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Molecular beam epitaxial growth of Si(001): a Monte Carlo study

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Abstract. The results of a Monte Carlo (MC) simulation study of epitaxial growth dynamics of Si(001) over a wide range of deposition rates (0.001–100 monolayers/s) and substrate temperatures (500–1000 K) are reported. The MC model, which allows the formation of bulk vacancies and overhangs in the tetrahedral coordination of silicon, is proposed. Surface relaxation (dimerization) and atom–atom interactions extending as far out as second-neighbour sites are included in the model. Our results demonstrate that the effect of the formation of vacant sites is pronounced only at low temperatures, where there is no active hopping of atoms, while at high temperatures this effect is washed out by intensive hopping of atoms.

1. Introduction

Monte Carlo simulation of the growth of silicon has attracted great attention due to the increasing role of silicon vapour deposition techniques in producing new microelectronic devices. Molecular beam epitaxy (MBE) is one of the most promising techniques.

Two Monte Carlo models of the simulation of MBE growth of silicon have so far been developed. The most popular is the solid-on-solid (SOS) model [1]. In this model an atom is accommodated on the lattice site only if there is already an atom underneath that site. In this way one actually grows columns of atoms in which vacancies or overhangs are forbidden. By vacancies we mean unoccupied lattice sites completely surrounded by occupied ones, and by overhangs we mean unoccupied lattice sites partly surrounded by occupied lattice sites, i.e. having exposure to the vapour in their vicinity. However, vacancies and overhangs are present in real crystals, especially in those grown at low temperatures. The other MC model goes beyond the SOS approximation, allowing for bulk vacancies and overhangs, as proposed by Marmorkos and Das Sarma (MS) [2, 3]. Most papers published on silicon growth simulation are based on the SOS model [4–9]. To our knowledge, there are only two papers [2, 3] devoted to the MC simulation of crystal growth by the MS model.

In this work we extended the MS model to include the possibility of formation of bulk vacancies and overhangs in the real tetrahedral structure of silicon. Surface dimerization and atom–atom interactions out to second nearest neighbours were taken into account. Applying our MC simulation technique, we revealed the effect of including the possibility of forming bulk vacancies on the quality of a growing silicon crystal.

To reveal the role of two counteracting forces (i.e. substrate temperature and deposition rate) in the MBE growth of silicon, we made a set of simulations of growth over a wide range of these parameters.

2. Model

In this section we describe our MC model, which allows for the formation of bulk vacancies and overhangs in the growing silicon material.

Figure 1(*a*) shows a fragment of tetrahedral coordination of silicon. In the SOS model, in which the formation of vacancies is forbidden during growth, an impinging atom is accommodated at lattice site A (figure 1(*b*)) only if both nearest-neighbour sites (B and C) in the layer below are occupied.

In the model we propose here, we allow for an impinging atom to reside at lattice site A if two conditions are satisfied: first, there is at least one nearest-neighbour atom (B or C) in the layer below (B in this particular case). Second, there is at least one undimerized second nearest neighbour in the same layer (E or D). If these two conditions are satisfied, the impinging atom resides at lattice site A and forms a dimer with one of the second nearest neighbours (E or D). If both lattice sites E and D are occupied, a 'partner' with which atom A forms a dimer is chosen randomly.

We simulated a monoatomic system where the atoms were deposited on the (001) plane (taken to be the xy plane with the z direction as the growth direction in figure 1) of tetrahedral coordination. Periodic boundary conditions on the (001) plane were imposed and growth

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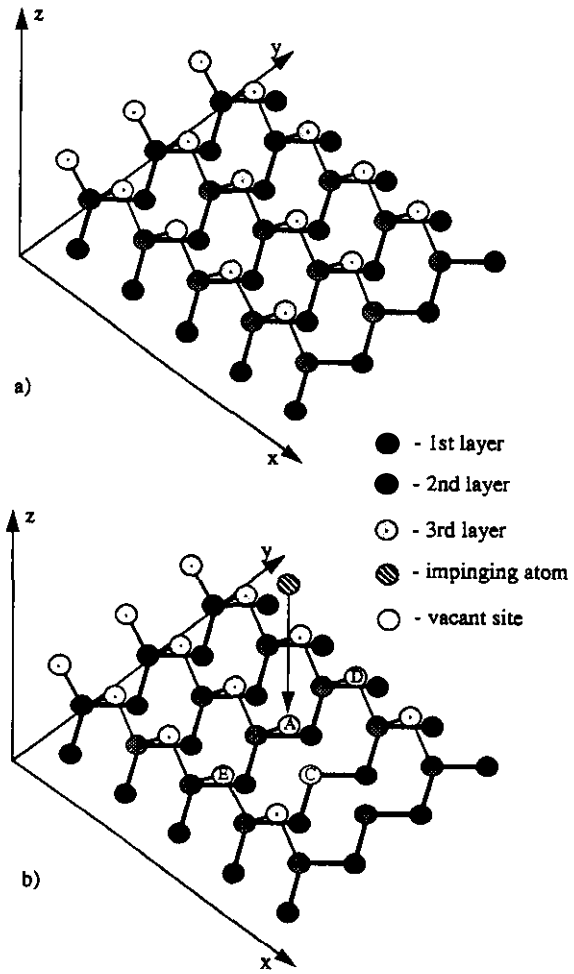

Figure 1. (*a*) A fragment of tetrahedral coordination of silicon. (*b*) Process of deposition of an atom within the framework of our model, allowing the formation of vacancies and overhangs. An impinging atom can be accommodated at site A even if there is no nearest neighbour at site C in the layer underneath site A.

took place on a substrate of similar atoms with the same lattice structure.

The complexity of four kinetic processes taking part in the growth dynamics (the deposition of the atom on the surface, the migration of this atom on the surface, the evaporation of deposited atoms from the surface and the surface relaxation) was simulated using the Arrhenius rate equation for each of these processes: $R = R_0 \exp[-(n_1E_1 + n_2E_2)/kT]$, where n_1 and n_2 are the number of first and second nearest neighbours and E_1 and E_2 are the first- and second-nearest-neighbour interaction energies respectively. Numerical values used in the simulation of the hopping event were chosen to be $E_1 = 0.6$ eV and $E_2 = 0.1$ eV, which are consistent with the experimental data [10, 11]. Energy terms for the evaporation event were taken to be $E_1 = 1.1$ eV and $E_2 = 0.2$ eV. The pre-exponential hopping rate or hopping attempt frequency R_0 was assumed to be $R_0 = 10^{13}$ s^{-1}.

The surface reconstruction process was simulated in a way similar to [8], i.e. it was assumed that dimer formation occurs spontaneously between two undimerized surface atoms located in the same layer at adjacent columns, and which have no upper nearest-neighbour atoms, that impinging atoms always break underlying atoms to chemisorb on the surface and that 'flip' events occur during growth, in which a dimerized atom 'swaps' partners by first breaking the dimer bond to an already-existing partner and then re-forms a new dimer with the undimerized atom in the opposite direction. The kinetic flipping rate was calculated according to the same Arrhenius-type equation, in which the activation energy E_f depends on the configuration of neighbouring dimers and can be expressed as $E_f = E_d - mE_{fi}$, where $E_f = 2$ eV is the dimer energy in the ideal (2×1) reconstruction, $E_{fi} = 0.2$ eV is an energy term used to describe the influence of the configuration of neighbouring dimers on the flip rate on lattice site i, and m is an integer having a value in the range 0–4, depending on the presence and orientation of adjacent dimers. The case when $m = 0$ represents the most stable perfect (2×1) reconstruction with the lowest rate of flip events. In cases $m = 1$–4 we have less stable dimer pairs with a higher probabilities of flip events.

The Monte Carlo algorithm used was similar to the fast MBE growth algorithm of Maksym [12]. According to this algorithm, the time, type and site of each of the events mentioned above were chosen randomly with a probability of occurrence that depends on the kinetic rates for the individual events at each lattice site.

The time for the event to occur was obtained from the total kinetic rate

$$R = \sum_{i=1}^{N} (R_{di} + R_{hi} + R_{ei} + R_{fi})$$

where N is the number of surface sites, R_{di}, R_{hi}, R_{ei} and R_{fi} are kinetic rates of deposition, hopping, evaporation and flip events respectively. The time t between successive events was determined from

$$t = -\frac{1}{R} \ln r$$

where r is a random number distributed uniformly between 0 and 1.

The conditional probabilities of the event being deposition, hopping, evaporation or flipping are R_d/R, R_h/R, R_e/R and R_f/R respectively, where R_d, R_h, R_e and R_f are the total rates of deposition, hopping, evaporation and flipping

$$R_d = \sum_{i=1}^{N} R_{di} \qquad R_h = \sum_{i=1}^{N} R_{hi}$$

$$R_e = \sum_{i=1}^{N} R_{ei} \qquad R_f = \sum_{i=1}^{N} R_{fi}.$$

Numerically, the selection of the type of event was done with a second random number r_2. The event was hopping of an atom on the surface for $Rr_2 < R_h$, evaporation for $R_h < Rr_2 < R_h + R_e$, flipping for $R_h + R_e < Rr_2 < R_h + R_e + R_f$ and deposition for $Rr_2 > R_h + R_e + R_f$.

The site of the event was located in a similar way. Thus, if hopping takes place the site is found by looking for the largest i such that

$$Rr_2 > \sum_{j=1}^{i-1} R_{hj}.$$

The sites of evaporation and flipping were found by testing the inequalities

$$Rr_2 - R_h > \sum_{j=1}^{i-1} R_{ej}$$

$$Rr_2 - R_h - R_e > \sum_{j=1}^{i-1} R_{fj}$$

respectively. The x and y coordinates of the lattice site for the deposition of an adatom were determined randomly.

3. Results and discussion

Using the model described in section 2, we performed a set of computational experiments on the simulation of the growth of Si(001). Most of the results presented here are for a 40×40 lattice with, typically, 10 layers grown on the substrate. Most of our results are means of 10 simulations run using different random number sets.

For quantitative characterization of the quality of the growing material we analysed several characteristics. To describe vertical disorder of the surface morphology we introduced interface width (roughness) Δ [9]

$$\Delta = \langle (h_i - \langle h \rangle)^2 \rangle^{1/2}.$$

Here h_i is the height of the ith column of the structure. The angle brackets denote an average over all surface sites. Δ is expressed in units of monolayers (ML).

During our simulations we also kept a dynamical record of layer coverage, number of vacant sites and RHEED intensity. RHEED intensity was calculated in the following way:

$$I(t) = \left(\sum_n (-1)^n S_n(t) \right)^2$$

as is in [3], where n is the number of layers and $S_n(t)$ is the so-called exposed coverage of the nth layer. $S_n(t)$ means the nth layer coverage due to the atoms of that particular layer, which are unscreened by other atoms directly above them.

It is well known that MBE growth of semiconductors is controlled by two driving forces, namely the substrate temperature and the deposition rate. For our first set of simulations we investigated the influence of the substrate temperature and the deposition rate R_d on the quality of the growing silicon crystal. For deposition rates R_d = 0.001–100 ML s^{-1} we changed the substrate temperature T from 500 to 1000 K. The results of this study are presented in figures 2–7.

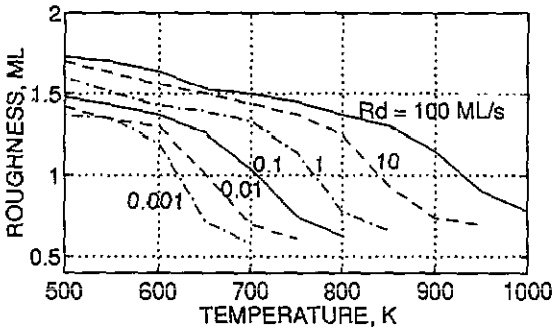

Figure 2. Dependence of interface width (roughness) on substrate temperature at different deposition rates (corresponding deposition rates in monolayers per second are indicated near each curve.

Figure 2 shows the dependence of the interface width (roughness) Δ on the substrate temperature at different deposition rates after the deposition of 10 monolayers of silicon atoms on an Si(001) substrate. From this picture we can reach three conclusions about the result of the interplay of two driving forces (substrate temperature and deposition rate) in the growth of Si(001).

First, in the low-temperature region, where the temperature is low enough to 'keep' deposited atoms in the very first lattice site reached during the deposition process, the growth mode is clearly rough and three-dimensional with interface width (roughness) $\Delta > 1.3$–1.4. The difference in the value of Δ for different deposition rates observable in this temperature region is caused by the fact that the migration of deposited atoms is not completely halted by the incoming flux of new adatoms. The higher the deposition rate (more incoming atoms), the lower the surface migration of deposited atoms (higher Δ).

Second, increasing the substrate temperature at a fixed deposition rate results in a change of the growth mode from rough three-dimensional growth $\Delta > 1.3$–1.4, to smooth two-dimensional growth with $\Delta < 1$.

Illustrating the role of substrate temperature T on the quality of the growing material, in figure 3 we present the simulation results of the growth of Si(001) at different T for the deposition rate $R_d = 0.1$ ML s^{-1}. The temporal evolutions of interface width (roughness) Δ at substrate temperatures T = 600, 700, 750 and 800 K are shown in figure 3(a). It can be seen from this figure that at T = 600 K the growth is clearly rough and three-dimensional with Δ increasing over time. The temperature range T = 700–750 K can be called intermediate between the rough and smooth growth modes. In this temperature regime the interface width still does not saturate in time, although its value is much lower than in the case of T = 600 K. It should be pointed out here that at T = 750 K the growth is almost smooth layer-by-layer growth, while in the temporal evolution of Δ we still cannot observe oscillations of Δ which, along with the saturation in time, is a peculiarity of Δ indicating layer-by-layer growth mode with the filling of individual layers during growth. Meanwhile, these oscillations

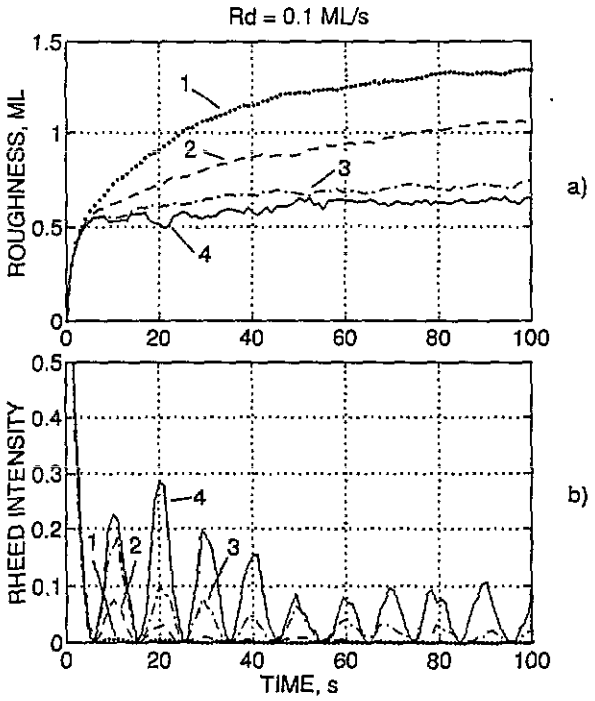

Figure 3. Temporal evolution of the surface roughness (*a*) and RHEED intensity (*b*) during deposition of 10 monolayers of Si at different substrate temperatures (deposition rate $R_d = 0.1$ ML s^{-1}). Curves 1, 2, 3 and 4 correspond to substrate temperatures 600, 700, 750 and 800 K respectively.

are clearly pronounced in Δ at $T = 800$ K, which indicates smooth two-dimensional growth of silicon. The results of RHEED intensity depicted in figure 3(*b*) confirm the evaluation of the temperature of change of growth mode from rough three-dimensional to smooth two-dimensional. The temporal oscillations of RHEED intensity are good indicators of the growth of a high-quality surface. Indeed, at $T = 800$ K (full curve) we see deep and clearly pronounced intensity oscillations, while at $T = 750$ K those oscillations (chain curve) are damped and almost disappear after the deposition of eight layers. At lower temperatures we can observe only a few of these oscillations ($T = 700$ K, broken curve), or there are no oscillations at all ($T = 600$ K).

Third, the critical temperature T_c for this change of growth mode depends on the deposition rate. Increasing R_d moves T_c into the region of higher temperatures. This result is depicted in figure 4. It can be seen from this figure that T_c moves from 650 K for deposition rate $R_d = 0.001$ ML s^{-1} to $T_c = 950$ K for $R_d = 100$ ML s^{-1}. From this picture the regimes for smooth two-dimensional growth of silicon can be determined. To achieve this growth regime, the point of intersection of substrate temperature and deposition rate values should be in the upper part of the plane divided by the $R_d(T_c)$ dependence.

To illustrate the dependence of the growth mode on the deposition rate, in figures 5–7 we show the results of the growth of silicon layers at $T = 700$ K for three different R_d: 100, 0.1 and 0.001 ML s^{-1} respectively.

The temporal evolution of interface width (roughness), layer coverage and RHEED intensity during the

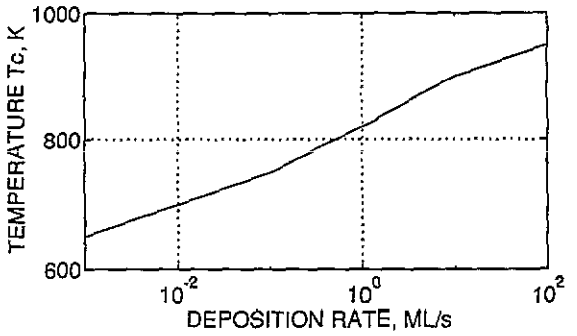

Figure 4. Critical substrate temperature T_c for smooth two-dimensional growth versus deposition rate.

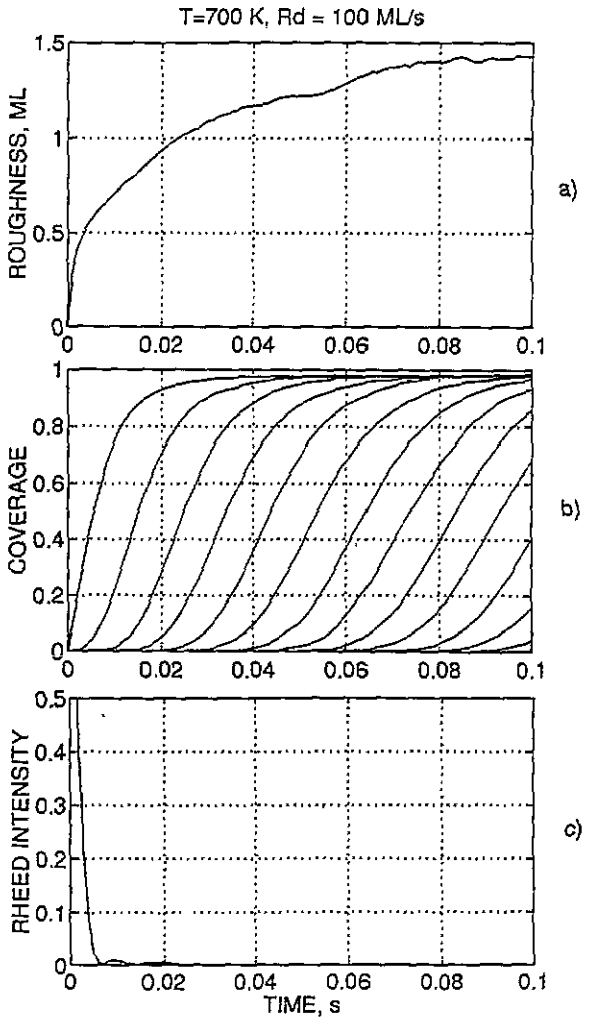

Figure 5. Time dependence of interface width (roughness) (*a*), layer coverage (*b*) and RHEED intensity (*c*) during deposition of 10 monolayers of Si at $T = 700$ K for deposition rate $R_d = 100$ ML s^{-1}.

deposition of 10 monolayers at the deposition rate $R_d = 100$ ML s^{-1} is depicted in figures 5(*a*), (*b*) and (*c*) respectively. As can be seen from figure 5(*a*), the growth is clearly rough, with three-dimensional growth morphology as indicated by Δ, increasing with time and reaching $\Delta \approx 1.45$ ML at $t = 0.1$ s. We note that the results shown in figures 5(*b*) and (*c*) also confirm this conclusion. Indeed, the temporal evolution of different layer coverages (figure 5(*b*)) with many (five or six) monolay-

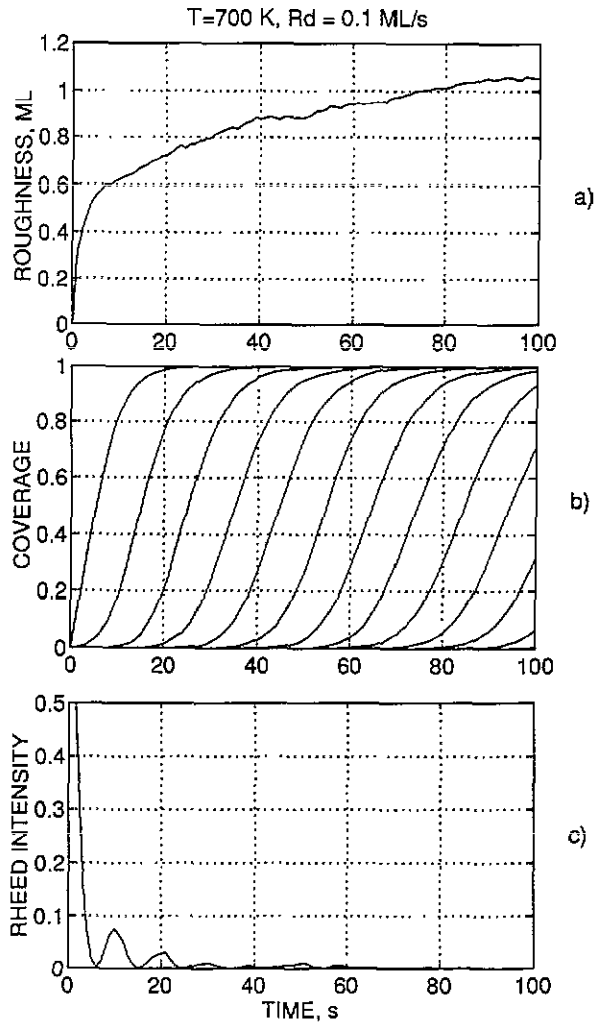

Figure 6. Temporal evolution of interface width (roughness) (*a*), layer coverage (*b*) and RHEED intensity (*c*) during deposition of 10 monolayers of Si at $T = 700$ K for $R_d = 0.1$ ML s^{-1}.

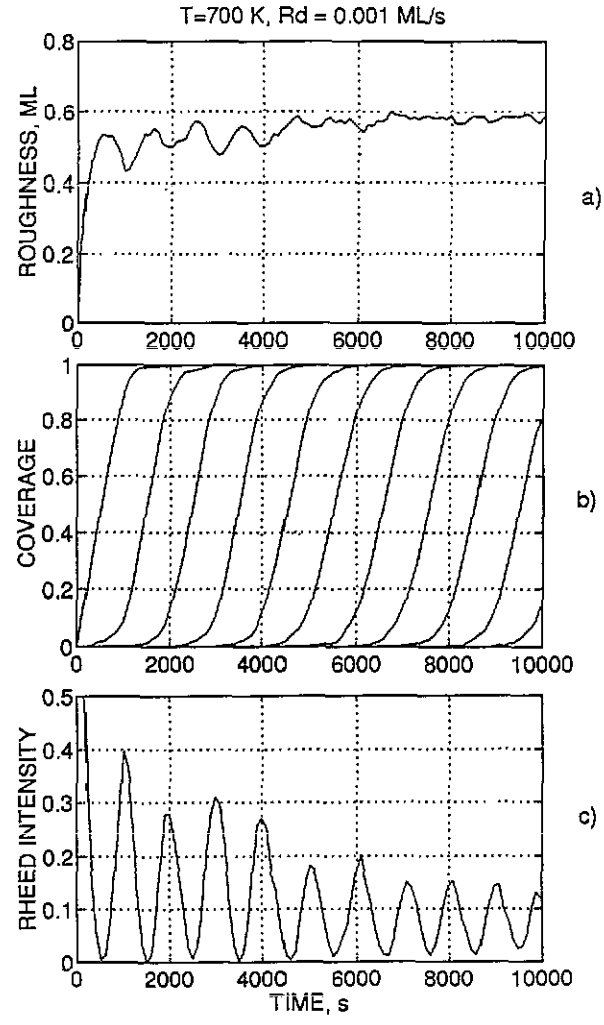

Figure 7. Interface width (roughness) (*a*), layer coverage (*b*) and RHEED intensity (*c*) during deposition of 10 monolayers of Si at $T = 700$ K for $R_d = 0.001$ ML s^{-1}.

ers growing together at the same time moment, as well as the absence of temporal oscillations in the RHEED intensity (figure 5(*c*)), indicate a rough growth mode. It should be noted here that growing layers of silicon in this case are not completely filled, as follows from layer coverage results (figure 5(*b*)). This means that under these conditions bulk vacancies and overhangs are formed in the crystal.

The same set of parmaters (Δ, layer coverage and RHEED intensity) for the same substrate temperature ($T = 700$ K) but at a different deposition rate ($R_d = 0.1$ ML s^{-1}) are shown in figure 6. We see from figure 6(*a*) that, as in the case of $R_d = 100$ ML s^{-1}, the interface width still does not saturate during growth ($\Delta \approx 1.05$ after the deposition of 10 monolayers), but the value of Δ is clearly smaller in this case. Figure 6(*b*) also exhibits the difference between these growth modes. As follows from this picture, the layers are now completely filled out, without any vacancies and overhangs. However, the growth is still not two-dimensional because of three or four layers growing together at the same moment. Two clearly pronounced peaks in RHEED intensity (figure 6(*c*)) also indicate that under these conditions the growth is intermediate between rough three-dimensional and smooth layer-by-layer.

A different situation in the growth of Si(001) is in the case of $R_d = 0.001$ ML s^{-1}. The results of simulations are shown in figure 7. Interface width (roughness), as can be seen from figure 7(*a*), tends toward saturation with $\Delta = 0.58$. Moreover, the temporal oscillations of Δ can be clearly seen in this graph. The period of these oscillations is about 1000 s, which exactly corresponds to the time of deposition of one complete monolayer at a deposition rate of 0.001 ML s^{-1}. Figure 7(*b*) shows the growth of high-quality silicon crystal. In this case, not more than two layers are being filled at the same time moment. As follows from figure 7(*b*), filling of the next layer starts just after the previous layer is almost filled out. RHEED intensity (figure 7(*c*)) also exhibits clear temporal oscillations with the period of completion of one monolayer.

Thus, at fixed substrate temperature $T = 700$ K, it is possible to observe three different growth regimes. At $R_d = 100$ ML s^{-1} the growth mode is clearly rough and three-dimensional, while at $R_d = 0.001$ ML s^{-1} it is layer-by-layer and two-dimensional. The growth regime at $R_d = 0.1$ ML s^{-1} is intermediate between the first two. Similarly to the critical temperature T_c of change

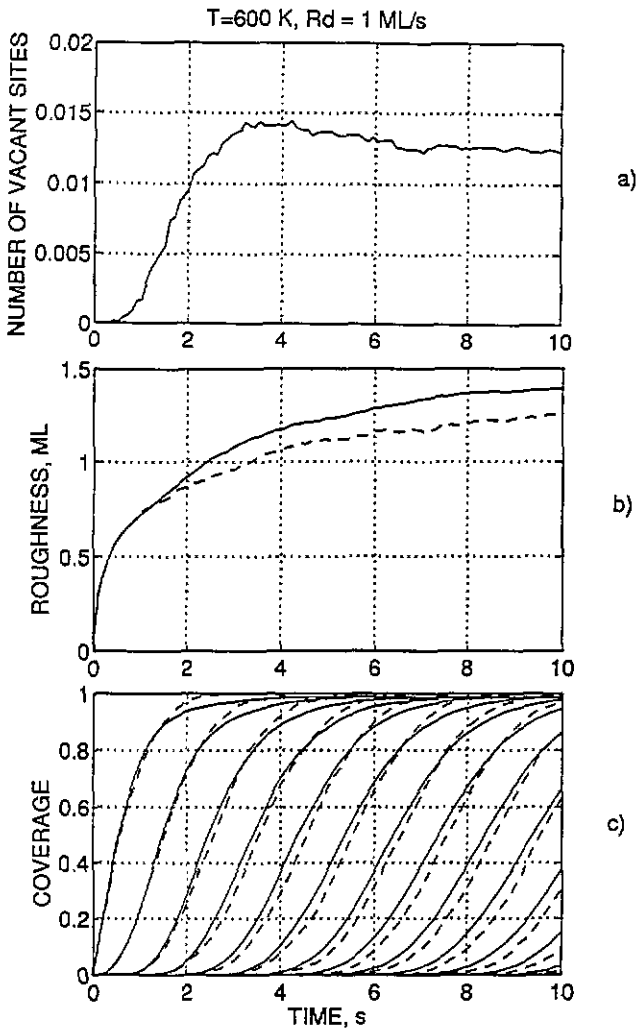

Figure 8. Temporal evolution of the number of vacant sites normalized to surface lattice sites (*a*), surface roughness (*b*) and coverage (*c*) during deposition of 10 monolayers of Si at $R_d = 1$ ML s^{-1} and $T = 600$ K. Full curves in (*b*) and (*c*) represent the results of calculations by our model allowing for vacancies. Broken curves represent the results of simulations within the framework of the sos model.

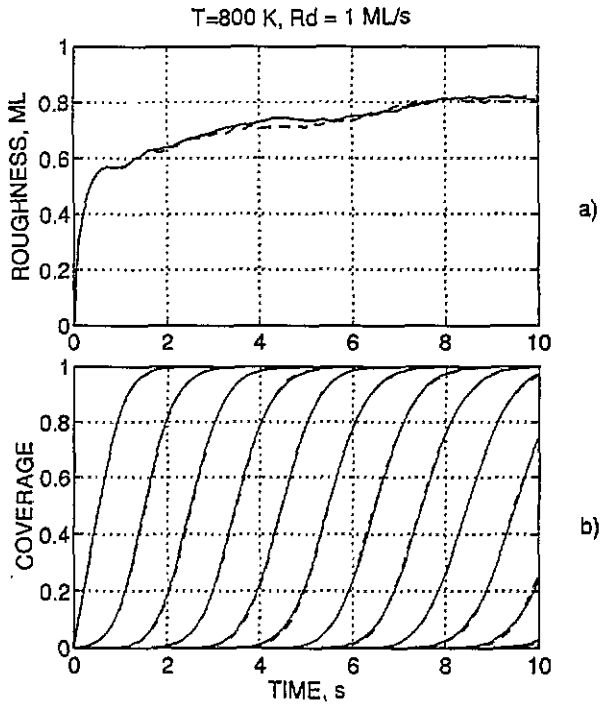

Figure 9. Time dependence of surface roughness (*a*) and layer coverages (*b*) during deposition of 10 monolayers of Si at $T = 800$ K and $R_d = 1$ ML s^{-1}. Full curves represent the results of calculations by our model allowing for vacancies. Broken curves represent the results of simulations within the framework of the sos model.

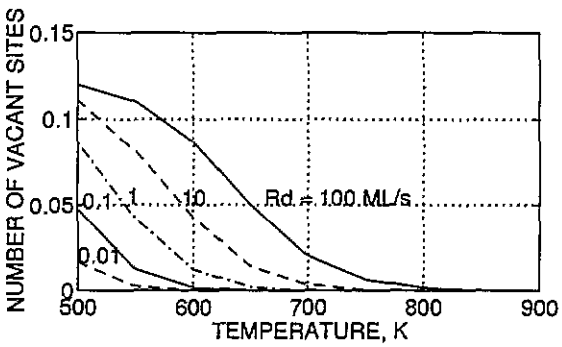

Figure 10. Dependence of the number of vacant sites normalized to surface lattice sites on the substrate temperature at different deposition rates after deposition of 10 monolayers.

in growth mode, we can introduce a critical deposition rate for a particular temperature. This critical rate can be found from the same figure (figure 4) as the critical substrate temperature.

Our second set of simulations was devoted to the investigation of the influence of the formation of vacancies and overhangs on the quality of growing silicon crystal. We simulated the growth of Si(001) using our model, which allows for the formation of bulk vacant sites, as well as using the SOS model, and compared the simulation results.

In figures 8 and 9 we show simulated dynamical growth profiles of layer coverages, number of vacant sites (i.e. lattice sites, which are forbidden in the SOS model, normalized to the number of surface lattice sites), as well as interface width (roughness) Δ for substrate temperatures of 600 K and 800 K respectively, for a fixed deposition rate $R_d = 1$ ML s^{-1}.

As shown in figure 8, the growth at $T = 600$ K is rough, as indicated by a roughness Δ increasing with time (figure 8(*b*)) according to both our model and the SOS model. The difference in Δ obtained by the two different models is caused by the presence of vacant sites in growing silicon (figure 8(*a*)), which are allowed in our model but forbidden in the SOS model. The temporal evolution of layer coverages depicted in figure 8(*c*) also indicates rough growth with many (five or six) layers growing together at the same time, and the effect of allowing the formation of vacant sites.

Growth at $T = 800$ K, as can be seen from figure 9, is intermediate between rough three-dimensional growth and epitaxial layer-by-layer growth. From figure 9(*a*) we can see that Δ tends toward saturation with time, reaching $\Delta = 0.8$ after the deposition of 10 complete monolayers. On the other hand, at the very beginning of growth ($t = 1$ s) at least one temporal oscillation

of Δ can be detected, which indicates a tendency to two-dimensional layer-by-layer growth. It should be pointed out also that there is no difference between the results obtained by our model and the SOS model at this temperature. The temporal evolution of both Δ and surface coverage (figures 9(*a*) and (*b*)) coincide for both models at $T = 800$ K. The reason for this is the absence of vacant sites in the growing material simulated within the framework of our model, which is caused by a temperature ($T = 800$ K) high enough to provide intensive hopping of atoms from one site to another. Due to the fact that atoms accommodated in the vicinity of vacant sites have fewer first or second nearest neighbours, their hopping kinetic rate is higher, so that they are the most 'active': they leave their sites and occupy vacant sites very quickly.

Thus the results shown in figures 8 and 9 demonstrate that the effect of the formation of vacant sites on the quality of growing silicon is pronounced only at low temperatures, where there is no active hopping of atoms. At higher temperatures this effect is washed out by intensive hopping of atoms. Results similar to those of $R_d = 1$ ML s^{-1} were obtained for a whole range of deposition rates. The dependence of the number of vacant sites formed during growth on the substrate temperature at different deposition rates is presented in figure 10. From this figure we can see that the number of vacant sites decreases quickly with increasing temperature. At higher deposition rates the effect of vacant sites moves into the region of higher temperatures.

4. Conclusions

We have developed a new MC model for the simulation of the growth of an Si(001) 2×1 surface. Apart from the explicit incorporation of surface dimerization, tetrahedral coordination and atom–atom interactions out to second nearest neighbours, we have extended the MC model by allowing the formation of bulk vacancies and overhangs in the growing crystal.

Our results demonstrate that the effect of the formation of vacant sites is pronounced only at low temperatures where there is no active hopping of atoms. At higher temperatures this effect is washed out by intensive hopping of atoms. Increasing the deposition rate R_d moves the influence of this effect into the range of higher temperatures.

We have learned that increasing the deposition rate R_d from 0.001 to 100 ML s^{-1} moves the temperature range for the change of growth mode from rough three-dimensional growth to smooth two-dimensional growth toward higher temperatures: from 650 K ($R_d =$ 0.001 ML s^{-1}) to 950 K ($R_d = 100$ ML s^{-1}).

References

[1] Weeks J D, Gilmer G H and Jackson K A 1976 *J. Chem. Phys.* **65** 712
[2] Marmorkos I K and Das Sarma S 1990 *Surf. Sci. Lett.* **237** L411
[3] Marmorkos I K and Das Sarma S 1992 *Phys. Rev.* B **45** 11262
[4] Clarke S, Wilby M R, Vvedensky D D and Kawamura T 1989 *Phys. Rev.* B **40** 1369
[5] Clarke S, Wilby M R and Vvedensky D D 1991 *Surf. Sci.* **255** 91
[6] Keršulis S and Mitin V 1995 *J. Mater. Sci. Eng.* B **29** 34
[7] Kawamura T and Wilby M R 1993 *Surf. Sci.* **283** 360
[8] Barnett S A and Rockett A 1988 *Surf. Sci.* **198** 133
[9] McCoy J M, Maksym P A and Kawamura T 1991 *Surf. Sci.* **257** 353
[10] Ichikawa M and Doi T 1987 *Appl. Phys. Lett.* **50** 1141
[11] Kaspar E 1982 *Appl. Phys.* A **28** 129
[12] Maksym P A 1988 *Semicond. Sci. Technol.* **3** 594