computational convenience in dealing with group IV multicomponent systems. For the sake of comparison, the depositions of the three kinds of atoms are simulated by using the same potential. Equations used in the Tersoff potential are as follows:

$$E = \sum_i E_i = \frac{1}{2}\sum_{i\neq j} V_{ij}, \quad V_{ij} = f_c\left(r_{ij}\right)\left[f_R\left(r_{ij}\right) + b_{ij} f_A\left(r_{ij}\right)\right], \tag{1a}$$

$$f_R\left(r_{ij}\right) = A_{ij}\exp\left(-\lambda_{ij} r_{ij}\right), \quad f_A\left(r_{ij}\right) = -B_{ij}\exp\left(-\mu_{ij} r_{ij}\right), \tag{1b}$$

$$f_c\left(r_{ij}\right) = \begin{cases} 1, & r_{ij} < R_{ij}, \\ \dfrac{1}{2} + \dfrac{1}{2}\cos\left[\pi\left(r_{ij} - R_{ij}\right)/\left(S_{ij} - R_{ij}\right)\right], & R_{ij} < r_{ij} < S_{ij}, \\ 0, & r_{ij} > S_{ij}, \end{cases} \tag{1c}$$

$$b_{ij} = \chi_{ij}\left(1 + \beta_i^{n_i}\zeta_{ij}^{n_i}\right)^{-1/2n_i}, \quad \zeta_{ij} = \sum_{k\neq i,j} f_c\left(r_{ik}\right)\omega_{ik} g\left(\theta_{ijk}\right), \tag{1d}$$

$$g\left(\theta_{ijk}\right) = 1 + c_i^2/d_i^2 - c_i^2/\left[d_i^2 + \left(h_i - \cos\theta_{ijk}\right)^2\right], \tag{1e}$$

$$\lambda_{ij} = \left(\lambda_i + \lambda_j\right)/2, \quad \mu_{ij} = \left(\mu_i + \mu_j\right)/2, \tag{1f}$$

$$A_{ij} = \left(A_i A_j\right)^{1/2}, \quad B_{ij} = \left(B_i B_j\right)^{1/2}, \quad R_{ij} = \left(R_i R_j\right)^{1/2}, \quad S_{ij} = \left(S_i S_j\right)^{1/2}, \tag{1g}$$

The energy is modeled as a sum of pairing interactions, where, however, the coefficient of the attractive term in the pairing potential (which plays the role of a bond order) depends on the local environment, giving rise to a many-body potential. Here i, j, and k label the atoms of the system, r_{ij} is the length of the ij bond, and θ_{ijk} is the bond angle between bonds ij and ik. Singly subscripted parameters, such as λ_i and n_i, depend only on the type of atom (C, Si, or Ge). The parameter χ strengthens or weakens the heteropolar bonds, relative to the value obtained by simple interpolation. The suggested parameters for C, Si, and Ge are given in Table 1.[18]

Table 1. Values of parameters of C, Si, and Ge to be used in expression (1).

	C	Si	Ge
A/eV	1.3936×10^{3}	1.8308×10^{3}	1.769×10^{3}
B/eV	3.467×10^{2}	4.7118×10^{2}	4.1923×10^{2}
λ/nm^{-1}	34.879	24.799	24.451
μ/nm^{-1}	22.119	17.322	17.047
β	1.5724×10^{-7}	1.1000×10^{-6}	9.0166×10^{-7}
n	7.2751×10^{-1}	7.8734×10^{-1}	7.5627×10^{-1}
c	3.8049×10^{4}	1.0039×10^{5}	1.0643×10^{5}
d	4.384×10^{0}	1.6217×10^{1}	1.5652×10^{1}
h	-5.7058×10^{-1}	-5.9825×10^{-1}	-4.3884×10^{-1}
R/nm	0.18	0.27	0.28
S/nm	0.21	0.3	0.31
		$\chi_{\mathrm{C-Si}} = 0.9776$	$\chi_{\mathrm{Si-Ge}} = 1.00061$

3. Method of simulation

In order to have sufficient equilibration time after each deposition of an atom, we adopt a small computational cell, but it is large enough for the simulation results, little affected by the periodic boundaries; this simulation cell is similar to that in Refs.[13] and [16].

The substrate in the simulation cell is assumed to be of a cube consisting of 216 Si atoms. Its sides are along the three crystallographic axes of the silicon diamond structure, and they are $3a_0$ in length, where a_0 is the lattice constant of Si at a specified temperature. The coordinates x, y, and z are taken along the sides of the cube. The growth direction is the [001] direction. The periodic boundary conditions are applied in the x and the y directions. To prevent crystal drift due to adatom momentum transfer, the lowest four atomic layers within the substrate are fixed. During atom impact, the adatom initial kinetic energy and latent heat of condensation are partitioned into the vibrational modes of the system. This will then result in a continuous increase of system temperature. To simulate the approximately isothermal conditions under which growth usually occurs, the top eight atomic layers are set to be velocity-scaling layers. This allows the heat generated on the surface to be conducted to the thermostat region where it is then removed from the calculation.

Growth is simulated by periodically injecting a single atom towards the top (001) surface from points whose x and y coordinates are selected at random from 0 to $3a_0$ and whose z coordinate is $6a_0$. Atoms with the velocity whose magnitude is corresponding to 0.2 eV in the direction towards the substrate successively appear in the simulation cell, move along the minus z direction, and arrive at the surface of the substrate. In the first simulation, one atom (Si, Ge or C) is deposited in 20 ps; in the second simulation, 15 atoms (Si, Ge or C) are deposited in 200 ps; in the third simulation, 100 atoms (Si, Ge or C) are deposited in 2000 ps. The equations of motion are integrated by the Gear method with a time step of 0.2 fs.

The deposition rate is extremely high compared with the experimental ones, which cannot be avoided because of the restriction on the size of the MD time step. However, it is low enough if it is compared with the deposition rates of simulations in the literature; e.g. the deposition rate adopted by Srivastava *et al* [19] was one atom per 3 ps. Despite the lack of steps and the small diffusion length of adatoms, the limited-thickness Si (001) epitaxy in the simulation can suggest the mechanism of atomic self-assembling occurring locally on the flat terraces between steps.[16]

4. Results and discussion

We have found that 20 ps is enough to observe the diffusion processes of one adatom in our above conditions. The trajectories (black lines) of a single deposited Si atom during 20 ps after its arrival at the simulation cell at 300, 500 and 900 K are shown in Fig.1. The diffusion is along the $[1\bar{1}0]$ direction. Since the distance between the nearest neighbour atoms on the uppermost substrate surface without reconstruction is about 0.38 nm, it is easy to see that an atom deposited on the substrate at 300 K does not move around beyond the range of the unit square lattice. The adatom is not active to reach the equilibrium position and will search for the equilibrium position until the end of the simulation, so the trajectory line at 300 K is broad. On the other hand, an atom deposited on the substrate at 900 K is relatively active. It can move beyond the range of the unit square lattice on the substrate surface and find the equilibrium position easily. When the adatom reaches the equilibrium position, it just vibrates around the equilibrium position where the trajectory line is dense. Note that the continuous trajectory at 900 K is described as a split one, owing to the periodic boundary condition. As the obvious thermal motions of the surface atoms, some atoms of the substrate surface break away from the initial positions at high temperatures. The results are analogous when the deposited atoms are C and Ge.

Figure 2 shows the trajectories (black lines) of single deposited Ge and C atoms during 20 ps after their arrival at the simulation cell when the temperature of the substrate is 500 K respectively. The diffusion is along the $[1\bar{1}0]$ direction too. Different kinds of adatoms have different diffusion velocities along the surface, C adatom moves a longer distance and reaches the equilibrium position quickly, then vibrates around the equilibrium position and the vibration range is the smallest. The diffusion length of the Ge adatom is small, it is not active to reach the equilibrium position and will search for the equilibrium position until the end of the simulation; this is the reason why the trajectory line is broad. The results are analogous when the temperatures are 300 K and 900 K.

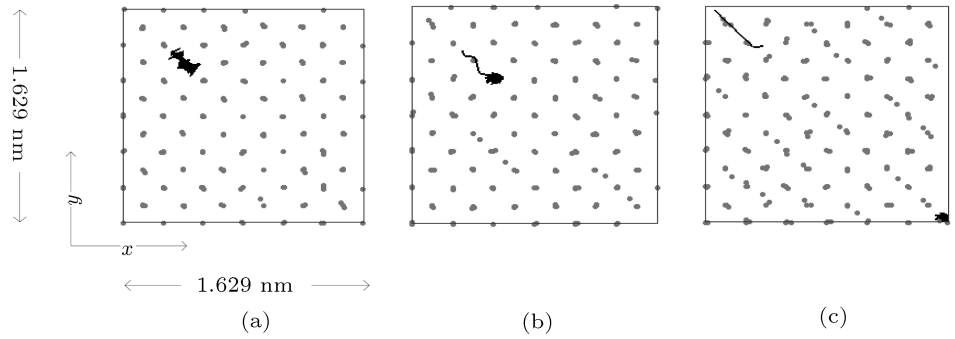


Fig.1. Trajectories (black line) of a deposited single Si atom during 20 ps after its arrival at the simulation cell when the temperature of the substrate is (a) 300 , (b) 500 and (c) 900 K respectively.

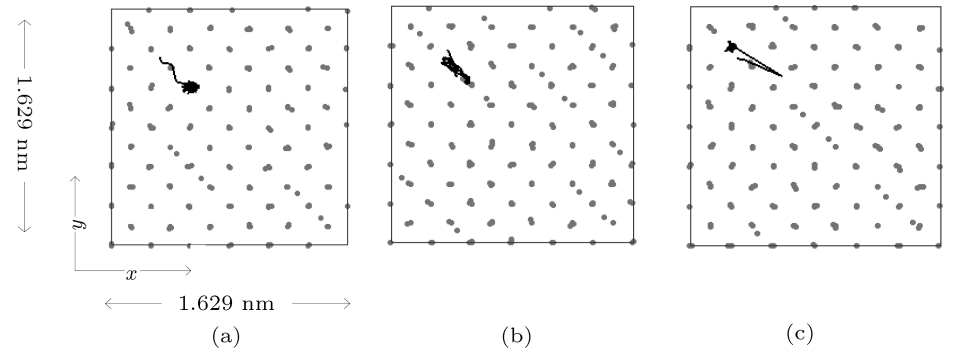


Fig.2. Trajectories (black line) of deposited single atoms (a) Si, (b) Ge, and (c) C, during 20 ps after their arrival at the simulation cell when the temperature of the substrate is 500 K, respectively.

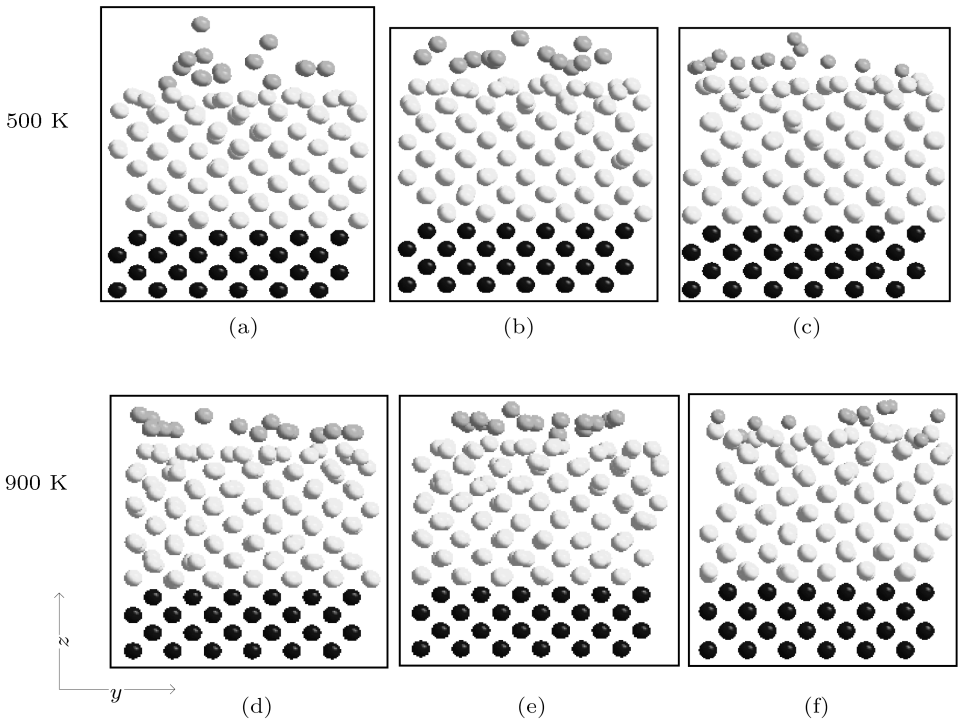


Fig.3. Side views of the deposited atoms and the substrate after the deposition of 15 atoms, where (a), (b), (c) are for Si, Ge, C deposited atoms respectively at 500 K and (d), (e), (f) are for Si, Ge, C deposited atoms respectively at 900 K. Black solid circle is for the fixed layer of the substrate, white one is for the temperature controlled layer of the substrate and grey one is for the deposited atoms.

Gilmer and Roland[14] evaluated the diffusion constant of an adatom with an initial kinetic energy of 0.17 eV by calculating the mean-squared displacements measured in the systems containing a single adatom. They used a classical MD method with the SW potential. They obtained the Arrhenius expression for adatom diffusion constant $D = 1.3 \times 10^{-3} \exp(-0.54 \text{ eV/kT}) \text{ cm}^2/\text{s}$, where k and T are the Boltzmann constant and the absolute temperature, respectively. Our diffusion lengths of an adatom at 500 K and 900 K in Fig.1 are about 0.192 and 0.384 nm, respectively, which are consistent with the diffusion lengths estimated from the diffusion constant expression of Gilmer and Roland.

Figure 3 shows the side views of the deposited atoms and the substrate after the deposition of 15 atoms in 200 ps at 500 K and 900 K. Obviously, the deposited atoms make ordered arrangements and are more likely to form dimers with the atoms of substrate at 900 K. From Figs.3(c) and 3(f), some C adatoms are implanted into the substrate by breaking and reconstructing the dimers due to the impingement of deposited atoms. However, exchanges between Si (or Ge) adatoms and substrate are not obvious.

Bird's-eye views of the deposited atoms after the deposition of 15 atoms in 200 ps are shown in Fig.4. The substrate temperature is maintained at 500 and 900 K respectively. Since an adatom is likely to move in the $[1\bar{1}0]$ direction as shown in Figs.1 and 2, 2×1 dimer rows are likely to be along $[1\bar{1}0]$ direction on the substrate surface. Diffusion is more likely to occur in the direction along the dimer rows than in the direction perpendicular to the dimer rows. Such a tendency can be seen more clearly at 900 K than at 500 K. Some deposited atoms are excluded from the bird's-eye views of snapshots because they are not on the substrate surface. In Figs.4(b) and 4(d), some atoms can make a dimer, owing to the periodic boundary condition, and in Figs.4(c) and 4(f), one C atom reevaporates rapidly after briefly interacting with the substrate.

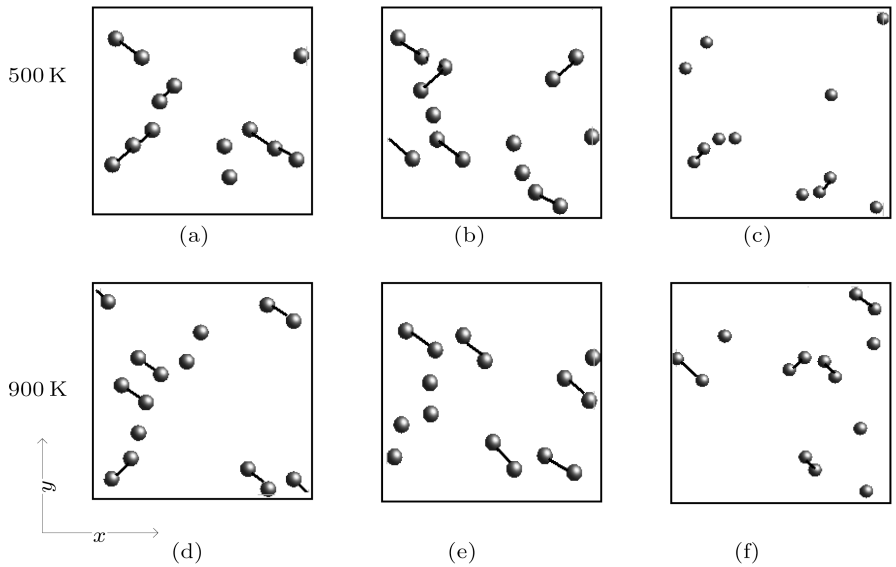


Fig.4. Bird's-eye views of the adatoms after the deposition of 15 atoms, where (a), (b) and (c) are for Si, Ge, and C atoms respectively at 500 K and (d), (e), (f) are for Si, Ge, C atoms respectively at 900 K. Si atoms of substrates are left out from the view to make the alignments clear.

Figure 5 shows the time evolutions of the total potential energies of adatoms and substrate atoms involved in the simulation cell at 500 K. The potential energies of the entire system will gradually decrease as time increases and the curves present a ladder-like tendency. This is because a newly arrived adatom gains its own potential energy from the potential energy of the entire system when it settles down at its stable position. The system becomes more and more energetically stable and the potential energies of the dimers constructed at the transient surface also decrease, these dimers tend more and more difficult to be broken. The flat parts of the ladder-like curves represent the equilibrium state when a newly arrived

adatom reaches the stable position, and the total potential maintains the same value before the deposition of the next atom. Note that C adatoms can lead to more reduction of the system energy because the adsorption heat of C is larger and then it is removed from the system through the thermostat region. The results are analogous when the temperatures are 300 and 900 K.

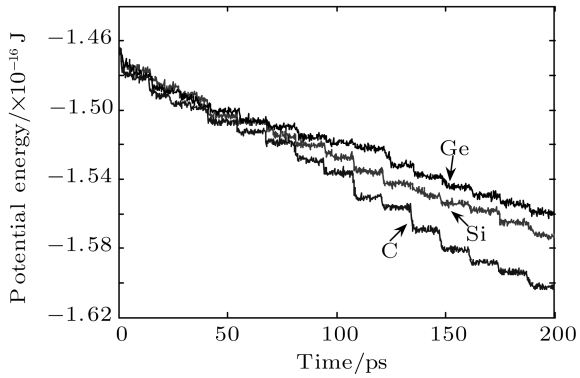


Fig.5. Time evolutions of potential energies of adatoms and substrate atoms in simulation cell after the deposition of 15 atoms, with the substrate maintained at 500 K.

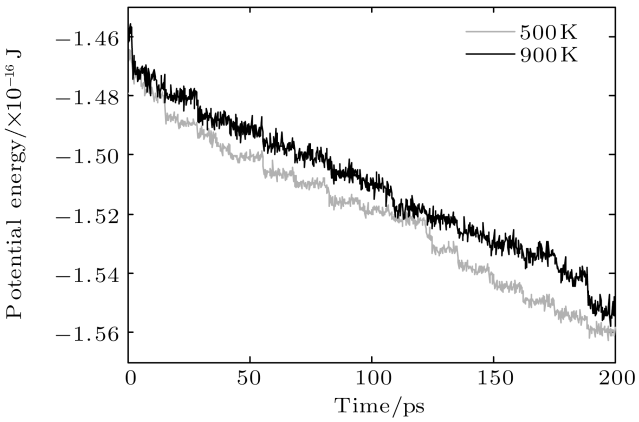


Fig.6. Time evolutions of the potential energies of adatoms and substrate atoms in the simulation cell after the deposition of 15 Ge atoms with the substrate maintained at 500 and 900 K respectively.

Figure 6 shows the time evolution of the total potential energies of adatoms and substrate atoms involved in the simulation cell after the deposition of 15 Ge atoms at different temperatures. The system becomes more and more energetically stable at 500 K and 900 K separately. The average distance between the neighbouring atoms in condensed matters depends on temperature and increases with the increase of temperature. The interatomic potential energy plotted against the interatomic distance will shift toward the right (to the larger distance) and upwards as temperature increases. Accordingly the minimum of the potential energy function, which shows the time-averaged value of the potential energy when the system is in equilibrium, will increase as temperature increases. So, the potential energy at every time step at 900 K is larger than that at 500 K.

At 900 K, the amplitude excursion of interatomic distance is larger. So, the amplitude excursion of the potential energy is larger and the flat parts of the curves are not obvious. The results are similar when the deposited atoms are C and Si.

Images of the deposited atoms and the substrate after the deposition of 100 atoms in 2000 ps at 900 K are shown in Fig.7. The deposited atoms are (a) Si, (b) Ge, and (c) C respectively. It is revealed that the transient anisotropic surface structures are created by the break and the reconstruction of dimers due to the impingement of deposited atoms and the epitaxy occurs when such a renewal of surface dimers is repeated.[16] Owing to the thermal motion of the surface atoms, the fluctuation of the atom positions is observed, which leads to the fluctuation of the binding energies. Different positions of the surface have different adsorption energies. If the vertical energy of the deposited atom is big enough to exceed the adsorption energy, the deposited atom will reevaporate from the substrate surface. There are 99 Si, 100 Ge, 84 C atoms left on the substrate surface. 1 Si and 16 C adatoms have reevaporated from the substrate. As C adatoms move more actively than Si and Ge adatoms, exchanges between C adatoms and substrate atoms are obvious, some C adatoms are implanted into the substrate which is the main reason for small epitaxial thickness of the deposited C atoms in Fig.7(c). The epitaxial thickness of the deposited Ge layers in Fig.7(b) is a little larger than that of the deposited Si atoms in Fig.7(a) because the lattice constant of Ge is a little bigger than that of Si.

It is also found that the limited thicknesses indicated in Fig.7 are much smaller than those observed in experiment.[20,21] This is because the deposition rate in MD simulations must be of the orders of magnitude greater than that measured in experiment, namely our beams of atoms in the simulations are extremely dense compared with those in experiment, which cannot be avoided because of the restriction on the size of the MD time step.

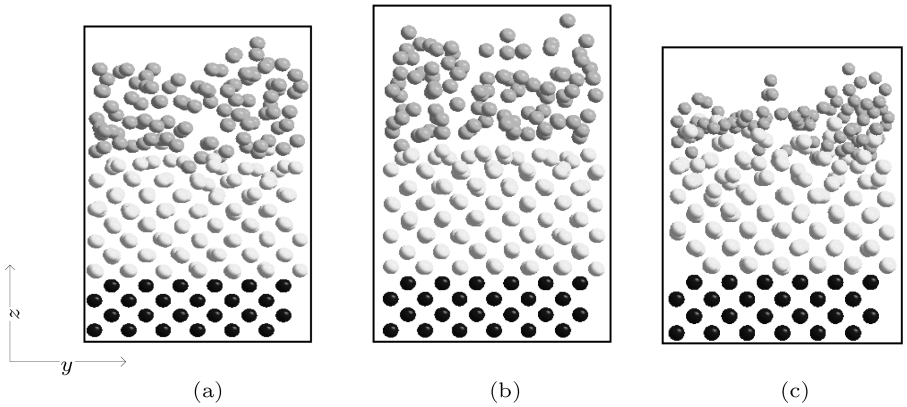


Fig.7. Side views of the deposited atoms and the substrate after the deposition of (a) 100 Si atoms, (b) 100 Ge atoms and (c) 100 C atoms in 2000 ps at 900 K. Blcck is for the fixed layer of the substrate, white is for the temperature controlled layer of the substrate and grey is for the deposited atoms.

5. Concluding remarks

Molecular dynamics simulations with a Tersoff potential are used to investigate the atomic assembly and surface diffusion of Si, Ge and C adatoms on Si (001) surface respectively. In the simulation, the adatoms are likely to move along the $[1\bar{1}0]$ direction and the dimer rows are more likely to align in the $[1\bar{1}0]$ direction on the substrate surface at higher temperatures. C adatoms are more likely to break and reconstruct the dimers of the substrate surface because C adatoms move more actively than Si and Ge adatoms. The epitaxial thickness of the deposited C layers is smaller than that of the Si or Ge. The total potential energies of adatoms and substrate atoms involved in the simulation cell will decrease as time increases. It is also found that C adatoms can lead to a larger reduction of the system energy and the potential energy of the system will increase as the temperature increases. The calculations support the previous results published in the literature.

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