

# Molecular dynamics simulations of the growth of Ge on Si

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## ABSTRACT

The initial stages of the growth of germanium on the dimer reconstructed Si(100) surface is modelled using molecular dynamics (MD). Pyramidal island structures are observed to form despite MD being carried out at a deposition rate faster than experiment. By an examination of transitions that can occur from intermediate structures that form in the MD simulations, growth mechanisms can be identified. The initial wetting occurs as a result of Ge atoms diffusing into the trenches between the dimer rows. This results in Ge-Ge or Ge-Si dimer chains growing in rows perpendicular to the original Si-Si dimer rows on the surface. It is shown how strained Ge pyramids with square bases can form by diffusing atoms joining together adjacent dimer rows. From these initial square-based structures, complex concerted motions are observed in which atoms in lower layers 'climb up' to higher layers. Similar structures grown in the pure Si case exhibit much higher energy barriers for the 'climbing up' process indicating that the effect of strain is to reduce the energy barriers for pyramid formation. In addition to the investigation of atomistic growth processes, surface energy effects are also examined, which show that a germanium-covered Si(100) surface containing shallow-angled pyramids is energetically more favourable than that grown as a flat monolayer.

## 1. Introduction

Experiments reporting the growth of quantum dots of germanium on silicon first appeared in the literature 30 years ago [1,2]. Originally, hut structures with square (pyramids) and rectangular (wedges) bases were observed and since then both pyramids and wedges have been seen dependent on the precise growth conditions [3,4]. Due to a lattice mismatch of about 4.2% in the Ge/Si system, the Stranski-Krastanow growth mode is realised [5–8]. Experiments indicate that the nucleation of large 3D clusters only occurs after the deposition of a wetting layer (WL) with a critical thickness of typically, 3–5 monolayers [9,10].

There have been numerous experimental and theoretical studies over the years aiming to understand the precise mechanisms for the formation of the growth structures which continue to this day. A good overview of experimental work up to 2013 is given in [11]. Over a number of years heterostructures with quantum dots have been actively used for the creation of photodetectors, solar cells and light emitting devices [12,13]. They have also found application in emerging fast-speed transistors where the engineered strain induces very high mobilities of the charge carriers [14].

Theoretical models can be broadly categorised in terms of (1) free

energy models [15] (2) Kinetic Monte-Carlo (KMC) models [16,17] (3) Quantum mechanical (Density Functional Theory, DFT) models. Whereas the DFT models can give relatively accurate values for the energies and stresses of the Ge 'hut' islands [18,19] they are too expensive to be used in dynamical growth simulations. The KMC models can predict the growth of pyramids with the observed (105) facets by both including the effect of strain and by artificially forcing cells that lie locally on such a face to be less mobile than other cells [16].

Larger scale free energy models have also been used to explain the growth process such as the effect of the edge energy [20], the transition from two dimensional to three dimensional growth [21], the influence of the wetting layer [22] and the role of elastic interactions between islands [23,24]. Moreover, such models have been successfully used to describe Volmer-Weber growth of islands directly on the surface of the substrate in highly-mismatched systems [25,26], as well as the formation of 2D layers according to Frank-van der Merwe mechanisms in systems with close lattice parameters [27,28]. However, precise information about surface diffusion coefficients [29] and thickness-dependent surface energies [18,19] is required for constructing these models. These are still less well-defined input parameters [30], because direct experimental measurements of these values are impossible.

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Despite the large amount of theoretical work which we only touch upon briefly in this introduction, there are still gaps in the theory that make direct prediction of experimental results quite difficult.

One type of model that to our knowledge has not been fully explored is the use of molecular dynamics (MD). MD is generally not so suitable for atomistic growth modelling because it cannot capture experimental growth rates. This is because time scales accessible by MD are usually of the order of microseconds at most and so diffusion between successive particle impacts is generally not so well captured. This has led to other methods such as temperature accelerated dynamics (TAD) [31] and adaptive KMC [32]. In the case of Ge growth on Si, the adaptive KMC is difficult to implement because the dimer reconstruction enlarges the search volumes in which transitions are located, making it too computationally expensive to find a representative set of transitions. However recent work [33] has shown that in certain circumstance MD at elevated temperature can be a useful tool in modelling growth on surfaces and indeed more than 30 years ago MD at elevated temperature was used on quite small systems to show how the first layer of growth of Si on the dimer reconstructed Si(100) surface occurred [34]. Another potential drawback of MD using classical potentials is that it cannot capture all the electronic details of chemical interactions. Generally ab initio methods give a better representative model; for example in the case of the dimer reconstructed Si(100) surface, ab initio methods can capture the dimer tilting observed experimentally whereas classical potentials do not. However due to the computations involved ab initio methods are impractical for growth simulations and it is expected that because a key feature of the pyramidal growth is the lattice size mismatch between Si and Ge, which the classical potentials are fitted to, MD should be able to shed some light on the growth mechanisms on the atomic scale.

Computing power has significantly increased since that initial work of Si growth on Si [34] allowing for larger systems to be investigated but the problem of enhanced deposition rates compared to experiment still exists. Notwithstanding that, elevated temperature MD can be a powerful tool for analysing complex transitions that occur in atomistic growth. This is the approach adopted here, combined with an analysis of some specific transitions which can form the explanation for how the pyramidal structures grow.

## 2. Methodology

Depositions were modelled via MD using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [35] package. The Tersoff potential [36] for Si–Ge was used for simulations. The potential energy surface for the system is quite rough with a combination of both very small energy barriers where the atoms change position only over a distance of fractions of an Å and larger barriers where hops are quite rare. This makes the speed-up of both TAD and adaptive KMC quite marginal. In addition because of the dimer reconstruction, quite large search volumes are required for adaptive KMC which also renders the method very slow. As a result it was decided to use MD with a deposition rate faster than experiment to investigate the system.

The largest simulation cell used for the Si substrate had dimension  $8.7 \times 8.7 \times 1.2$  nm comprising of 10 layers with 512 atoms in each layer. The (100) surface was dimer reconstructed. The bottom layer of the substrate was fixed and the next layer above the fixed zone was heated to 1000 K with a Berendsen [37] thermostat which scales velocities. The entire system was thermalised to 1000K before deposition. Ge atoms were deposited normal to the surface and initially placed randomly 10 Å above the surface beyond the cut-off distance of the potential. 4900 Ge atoms were deposited equivalent to around 10 added layers. The temperature of 1000 K was chosen to allow for some diffusion between particle impacts and also so as to be not that much larger than that used in the experiments (475–875 K as reported in [1]). The deposition energy was chosen as 1 eV and each deposition was run 0.1 ns before the next deposition started. Throughout the simulation,

because of the thermostat the average temperature remained at around 1000 K.

Simulations at the same temperature but with a smaller cell and 1 ns between impacts was also studied to allow for more diffusion of atoms and the identification of new diffusion pathways. Despite the time between impacts being reduced by a factor of 10, the revised model cannot capture all the diffusion that takes place between impacts. For example, if experimentally there was a fast deposition rate of 10 monolayers per second, this would correspond to the impact in our system of a Ge atom arriving every  $200 \mu\text{s}$  so the simulation is still  $2 \times 10^5$  faster than experiment. Nonetheless, using MD to identify diffusion mechanisms and then using the nudged elastic band (NEB) [38] method to determine energy barriers can give valuable insight into the main processes behind pyramid formation. In addition to the dynamical simulations, some surface energies  $E_{\text{Surf}}$  were also calculated following [39]

$$E_{\text{Surf}} = \frac{(E_{\text{Tot}} - N_{\text{Si}}E_{\text{Si}} - N_{\text{Ge}}E_{\text{Ge}})}{2A}, \quad (1)$$

where  $E_{\text{Tot}}$  is the total energy of the system,  $A$  is the surface area,  $N_{\text{Si}}$  and  $N_{\text{Ge}}$  are the number of Si and Ge atoms in the system and  $E_{\text{Si}}$  and  $E_{\text{Ge}}$  are cohesive energies of Si and Ge respectively. The energies are all calculated using the Tersoff potential for which the cohesive energies of Si and Ge in bulk are  $-4.63$  eV and  $-3.76$  eV respectively.

## 3. MD deposition results

### 3.1. Simulations using a ten layer Si substrate with an area $8.7 \text{ nm} \times 8.7 \text{ nm}$ and a Ge deposition every 0.1 ns

Before discussing individual diffusion pathways and mechanisms we first present the results from the fast deposition of about 10 added Ge layers under the conditions as described above. The results are shown in Fig. 1 after the deposition of 400 Ge atoms in Fig. 2 after 2174 atoms.

Fig. 1 shows clearly dimer rows of Ge and mixed Ge–Si atoms

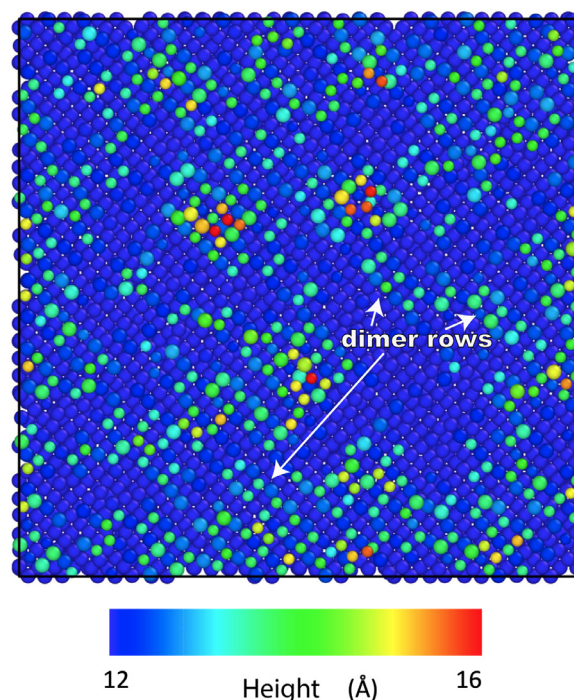
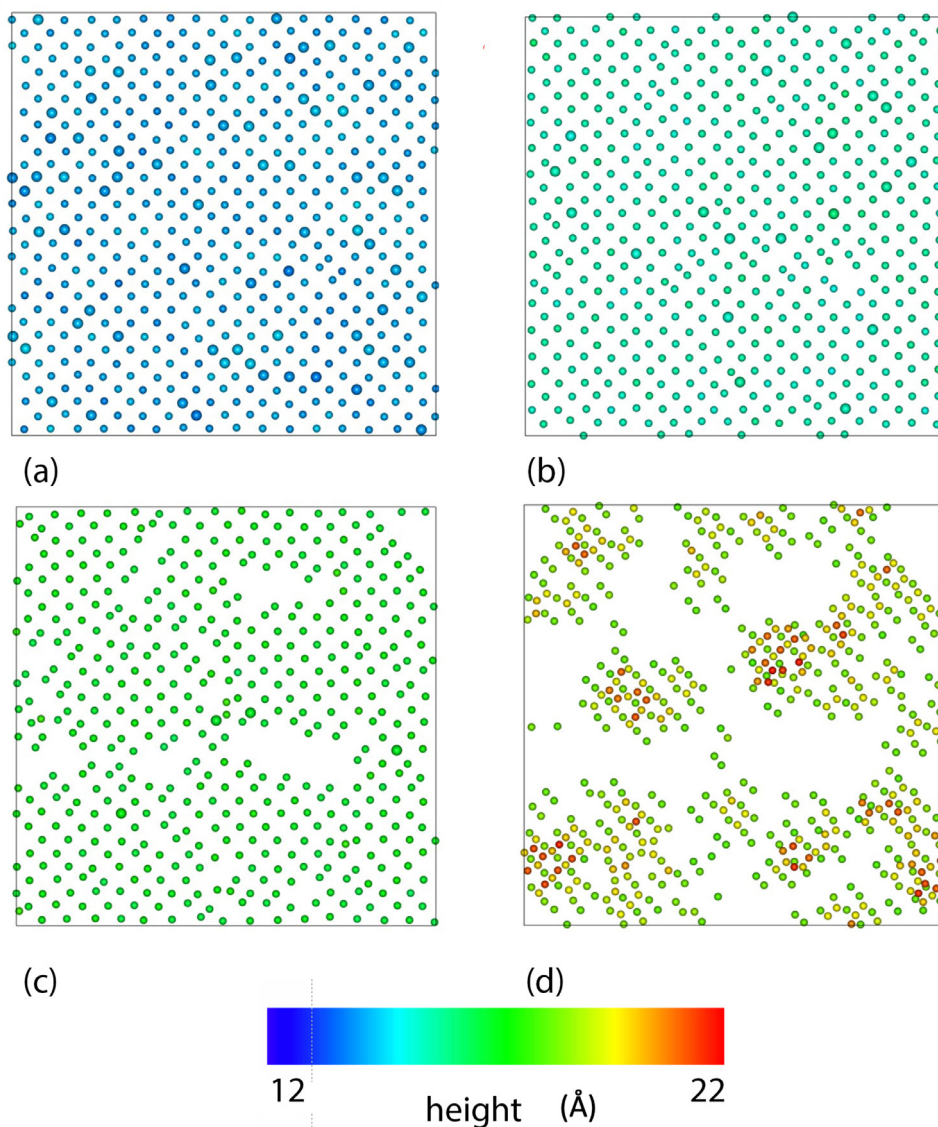
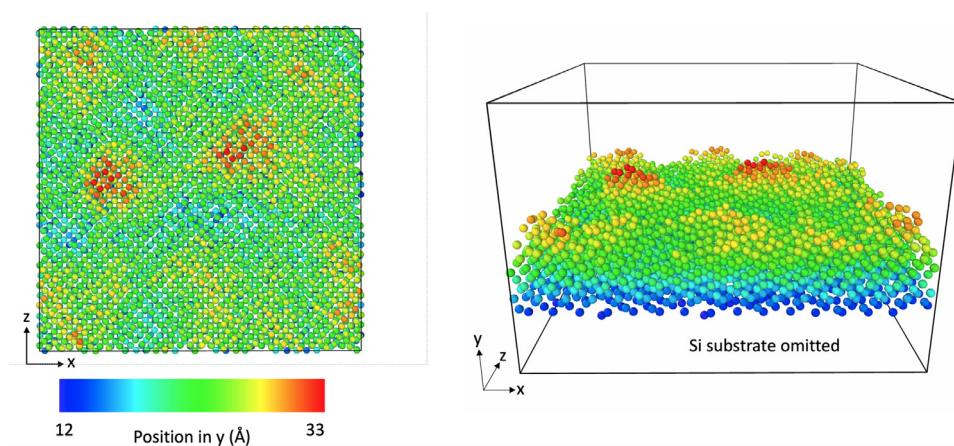


Fig. 1. The spatial distribution of 400 Ge atoms that have been deposited every 0.1 ns, normal to the surface with an energy of 1 eV at 1000 K. The larger spheres represent Si atoms and the smaller, spheres, the added Ge. Note that the highlighted dimer rows contain both Ge–Ge and Si–Ge dimers.



**Fig. 2.** The structure after the addition of atoms equivalent to 4 added layers. The atoms are deposited every 0.1 ns, normal to the surface with an energy of 1 eV. (a) The first monolayer showing complete coverage of the surface; (b) The second added layer; (c) the third added layer; (d) Atoms added in layer 4 and above.



**Fig. 3.** The formation of small Ge islands after 4900 deposited Ge atoms at 1000 K. The atoms are deposited every 0.1 ns, normal to the surface with an energy of 1 eV.



perpendicular to the original Si-Si dimer rows together with some regions where clustering has started to occur. The Si-Ge dimers have a spacing between 2.42 and 2.43 Å whereas the Ge-Ge dimer spacing is 2.49–2.50 Å. This compares with the Si-Si dimer spacing of 2.37 Å. It can be seen that there are some areas of the surface that remain uncovered by Ge atoms and some small island clusters which form the basis of the pyramidal island structures that ultimately form. The first added layer consists mainly of Ge adatoms with a few Si atoms that are produced by a replacement mechanism described later. Atoms in the second added layer are coloured yellow and in the third added layer, red. After the deposition of about 10 monolayers as shown in Fig. 3 islands have clearly started to form.

Fig. 2 shows that after the addition of 4 layers the surface is completely wetted by the first monolayer that consists of a mixture of Ge and Si atoms displaced from the substrate in perfect crystalline form. The second layer is almost complete and the third layer has a few patches of missing atoms but island structures. In Fig. 2(d) clustering on the surface has occurred which form the seed points for the nucleating island structures.

### 3.2. Simulations using a ten layer Si substrate with an area $1.1 \text{ nm} \times 1.1 \text{ nm}$ and a Ge deposition every 1 ns.

Fig. 3 shows the surface topography after 4900 atoms have been deposited, equivalent to about 10 added layers. By this stage clear island structures have begun to form on top of the completed wetting layers.

To understand the clustering and surface diffusion processes in more detail some simulations were also carried out at a deposition rate ten times slower where a Ge atom was deposited every nanosecond onto a smaller surface. In this case more uniform clusters form as shown in Fig. 4. The cluster that has formed in Fig. 4 has a rectangular base where the outer part consisting of dimerised Ge atoms. The central part has second layer dimerised Ge atoms, shown coloured yellow and other Ge atoms that have split the added dimers to form a more bulk-like structure (atoms coloured cyan and green). In the next section the

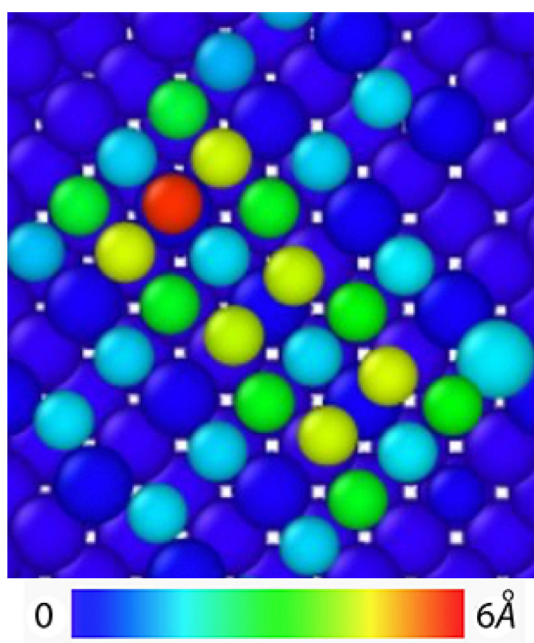


Fig. 4. An example of a small Ge island grown on Si(100) when the deposition rate is one Ge impact every nanosecond. Colouring is by height on a scale 0 to 6 Å. The larger spheres are Si atoms and the smaller spheres Ge. The letter X represents a Ge atom that has become incorporated in the substrate and Y the Si adatom from the same substrate site.

surface diffusion mechanisms and growth processes that can produce such a structure will be examined in more detail.

## 4. Diffusion pathways and growth mechanisms

### 4.1. Mechanisms in the first added layer

Growth occurs by Ge atoms diffusing over the surface to two favoured sites. These sites are where the Ge atom attaches to an Si dimer or resides in the trench between adjacent dimers, pulling the adjacent Si atoms towards it. Fig. 5a shows a typical diffusion path seen in MD with the associated energy barriers determined by the nudged elastic band (NEB) method shown in 5 b. The final state is the equilibrium structure in the trench between dimer rows and the intermediate structure with the local minimum of  $-0.5 \text{ eV}$  is the atom attached to the dimer row. The final state referred to as the ‘long bridge site’ has already been noted as the global minimum site on the surface by Srivastava and Garrison [40]. The initial site over the bulk-terminated first-layer atom is called the ‘dangling bond’ or ‘radical’ site and was identified in [40] as the most probably site at which an arriving Ge atom would first bind to the surface. The energy barrier for diffusion between adjacent ‘long bridge’ sites is  $1.05 \text{ eV}$  and the barrier to jump out of this site to the flatter part of the surface is  $1.2 \text{ eV}$  as was also calculated in [40] but can also be seen from Fig. 5a. The reason why the Ge dimer rows are perpendicular to the original Si surface dimer rows is because surface Ge atoms migrate to the ‘long bridge sites’ and when another Ge atom arrives at an adjacent ‘long bridge site’ the bond between them is shortened due to their mutual attraction forming a Ge surface dimer whose axis is perpendicular to that of the surface Si dimers.

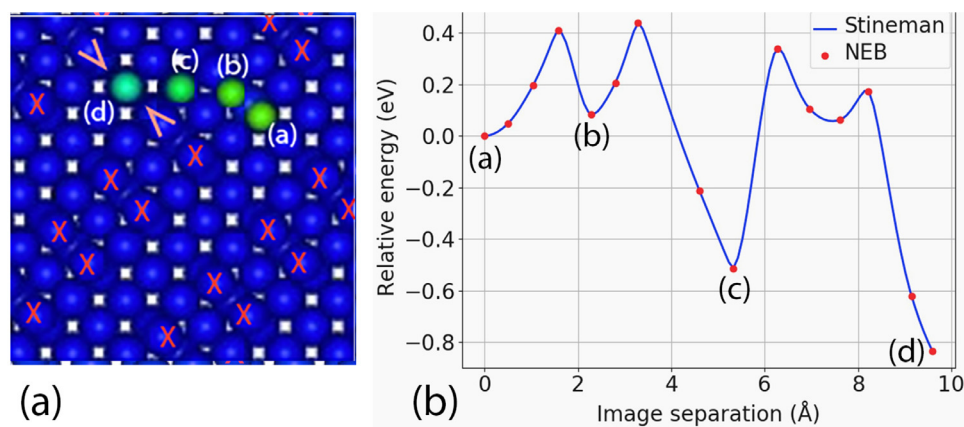
In some cases split Ge-Si dimers can form as shown in Fig. 6. The formation of such mixed dimers was previously found experimentally [42]. In this case the split dimer forms by a replacement mechanism whereby an Si atom in the substrate is pushed up and is replaced by the diffusing Ge atom as shown in Fig. 6.

The obtained mechanism of silicon and germanium atoms replacement coincides with the experimentally observed picture of Si-Ge intermixing in strained quantum dots and 2D layers [43–45]. The experimental composition profiles across the islands show how the concentration of germanium atoms gradually increases from the base of an island, reaching its maximum at the top of an island, due to incorporation of Si material into an island. Moreover, experimental data clearly demonstrate the penetration of germanium atoms into the silicon substrate, which is confirmed by our results.

Atoms can diffuse over the surface and form links between adjacent dimer rows as shown in Fig. 7. Fig. 7 shows a typical mechanism as to how the bases of the pyramidal structures form, whose sides are parallel and perpendicular to the original Si dimer rows. These structures attract other diffusing atoms to form base layer seeds onto which the pyramids can grow. This mechanism and alignment of islands along two orthogonal directions defined by dimer rows orientation are confirmed by in situ and ex situ STEM observations in numerous experiments [3,11,24]. In Fig. 7 the sites between the two parallel Ge dimer rows are favourable sites for bonding but the internal sites are difficult to access by diffusing Ge atoms so the edges of the pyramidal bases are first formed. The internal sites can be accessed by concerted motions involving mechanisms such as those as shown in Fig. 8.

### 4.2. Mechanisms for pyramidal growth

Fig. 8 shows a concerted mechanism, identified from the MD simulations, by which an atom can attach itself to an existing island and push atoms up into the next layer. The relative energies along the pathway for this mechanism are shown in Fig. 9. The energy barrier for this mechanism is  $1.3 \text{ eV}$  but the final state is  $2.4 \text{ eV}$  lower in energy than the initial state. It can be seen that the mechanism for this transition is complex involving at least 3 atoms whose movements are



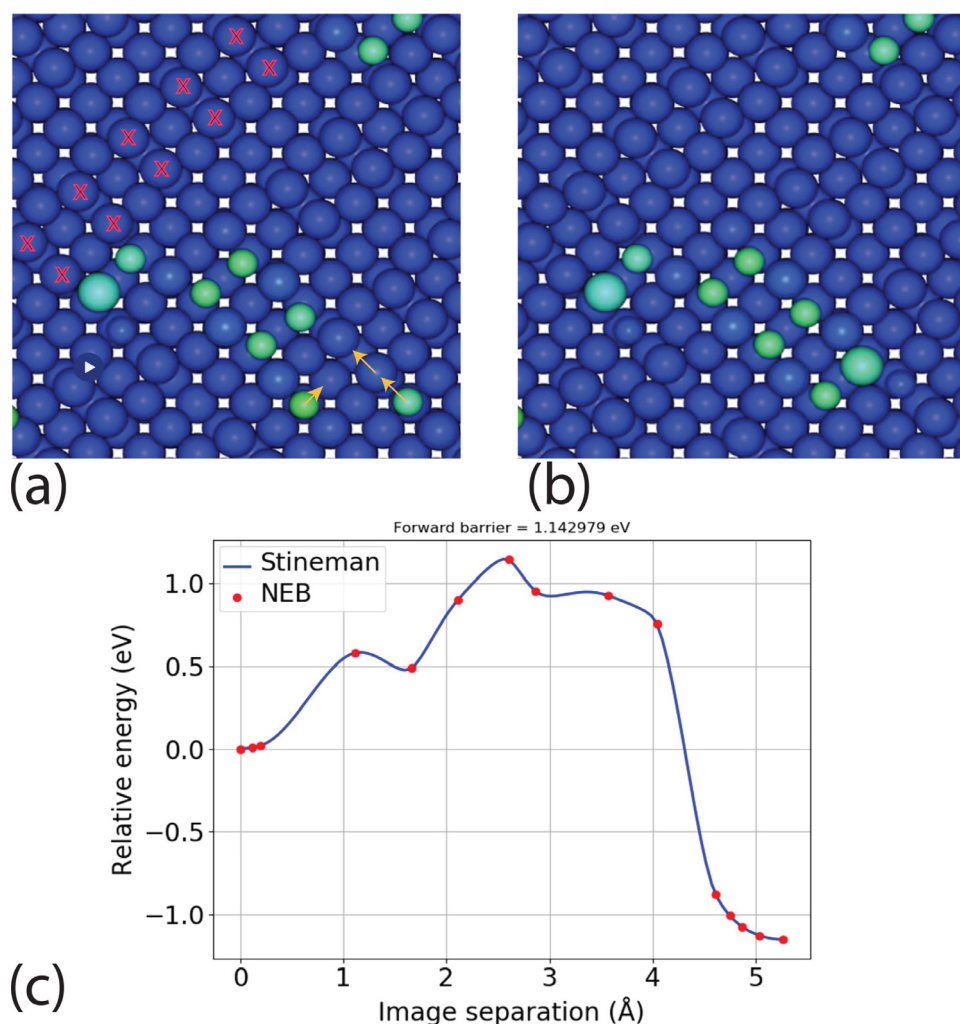
**Fig. 5.** (a) A typical diffusion pathway for an isolated Ge atom moving over the dimer-reconstructed Si(100) surface. The Ge atom is deposited in the right-hand part of (a), eventually resting in its preferred site in the trench between two Si dimer rows on the surface, in line with the Si dimers which are pulled slightly apart by the Ge atom and marked by the pink arrowheads. The X's mark the original dimer rows on the surface and the dotted white line, the trench between the dimer rows. In (b) the pathway is shown with the curve through the points being produced by Stineman interpolation [41] (a well behaved method of interpolation based on piecewise rational functions) and the turning points on the pathway joining the initial and final image represent the metastable local minima on the energy

pathway curve. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

shown by the arrows in Fig. 8. In the final part of the transition from (c) to (d) the Ge atoms marked with the black crosses are pushed up into their final position due to the motion of the atom marked with the arrow in (c).

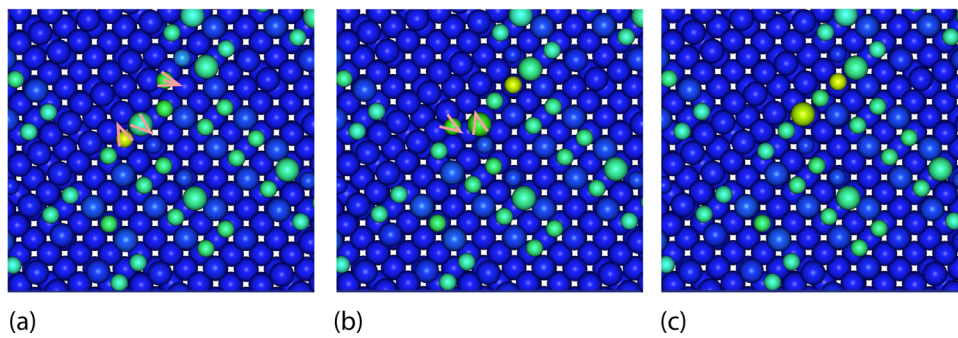
Another example of a transition in which atoms diffuse upwards is

shown in Fig. 10. In this example atoms in the second added layer rearrange themselves with one atom pushed up into the third added layer. The rearrangement also affects an atom in the first added layer as shown in (c) and (d). For this transition the energy barrier is 1.8 eV with the final state being 1.6 eV lower than the initial state. Note that



**Fig. 6.** A typical concerted mechanism that occurs in the formation of the surface dimer rows in the first added layer. In (a) a dimer row in the original surface is marked for clarity by the X's. The smaller circles represent Ge atoms. The lighter colour represents the first added layer. The yellow arrows mark the atom movement that occurs to form a split Si-Ge dimer by a replacement mechanism; (b) the reaction pathway for the transition determined by NEB. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)





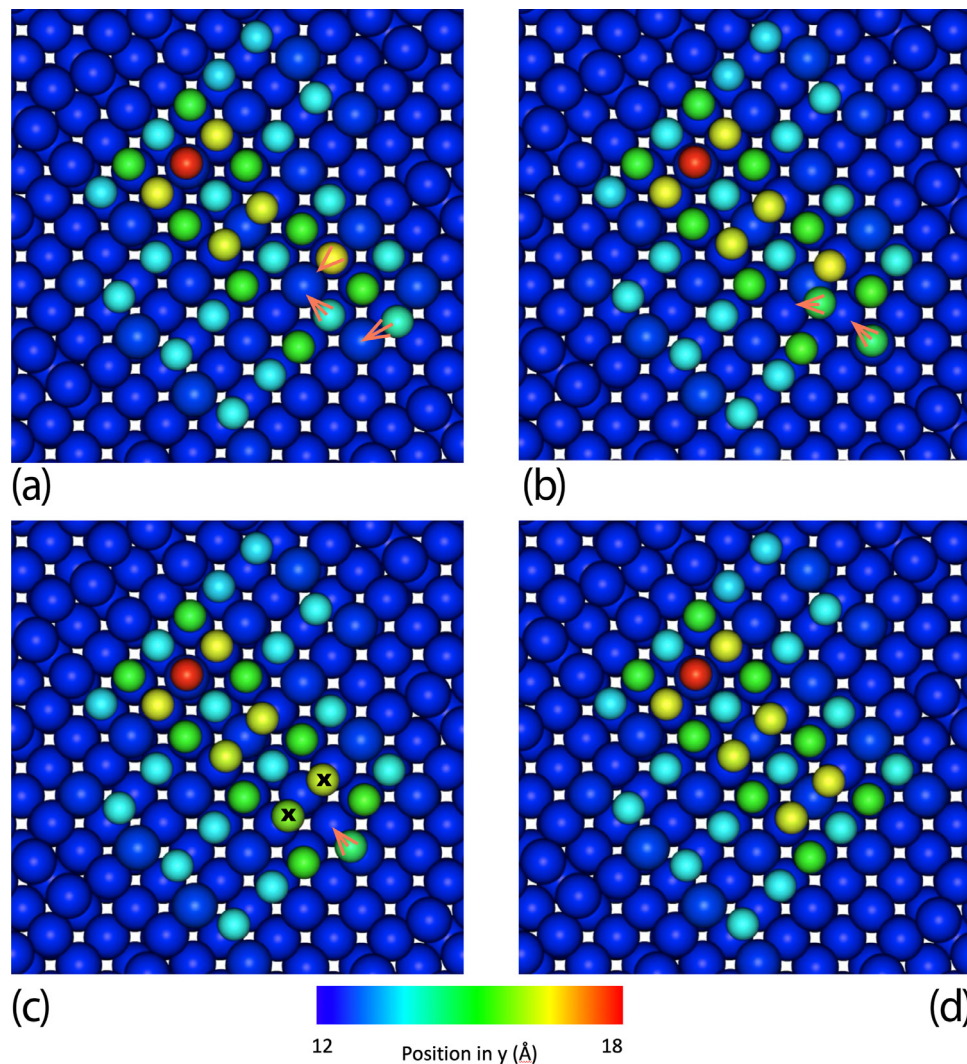
**Fig. 7.** Illustration of how the bases of the square pyramids can form by concerted mechanisms. In this case there are two processes with barriers of 0.5 eV (a) to (b) and 1.2 eV (b) to (c). In (a) and (b) the arrows mark the motion of the atoms in the surface that have moved the most. The lighter colours indicate that the atoms lie above the level of the other adatoms on the surface.

the two red coloured atoms in Fig. 10(d) form a dimer in the same orientation as the Si dimers on the original Si (100) substrate.

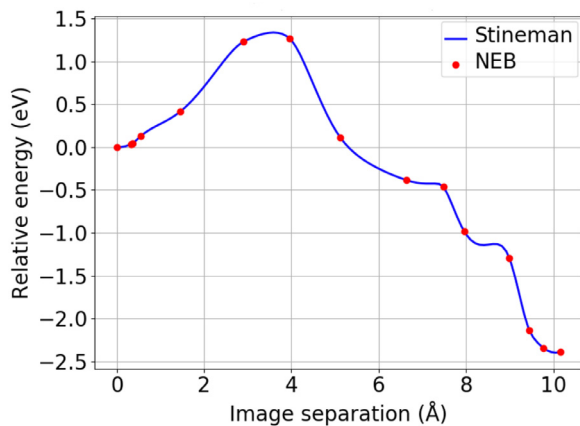
There are many other examples from the MD simulations where atoms can diffuse upwards into more stable positions which allow the island structures to increase in height but these are too numerous to mention here. The two that are shown in Figs. 8 and 10 are representative to illustrate the complexity of the processes involved but the MD simulations show many other complex transition involving multiple atom movements in which islands can increase in height, some

of these are shown as movies in the supplementary material.

It is instructive to investigate what would happen if instead of the Ge islands, the initial structures shown in Figs. 8, 10(a) had been Si. The corresponding barriers between the initial and final states were also determined. In the case of Fig. 8 the barrier height increased from 1.3 eV to 1.8 eV and in the case of Fig. 8 from 1.8 eV to 2.8 eV. Although we have not tested to see of the initial structures shown in the two figures would form in the case of Si grown on Si, the results suggest that energy barriers that need to be overcome for Si to form islands are



**Fig. 8.** Stages in the growth Ge islands on Si. (a) the initial structure showing an atom diffusing towards the base structure, with the red arrows indicating the ensuing motion. In (b) an atom in the edge row is pushed up into the next layer by the diffusing atom which dimerises with an existing second layer atom in (c). These two atoms are pushed up further as the arriving atom joins the edge of the cluster. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

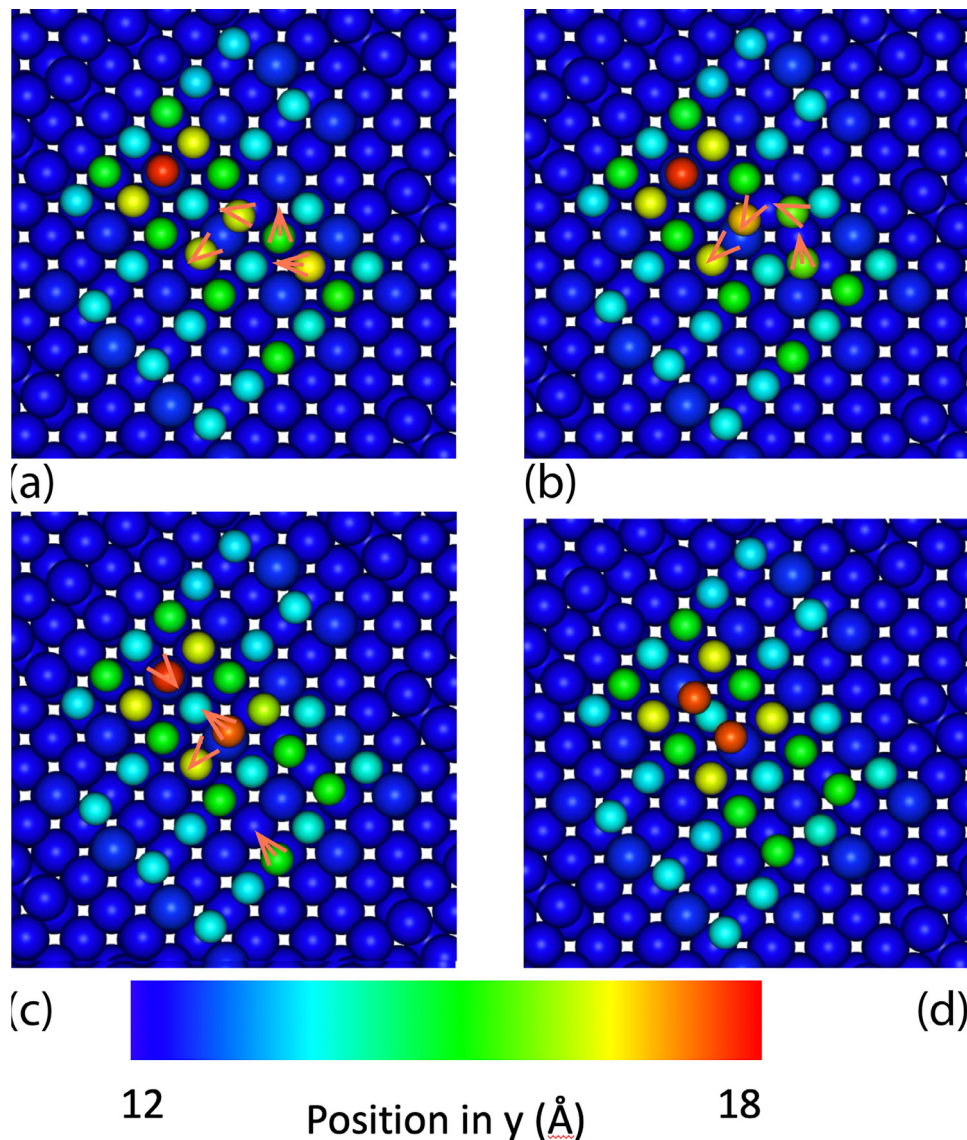


**Fig. 9.** The energy variation along the pathway for the transition shown in Fig. 8. The energy barrier is 1.3 eV and the final state is 2.4 eV more stable than the initial state.

much higher than in the case of Ge.

As a final calculation, it is noted from the literature that experimentally grown pyramids have faceted sides whose surface orientation is (105) i.e.  $11^\circ$  to the horizontal. We determined the surface energies of Ge pyramids formed from (105) planes on Si(100) with the addition of Ge layers. On the (100) Si surface without an added Ge monolayer the surface energy was determined as  $2.09 \text{ Jm}^{-2}$  with values of 1.90, 1.85,  $1.80 \text{ Jm}^{-2}$  after the addition of 1, 2 and 3 monolayers. The value for Si and Ge (100) surfaces in the pure crystal states are  $2.27$  and  $1.87 \text{ Jm}^{-2}$  respectively. For a single Ge monolayer on Si the value is  $1.97 \text{ Jm}^{-2}$  and for 2 monolayers  $1.93 \text{ Jm}^{-2}$ .

In addition if one considers a two-dimensional wedge of unit length whose sides are planes of angle  $11^\circ$  the surface area  $A$  of the sloping sides is greater than the surface area of the base by a factor  $\sec 11^\circ$ , i.e. 1.019. Taking the value of  $1.80 \text{ Jm}^{-2}$  for the surface energy these planes, the total surface energy per unit length is  $1.80A$ . The corresponding energy of the (100) base would be  $1.87A/1.019 = 1.84A$ , demonstrating that after the addition of 3 monolayers the total surface energy is less for a wedge than for the flat surface. This therefore indicates that the (105) facets would be energetically more favourable to



**Fig. 10.** An example of concerted atomic motions in which a first layer atom in an island structure can be pushed up into a second layer position to form a second layer dimer. The red arrow indicate the direction of motion at each stage. The energy variation involved in this transition is shown in Fig. 11. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



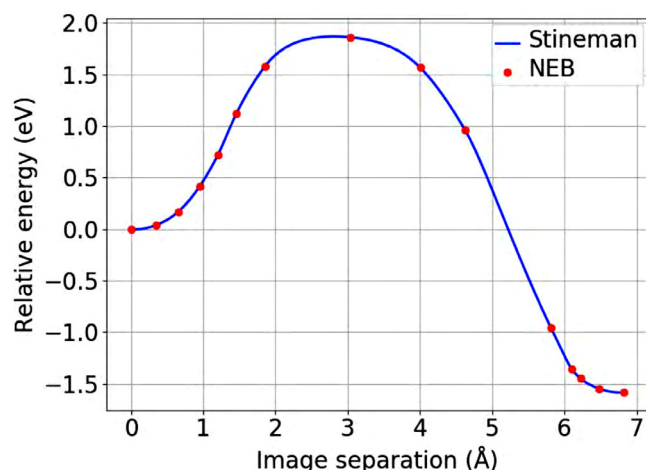


Fig. 11. The energy variation along the pathway for the transition shown in Fig. 10. The energy barrier is 1.86 eV and the final state is 1.6 eV more stable than the initial state.

form after the addition of 2 Ge monolayers on the Si surface.

## 5. Discussion

For many simple crystalline systems, whether island growth or layer by layer growth occurs can be roughly estimated from the Ehrlich-Schwoebel (E-S) barriers, i.e. the energy barrier for an adatom to climb up or drop off a step edge. See for example [46]. The Si(100) surface and the subsequent islands that form have complex structures with the simulations showing that addition of atoms to islands occurs by various multi-atom movements, so the concept of an E-S barrier involving single atom diffusion in our case makes no sense. Similarly the usefulness of defining a diffusion coefficient for a Ge atom moving over the surface is limited because of the presence of other Ge adatoms and as more Ge is added, the underlying Si reconstructs to a more bulk-like form.

Results from the static energy calculations show clearly that the surface energies of the Ge(100) and Ge(105) facets decrease with the increase in the number of the deposited germanium layers. This is often regarded as the key for understanding the mechanisms of germanium islands growth on the silicon substrate. As a standard picture, based purely on thermodynamic considerations, one might expect that at the first stage a flat germanium 2D wetting layer would be formed. Then, with the increase in the wetting layer thickness, the surface energy of the Ge(105) facet decreases so that the formation of this facet becomes thermodynamically possible. Once the small nuclei of the future 3D island occurs, the further growth of this island in size would become even more energetically favourable, as adatoms hop onto the higher layers to reduce the total energy of the substrate-WL-islands system.

The simulations however show that this is not the full story as small islands can begin to nucleate before a full wetting monolayer is achieved since kinetics plays an important role in the growth process. However once the equivalent of 4 monolayers are deposited the original surface is covered by 2 almost complete monolayers.

Once atoms have migrated to stable sites in higher layers the energy barriers for them to drop to lower layers are quite high, in the two cases discussed above in Figs. 8 and 10, the reverse energy barriers were over 3 eV.

From a macroscopic point of view the explanation of the growth of the pyramids is usually given in the following terms. i.e. that higher islands form despite the formation of the pyramids increasing the surface energy, due to the increase in the total surface area, as the shallow (105) facets on the strained pyramids have a lower surface specific energy than the (100) surface. This effect gradually diminishes as more

layers are added due to the decrease in strain.

From an atomistic point of view the explanation is that the strain in the added Ge layers reduces the energy barriers for Ge atoms to jump up into stable sites in higher layers. Without this strain as shown above for equivalent Si islands the barriers are much higher and atoms prefer to remain at a lower level.

This conclusion coincides well with the results obtained by other theoretical methods, including DFT calculations, KMC simulations and thermodynamic models [17–19,23,47–49].

## 6. Conclusion

Although the MD methodology used is too fast to capture all the diffusion processes that would occur experimentally between successive particle impacts, it gives a qualitatively accurate description of how deposited Ge atoms can develop into pyramidal structures as observed experimentally. Moreover, diffusion pathways and their associated energy barriers identified from MD calculations were used in NEB calculations to determine activation energies. The results have shown that the growth processes are complex with no single mechanism dominating with many transitions involving several atoms in concerted atomic motions.

Although the methods described above have estimated the activation energies of adatom diffusion on the surface of the substrate, values which are often input into larger scale models, the results show that the mechanisms involved are too complex to provide a well-defined set of values that can be used with confidence in such models. However the values of surface energies determined above from static calculations can be used in the parameterisation of larger scale models.

Although lower deposition rates could be achieved by using a method such as parallel trajectory splicing to determine more diffusion processes that can occur between impacts, the simpler direct MD method together with NEB have been able to determine a number of mechanisms for the early stages of growth of Ge on Si and explain qualitatively how the faceted pyramids can form.

## Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## CRedit authorship contribution statement

**Ying Zhou:** Conceptualization, Methodology, Validation, Software, Formal analysis, Investigation, Data curation, Writing - original draft, Visualization. **Adam Lloyd:** Conceptualization, Methodology, Validation, Software, Investigation. **Roger Smith:** Conceptualization, Methodology, Validation, Software, Formal analysis, Writing - original draft, Writing - review & editing, Visualization, Supervision, Project administration, Funding acquisition. **Kirill A. Lozovoy:** Conceptualization, Methodology, Validation, Investigation, Data curation. **Alexander V. Voitsekhovskii:** Conceptualization, Methodology, Validation, Supervision, Project administration, Funding acquisition. **Andrey P. Kokhanenko:** Conceptualization, Methodology, Validation.

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## Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.susc.2020.121594



## References

- [1] Y. Mo, D.E. Savage, B.S. Swartzentruber, M.G. Lagally, Kinetic pathway in Stranski-Krastanov growth of Ge on Si(001), *Phys. Rev. Lett.* 65 (1990) 1020.
- [2] D.J. Eaglesham, M. Cerullo, Dislocation-free Stranski-Krastanow growth of Ge on Si(100), *Phys. Rev. Lett.* 64 (1990) 1943.
- [3] L.V. Arapkina, V.A. Yuryev, Nucleation of Ge quantum dots on the Si(001) surface, *Phys. Rev. B* 82 (2010) 045315.
- [4] K.A. Lozovoy, A.P. Kokhanenko, A.V. Voitsekhovskii, Comparative analysis of pyramidal and wedge-like quantum dots formation kinetics in Ge/Si(001) system, *Surf. Sci.* 619 (2014) 1–4.
- [5] C. Priester, M. Lannoo, Origin of self-assembled quantum dots in highly mismatched heteroepitaxy, *Phys. Rev. Lett.* 75 (1995) 93–96.
- [6] P. Muller, R. Kern, The physical origin of the two-dimensional towards three-dimensional coherent epitaxial Stranski-Krastanov transition, *Appl. Surf. Sci.* 102 (1996) 6–11.
- [7] R. Kern, P. Muller, Elastic relaxation of coherent epitaxial deposits, *Surf. Sci.* 392 (1997) 103–133.
- [8] J.E. Prieto, I. Markov, Stranski-Krastanov mechanism of growth and the effect of misfit sign on quantum dots nucleation, *Surf. Sci.* 664 (2017) 172–184.
- [9] O.P. Pchelyakov, V.A. Markov, A.I. Nikiforov, L.V. Sokolov, Surface processes and phase diagrams in MBE growth of Si/Ge heterostructures, *Thin Solid Films* 306 (1997) 299–306.
- [10] O.P. Pchelyakov, Y.B. Bolkhovityanov, A.V. Dvurechenskii, L.V. Sokolov, A.I. Nikiforov, A.I. Yakimov, B. Voigtlander, Silicon-germanium nanostructures with quantum dots: formation mechanisms and electrical properties, *Semiconductors* 34 (2000) 1229–1247.
- [11] J. Aqua, I. Berbezier, L. Favre, T. Frisch, A. Ronda, Growth and self-organization of SiGe nanostructures, *Phys. Rep.* 522 (2013) 59–189.
- [12] J. Wu, S. Chen, A. Seeds, H. Liu, Quantum dot optoelectronic devices: lasers, photodetectors and solar cells, *J. Phys. D* 48 (2015) 363001.
- [13] S. Wirths, D. Buca, S. Mantl, Si-Ge-Sn alloys: from growth to applications, *Prog. Cryst. Growth Charact. Mater.* 62 (2016) 1–39.
- [14] T. David, K. Aqua J.N. Liu, L. Favre, A. Ronda, M. Abbarchi, J.-B. Claude, I. Berbezier, New strategies for producing defect free SiGe strained nanolayers, *Sci. Rep.* 8 (2018) 2891.
- [15] V.G. Dubrovskii, G.E. Cirlin, V.M. Ustinov, Kinetics of the initial stage of coherent island formation in heteroepitaxial systems, *Phys. Rev. B* 68 (2003) 075409.
- [16] P. Gaillard, J.N. Aqua, T. Frisch, Kinetic Monte-Carlo simulations of the growth of silicon germanium pyramids, *Phys. Rev. B* 87 (2013) 125310.
- [17] S.N. Filimonov, Y.Y. Hervieu, Kinetics of two-dimensional island nucleation on reconstructed surfaces, *Phys. Rev. B* 85 (2012) 045423.
- [18] G.H. Lu, F. Liu, Towards quantitative understanding of formation and stability of Ge hut islands on Si(001), *Phys. Rev. Lett.* 94 (2005) 176103.
- [19] G.H. Lu, F. Liu, First-principles study of strain stabilization of Ge(105) facet on Si(001), *Phys. Rev. B* 72 (2005) 125415.
- [20] K.A. Lozovoy, A.P. Kokhanenko, A.V. Voitsekhovskii, Influence of edge energy on modeling the growth kinetics of quantum dots, *Cryst. Growth Des.* 15 (2015) 1055–1059.
- [21] K.A. Lozovoy, A.P. Kokhanenko, A.V. Voitsekhovskii, Critical thickness of transition from 2D to 3D growth and peculiarities of quantum dots formation in GeSi<sub>1-x</sub>/Sn/Si and Ge<sub>1-y</sub>Sn<sub>y</sub>/Si systems, *Surf. Sci.* 669 (2018) 45–49.
- [22] K.A. Lozovoy, A.P. Kokhanenko, A.V. Voitsekhovskii, Generalized muller-kern formula for equilibrium thickness of a wetting layer with respect to the dependence of the surface energy of island facets on the thickness of the 2D layer, *Phys. Chem. Chem. Phys.* 17 (2015) 30052.
- [23] X.L. Li, G. Ouyang, G.W. Yang, A thermodynamic theory of the self-assembly of quantum dots, *New J. Phys.* 10 (2008) 043007.
- [24] K. Liu, I. Berbezier, L. Favre, A. Ronda, M. Abbarchi, P. Donnadiou, P.W. Voorhees, J.-N. Aqua, Capillary-driven elastic attraction between quantum dots, *Nanoscale* 11 (2019) 7798–7804.
- [25] A.A. Shklyayev, M. Ichikawa, Extremely dense arrays of germanium and silicon nanostructures, *Phys. Uspekhi* 51 (2008) 133161.
- [26] K.A. Lozovoy, A.P. Kokhanenko, V. Dirko, N.Y. Akimenko, A.V. Voitsekhovskii, Evolution of epitaxial quantum dots formed by Volmer-Weber growth mechanism, *Cryst. Growth Des.* 19 (2019) 7015–7021.
- [27] K.A. Lozovoy, A.P. Kokhanenko, A.V. Voitsekhovskii, Critical thickness of 2D to 3D transition in GeSi<sub>1-x</sub>/Si(001) system, *Surf. Sci.* 109 (2016) 021604.
- [28] K.A. Lozovoy, A.G. Korotaev, A.P. Kokhanenko, V. Dirko, A.V. Voitsekhovskii, Kinetics of epitaxial formation of nanostructures by Frank-van der Merwe, Volmer-Weber and Stranski-Krastanow growth modes, *Surf. Coatings Technol.* 384 (2020) 125289.
- [29] A.E. Dolbak, B.Z. Olshanetsky, Effect of adsorbed Sn on Ge diffusivity on Si(111) surface, *Cent. Eur. J. Phys.* 6 (2008) 634–637.
- [30] V.G. Dubrovskii, Calculation of the size-distribution function for quantum dots at the kinetic stage of growth, *Semiconductors* 40 (2006) 1123–1130.
- [31] M.R. Sorensen, A.F. Voter, Temperature-accelerated dynamics for simulation of infrequent events, *J. Chem. Phys.* 112 (21) (2000) 9599–9606.
- [32] C. Scott, S. Blackwell, L. Vernon, S. Kenny, J.M. Walls, R. Smith, Atomistic surface erosion and thin film growth modelled over realistic time scales, *J. Chem. Phys.* 135 (17) (2011) 174706.
- [33] A. Lloyd, Y. Zhou, M. Yu, C. Scott, R. Smith, S. Kenny, Reaction pathways in atomistic models of thin film growth, *J. Chem. Phys.* 147 (2017) 152719.
- [34] D. Srivastava, B. Garrison, D. Brenner, Anisotropic spread of surface dimer openings in the initial-stages of the epitaxial-growth of Si on Si(100), *Phys. Rev. Lett.* 63 (1989) 302–305.
- [35] S. Plimpton, P. Crozier, A. Thompson, LAMMPS-large-scale atomic/molecular massively parallel simulator, *Sandia Natl. Lab.* 18 (2007) 43.
- [36] J. Tersoff, Modeling solid-state chemistry: interatomic potentials for multi-component systems, *Phys. Rev. B* 39 (8) (1989) 5566.
- [37] H. Berendsen, J. Postma, W. van Gunsteren, A. DiNola, J. Haak, Molecular-dynamics with coupling to an external bath, *J. Chem. Phys.* 81 (1984) 3684–3690.
- [38] G. Henkelman, H. Jonsson, A climbing image nudged elastic band method for finding saddle points and minimum energy paths, *J. Chem. Phys.* 113 (2000) 9901–9904.
- [39] G.-H. Lu, M. Cuma, F. Liu, First-principles study of strain stabilization of Ge (105) facet on Si (001), *Phys. Rev. B* 72 (12) (2005) 125415.
- [40] D. Srivastava, B. Garrison, Adsorption and diffusion dynamics of a Ge adatom on the Si(100)(2x1) surface, *Phys. Rev. B* 46 (1992) 1472–1479.
- [41] R. Stineman, A consistently well-behaved method for interpolation, *Creative Comput.* 6 (1980) 54–57.
- [42] X.R. Qin, B.S. Swartzentruber, M.G. Lagally, Diffusional kinetics of SiGe dimers on Si(001) using atom-tracking scanning tunneling microscopy, *Phys. Rev. Lett.* 85 (2000) 3660–3663.
- [43] D.J. Smith, D. Chandrasekhar, S.A. Chaparro, P.A. Crozier, J. Drucker, M. Floyd, M.R. McCartney, Y. Zhang, Microstructural evolution of Ge/Si(100) nanoscale islands, *J. Cryst. Growth* 259 (2003) 232–244.
- [44] N. Paul, S. Filimonov, V. Cherepanov, M. Cakmak, B. Voigtlander, Identification of Ge/Si intermixing processes at the Bi/Ge/Si(111) surface, *Phys. Rev. Lett.* 98 (2007) 166104.
- [45] A. Rastelli, M. Stoffel, A. Malachias, T. Merdzhanova, G. Katsaros, K. Kern, T.H. Metzger, O.G. Schmidt, Three-dimensional composition profiles of single quantum dots determined by scanning-probe-microscopy-based nanotomography, *Nano Lett.* 8 (2008) 1404–1409.
- [46] S. Blackwell, R. Smith, S. Kenny, J. Walls, Modelling evaporation, ion-beam assist, and magnetron sputtering of thin metal films over realistic time scales, *Phys. Rev. B* 86 (3) (2012) 035416.
- [47] X.L. Li, G.W. Yang, Theoretical determination of contact angle in quantum dot self-assembly, *Appl. Phys. Lett.* 92 (2008) 171902.
- [48] Y.Y. Hervieu, I. Markov, Kinetics of second layer nucleation with permeable steps, *Surf. Sci.* 628 (2014) 76–81.
- [49] S.N. Filimonov, Y.Y. Hervieu, Step permeability effect and interlayer mass-transport in the Ge/Si(111) MBE, *Mater. Sci. Semicond. Process.* 8 (2005) 31–34.