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Computer simulations of the early-stage growth of Ge clusters at elevated temperatures on patterned Si substrate using the kinetic Monte Carlo method

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ABSTRACT

In this work we investigate the formation of Ge clusters on stepped Si substrate at elevated temperatures (≤300 °C) with the help of the kinetic Monte-Carlo (kMC) method. The modeling was performed for the case of low surface coverage in order to examine the process of Ge cluster growth at early stages. The temperature dependence of the development of Ge structures was explored and the transition from the growth in the middle of the steps to the growth at step edges was traced. Modeling shows that the formation of Ge clusters at the step edges begins at temperatures higher than 60 °C, whereas at temperatures below 60 °C clusters grow at the middle of the steps, and at 300 °C all Ge atoms are gathered at the bottom of the Si step edges. Results of the kMC simulations were compared to experiments and analytical evaluations. A cluster formation diagram linking deposition rate, terrace width, and transition temperature between different cluster formation modes is presented.

1. Introduction

Over the last 10 years interest in semiconductor nanostructures has steadily increased. This is mainly driven by the unique features of nanometric structures, whose optical properties strongly depend on their sizes. Recently, it has been demonstrated that nanosized Ge clusters exhibit intense photoluminescence. An interesting method to obtain Ge-based, highly efficient quantum dots is the self-organization method: atoms are deposited on a substrate at high temperature, and a Stranski–Krastanov or Volmer–Weber growth mode takes place.

Understanding the basic mechanisms of the formation of Ge quantum dots (Ge QDs) on either patterned Si or SiO_2 is of prime importance for the production of multi-junction solar cells and high electron mobility transistors by Selective Epitaxial Growth (SEG). Useful applications require a high density of quantum dots arrays, with good spatial ordering and sizes of the dots with narrow distribution functions. Literature contains several examples of attempts to reach such a target on either pre-patterned or un-patterned substrates [1–3]. For example, in [4,5] the formation of Ge nanostructures on Si(111) with atomically defined steps was studied experimentally. In [4] authors used low deposition rate ($8.9 * 10^{-4}$ to $5.0 * 10^{-2}$ biatomic layer per minute) and low coverage of the substrate (~0.1 biatomic layer), while the deposition in [5] was performed at higher rates (0.3 monolayer per minute) and the coverage was accordingly much higher (up to 19 monolayers). Nevertheless, if one focus only on the early stages of deposition (<1 atomic layer), it was clearly demonstrated that growing Ge nano structures depend on the temperature at which they were produced by deposition and optionally by subsequent annealing. At room temperature the formation of clusters was observed at the terraces; at temperatures > 300 °C deposited atoms form decorations at the bottom of the steps; and at 250 °C deposited atoms form individual clusters at the top of the step edges.

So it is clear that in order to grow the pattern of desired form, parameters such as substrate temperature must precisely controlled: if the temperature is too low, the deposited atoms stay at their landing sites and no self-organization takes place. On the contrary, if the temperature is too high, re-evaporation occurs, causing detachment from seed clusters, and no large clusters will form. Deposition rate has also a very strong effect as well will demonstrate in this work.

Several computational methods have been developed for the modeling of the structures formation and growth: mean field rate equations of non-equilibrium nucleation theory [6], stochastic continuum equations for the height profile of the growth surface [7], or kinetic Monte Carlo (kMC) simulations of the growth process [8–11]. In this study, we used kMC simulations to further understand and predict the Ge atomistic deposition and nucleation on Si substrates. We demonstrate that computer simulation which takes into account a set of simple physical phenomena (not involving complex stress-driven mechanisms or electromigration) might be useful to reproduce and therefore to predict the characteristic pattern of Ge clusters on patterned substrates. Simulation results are tested against published examples of Ge growth on patterned Si [4] and analytical derivation.

After a short description of the method used for the modeling in this study, we will present the results of modelization at 60 °C, 250 °C and 300 °C of Ge deposition and annealing on Si substrates with step

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edges. Analytical derivation of the transition temperature at which formation of Ge clusters occurs at the step edges and not on the terrace is also presented.

2. Simulation method and parameters

Details about the approach used have already been published [12]. We used the NASCAM code (NAnoSCale Modeling), a specific event kinetic Monte-Carlo approach. The evolution of the system is determined by the probabilities of the events that may happen during the actual physical process being simulated. Currently the following events are implemented: free diffusion at the substrate and layer level, diffusion along the step edges, detachment from an island or substrate feature, jumping up and down from one level to another, detrapping from a substrate defect, evaporation from a substrate surface as well as from deposited layers [13].

Probabilities are calculated from activation energies and Table 1 outlines the values used in this study. They originate either from experimental measurements or from theoretical evaluations.

Energy barrier for diffusion along the edges of Ge islands has not been found in literature. We evaluated it to be equal to 1.0 eV by comparing several simulations with the final morphology of Ge on Si as published in [4]: indeed, a too high value produces fractal like clusters. Starting from a high value, it was decreased down to 1.0 eV for which no more fractal like clusters were observed but rather compact ones, as observed in [4].

One may assume that the values for energy barriers for the jumping of atoms upwards or downwards are higher than for the surface diffusion as it was observed in the deposition of Si on Si and Ge on Si. The difference has been evaluated by [8] to 0.2 eV. Nevertheless, Li et al. [14] studied second-layer nucleation during Ge growth on Ge(001) by scanning tunneling microscopy at various temperatures. They concluded that the influence of step edge barriers on second layer nucleation on the Ge(001) surface is negligible. Therefore, the barrier values for jumping upward and downward (Ea_down or Ea _up) for Ge on Ge or Ge on Si should be within 0.8 to 1.0 eV. In this work the value of 1.0 eV was chosen.

The value for detachment activation energy (Ea_detach) was chosen using the work of Zhao et al. [15]: they used the density functional theory method to investigate the properties of free germanium clusters, including binding energies and fragmentation behavior. For Ge clusters in the range of 2–18 atoms, they adopted the lowest-energy geometries from literature. According to their results, the structure of the germanium clusters in the size range of 2–10 atoms is sphere-like and similar to silicon clusters. For sizes larger than 10, they adopt a trip-caped trigonal prism structure (Ge_{11} to Ge_{18}) and a more complex one for larger clusters. Whatever the size, the binding energy per atom for Ge dimer is 1.5 eV and increases very quickly to reach a value of 3.2 eV for Ge_9. In that range, the dissociation path called one-step fragmentation involves the liberation of a single Ge atom and a single Ge_{X-1} cluster. The energy required for one-step fragmentation is 3.8 eV, close to the cohesive energy of bulk germanium (3.85 eV). For larger clusters, the dissociation energy drops quickly to 1.2 eV. This has been measured in previous experiments by Hunter et al. [16]. As the dissociation of small clusters is the result of detachment of a single Ge atom, we have chosen the associated dissociation energy for Ge as activation energy for the detachment event, i.e. 3.8 eV. This value indicates that detachment is very improbable.

Finally, for Ge free diffusion on Si(111), we took the data published by Stepina et al. [9]. The value of 0.8 eV is close to the one derived by ab initio calculations, close to 1 eV [17,18].

In addition to the parameters listed in Table 1, the following assumptions were used in the simulation:

1. We used a hexagonal structure for the surface as there is a number of experiments where Si(111) was used as a substrate. Certainly the simple hexagonal structure of the substrate in the presented simulations is not totally equivalent to the surface structure of Si(111) but still may serve as a reasonable approximation. The size of the modeling box is 100×72 with the step width equal to 25 Si so that there are 4 steps in total. The step height is equal to 2 atomic layers in accordance with the Si(111) structure.
2. To mimic the non-uniformity of the surface morphology in the vicinity of the step edges we introduce regularly positioned "defects". It is possible to associate these "defects" with the unfaulted halves of the 7×7 structure which are positioned directly at the upper step edges. Such "defects" are the sites which have a larger potential barrier the atoms have to overcome to leave these sites. The way how the barrier was evaluated is presented later (Results and discussions)
3. All sizes are given in the Si lattice constant unit (0.543 nm).
4. For direct comparison with [4] deposition rate is set to $3 * 10^{-3}$ monolayer per second and the total number of deposited atoms is equal to 500, which is equivalent to the coverage 0.07 monolayer.
5. Periodical boundary conditions were implied.
6. The modeling included 2 steps. The first step is a deposition at a given temperature and the second step is annealing at the same temperature for 24 min as in [4]
7. We did not consider intermixing between Ge and Si nor stress effects.

One of the main ideas of the modeling was to reproduce the results of [4] and to find out what parameters of the system have the most influence on the process of the cluster formation at the early stages of deposition when the coverage of the surface is less than 1.

3. Results and discussions

First of all, sensibility study (data not shown) about the activation energies as listed in Table 1 revealed that the most critical parameters that govern the processes of cluster formation are the diffusion coefficient and detrapping energy. Indeed, energy barrier for the diffusion along the cluster edge mostly determines the form of the clusters and whether they are compact or not, and the detachment energy has a very low impact on the final morphology.

The results of the simulations are shown in Fig. 1 for three different temperatures (A = 60 °C, B = 250 °C, C = 300 °C). It shows that in the temperature range 60–250 °C the "defects" at the top of the step edges serve as nucleation centers for the growth of Ge clusters. This is due to the fact that Ge atoms spend more time at these places because of a higher potential barrier. The sizes of the clusters are in agreement with the experimental data of [4]. At higher temperatures (T = 300 °C) simulation shows that all deposited Ge atoms are gathered at the bottom of the step edges forming wires. This is also in agreement with the experimental data published in [4].

It is clear that there are three temperature ranges where one can observe three different patterns of Ge clusters. At low temperature, Ge clusters are formed at the middle of terraces as, because of reduced diffusion at that temperature, Ge atoms can't reach the step edges. The estimation for the upper temperature limit for this case will be given below. At higher temperature Ge atoms can reach the

Table 1
Parameters of modeling the Ge deposition.

Event	Energy barrier, (eV)	Reference
Ge diffusion on silicon	0.80	[9]
Ge diffusion along edges of Ge islands	1.0	This work
Jumping up and down from one level to another	1.0	[8,10]
Detachment from Ge island or substrate feature	3.8	[11]
Detrapping	1.3	This work