

# Atomic diffusion on vicinal surfaces: step roughening impact on step permeability

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**Abstract.** The problem of mass transport in material science for systems with reduced dimensionality holds special academic and technological attention since the fine diffusion control of adatoms could initiate exotic nanoscale patterning at epitaxial interfaces. The present study brings out important details of the atomic diffusion mechanisms on vicinal surfaces, accounting for the subtle competition between an external field imposed on the migrating adatoms and the roughening of the steps bordering the atomic terraces. The computational model reveals a temperature gap for breakdown of step permeability in the vicinity of the step roughening transition and sheds light on recently observed experimental results for atomic step dynamics on Si surfaces. The present study also demonstrates the extended capability of atomistic models in computer simulations to unravel simultaneous effects, to distinguish between them, and finally to assess their specific contribution to experimentally observed complex physical phenomena.

## 1. Introduction

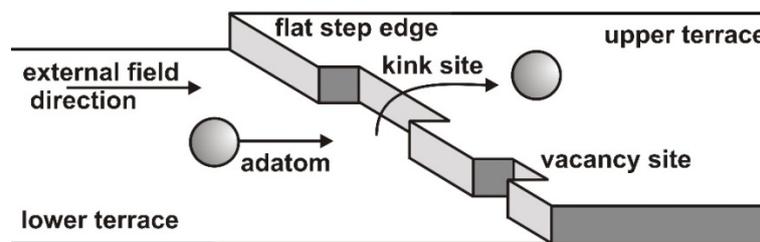
The surface diffusion phenomena play substantial role in the theoretical models of crystal growth and related physical scenarios for mass transport on epitaxial interfaces [1-4]. In this important field for materials science, an extensively studied problem is the step dynamics of vicinal surfaces. In some specific cases the enhanced step mobility causes formation of regularly spaced narrow groups of steps followed by step-free large terraces on the interface [5]. This effect, known as step bunching, has a large impact on the processes of nanoscale patterning of epitaxial interfaces [5-7]. The surface atomic diffusion is the basic phenomenon that controls step bunching and related mechanisms of step mobility. In the presence of external electromigration force acting on adatoms on Si surfaces as a result of the current heating the crystal, the atomic diffusion does not follow a simple Einstein-walk behavior [4]. The migration of adatoms is preferentially oriented in direction of the electric current which changes dramatically the surface step dynamics. An important role in this process plays the phenomenon of step permeability (or transparency), i.e. the ability of adatoms arriving at the terrace edge to overcome the step diffusion barrier and to jump to the upper terrace level. The step permeability opens a way for still unraveled temperature dependence of the step distribution on the crystal surface to be theoretically explained. This distribution varies from regular equidistant monatomic steps to bunches of steps and vice versa as the temperature (respectively the heating current) increases [5-8]. Hence, the step permeability influences the local adatom concentration on the terraces and is therefore expected to have essential impact on the terrace nucleation processes and the step propagation [3, 7].



In the present study, based on atomistic simulation experiments, we reveal important details of step permeability diffusion kinetics of adatoms in the vicinity of the edges of atomic terraces. We discuss the role of external field imposed on migrating atoms and the impact of fine atomic structure of steps on step permeability. We suggest a computational model and physical scenario for experimentally observed variation of step permeability as a function of temperature.

## 2. Physical and computational model

In the present study we consider homoepitaxial interface of atomically smooth Cu(111) crystal surface with a large single monatomic terrace and random adsorption of atoms and atomic clusters of the same material on top of the interface, figure 1. The system size is  $L_x = 76$ ,  $L_y = 44$  and  $L_z = 5$  lattice units in the corresponding space dimensions. Depending on the specific diffusion problem, we also apply an external field to direct adatoms and clusters in specific crystallographic direction and to evaluate the impact of the external force on the atomic diffusion kinetics. The computational model implies classical canonical Monte Carlo (MC) sampling with many-body Tight Binding Second Moment Approximation of Electron Density of States (TB SMA) potential between interacting atoms [8, 9].



**Figure 1.** Interface atomic scale morphology of monatomic step on vicinal surface and adatoms on which an external field acts. The adatom displacement on the upper terrace presents the step permeability phenomenon.

This semi-empirical TB SMA potential has been extensively applied in contemporary atomistic simulations of transition metals and intermetallic alloys [2, 10-12]. Its basic advantage relates to the ability of reproducing real physical properties of surfaces and interfaces including point defects, dislocations, vacancies, grain boundaries [9]. In the present many-body TB SMA interactions model, the energy  $E_i$  of atom  $i$  in the simulated system is a sum of repulsive,  $E_i^r$ , and attractive,  $E_i^b$ , interaction terms:  $E_i = E_i^r + E_i^b$ . These terms are given by the expressions:

$$E_i^r = A \sum_j \exp \left[ -p \left( \frac{r_{ij}}{r_0} - 1 \right) \right] \quad (1)$$

$$E_i^b = -\xi \left\{ \sum_j \exp \left[ -2q \left( \frac{r_{ij}}{r_0} - 1 \right) \right] \right\}^{\frac{1}{2}} \quad (2)$$

where  $r_{ij}$  is the distance between atoms  $i$  and  $j$ , and  $r_0$  is the nearest-neighbour distance in the metal lattice. The parameters  $A$ ,  $p$ ,  $q$  and  $\xi$  have values obtained by fitting to experimental data for the cohesive energy, lattice parameters and independent elastic constants of the metal system studied. For our monatomic homoepitaxial system Cu/Cu(111) interface we used the  $A$ ,  $p$ ,  $q$  and  $\xi$  values for Cu given in table I of Ref. 9. The energy calculation is performed over all atoms within a sphere of radius  $3r_0$ .

The statistical distribution is canonical, *i.e.* for an ensemble with fixed number of particles at constant temperature. In the state of equilibrium, the system energy is minimal and fluctuates around a constant value. Full lattice dynamics of the substrate, terrace and adatoms ensures complete thermodynamic relaxation of the system. The simulation experiments are done in the temperature range of 400 to 700 K. Hence, we can vary the adatom diffusion energy and the equilibrium atomic structure (density of kinks and vacancies) of the steps. The initial configuration at which all simulations start is a homoepitaxial interface with monatomic terrace on it and random distribution of adatoms on the lower terrace level. The external field having energy,  $E_e$ , is applied exclusively in direction normal to the step on the terrace. The strength of  $E_e$  is calculated as a part of Cu-Cu interaction energy,  $E_{Cu-Cu}$ , of the TB SMA potential given by Eq. 1 and Eq. 2. The step permeability  $P_s$  is defined as the ratio of the number  $N_p$  of atoms on the terrace at a given moment, and the initial number  $N_{all}$  of adatoms migrating towards the terrace:

$$P_s = \frac{N_p}{N_{all}} \quad (3)$$

The model enables to gain insight into the diffusion kinetics of adsorbed atoms and the variety of diffusion energy barriers depending on the fine atomic morphology of stepped surfaces.

### 3. Results and discussion

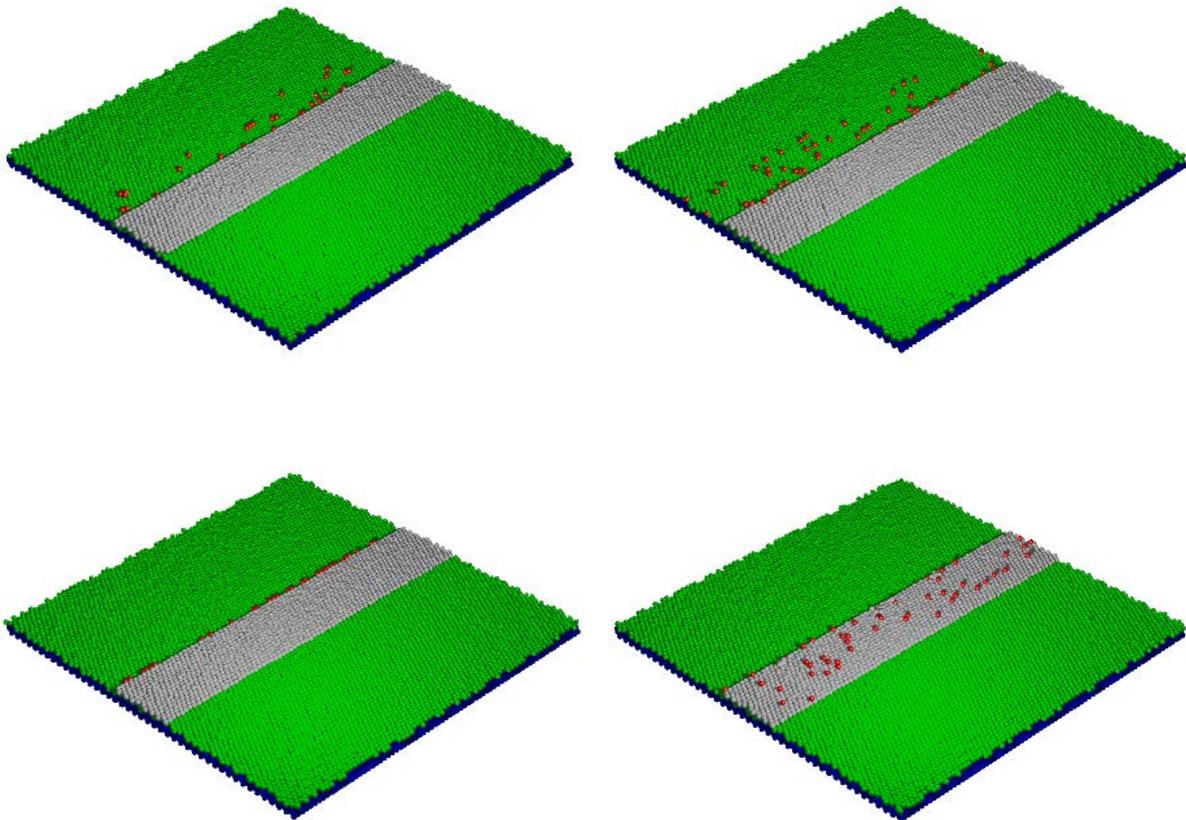
The step permeability takes place when an adatom arriving at the terrace periphery has energy exceeding the step diffusion barrier,  $E_s^d$ , and therefore can jump with a certain probability on the upper terrace, figure 1. In the general case, the adatom diffusion energy is related to the adatom thermal energy,  $kT$ , which makes the adatoms walk randomly in all space directions of the interface. Hence, the probability an adatom to jump on the upper terrace level is controlled by the system temperature. More complicated is the case of atomic diffusion in presence of external field imposed on the moving particles. Then the adatom energy  $E_a$  is enhanced and can be expressed by the sum of two terms:

$$E_a = E_T + E_e \quad (4)$$

where  $E_T$  and  $E_e$  are the thermal and external field energies, respectively. It is essential to note that in step bunching experiments the external field acts only in one direction which is perpendicular to the terrace steps. Typical example is the electromigration force, acting on Si adatoms on Si(111) surfaces and originating from the current, heating the sample. This is in contrast to the thermal energy which causes isotropic thermal fluctuations non-confined in space. Let us point out that an adatom jump to upper terrace level requires atomic shift in direction normal to the substrate. Therefore, the second term in Eq.4, contributes to the adatom move to the upper terrace level only in the case when the thermal energy already renders a fluctuation in direction normal to the interface. The energy contribution analysis based on Eq. 4 suggests an important conclusion related to the external field impact on step permeability phenomena. Being consisted of two terms with different physical origin, the adatom energy impact on adatom diffusion will depend on the dominant term in Eq. 4. Therefore, the step permeability could be suppressed or enhanced just by variation of the relative contribution of  $E_T$  or  $E_e$ . This result suggests that adatoms even with total energy  $E_a$  exceeding the step diffusion energy barrier could or could not lead to step permeability depending on the dominant term in the energy expression. Therefore, diffusion kinetics at low temperature under strong external field will differ substantially from the diffusion kinetics at high temperature under weak external field even when in both cases the absolute values of the adatom diffusion energies are identical. Hence, in a system satisfying the general requirement  $E_a > E_s^d$ , for adatom jump on the second terrace level, the step permeability could take or could not take place depending on the impact of thermal fluctuations resulting from non-zero system temperature.

### 3.1. Step permeability at constant temperature

Following the above analysis, we have performed simulation experiments to evaluate separately the influence of the system temperature and the magnitude of the external field. Apparently, at constant temperature the thermal energy of migrating adatoms is fixed and therefore the diffusion energy is controlled solely by the external field imposed on the adatoms. The Monte Carlo simulation data show that step permeability diffusion kinetics can be realized only if a certain critical strength of the external field is reached. The diffusion kinetics at 400 K in weak,  $E_e = 0.1E_{Cu-Cu}$ , external field is shown in figure 2. It is seen that the adatom energy is not sufficient for the adatoms to overcome the step diffusion barrier and therefore the step is impermeable. Keeping the temperature constant, 400 K, we have gradually increased the external field strength up to  $0.32E_{Cu-Cu}$ . The snapshots in figure 3 give clear evidence of complete step transparency for adatoms at overcritical external field. The value of  $0.17E_{Cu-Cu}$  was evaluated as the critical magnitude providing the adatom energy required to overpass the step diffusion barrier.

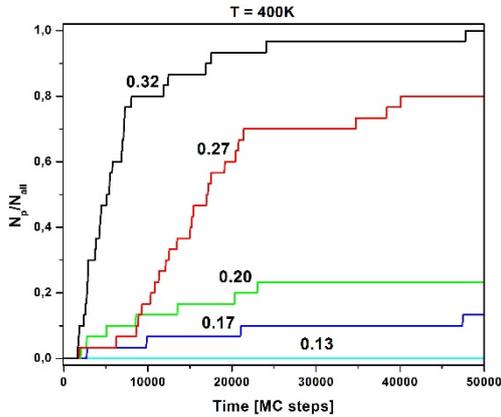


**Figure 2.** Atomic diffusion at 400 K in a weak external field. All adatoms “decorate” the step edge. The adatom diffusion energy is below the step energy diffusion barrier. Snapshots timescale is 1000 MCS (up) and 50000 MC steps (down). Green balls – substrate atoms, gray balls – terrace atoms, red balls – adatoms.

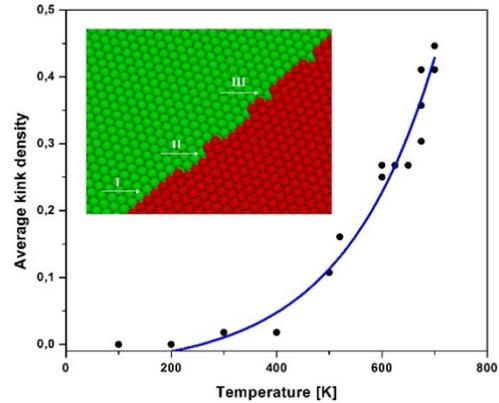
**Figure 3.** Atomic diffusion at 400 K and resulting step permeability at overcritical external field. The steps are transparent since the adatom energy exceeds the step diffusion barrier preventing their jump on the terrace. Snapshots timescale is 1000 MCS (up) and 50000 MC steps (down). Green balls – substrate atoms, gray balls – terrace atoms, red balls – adatoms.

The variation of  $P_s$  as a function of time is demonstrated in figure 4. The stronger external field causes also faster diffusion kinetic and enhanced step transparency for migrating adatoms. This is

distinctly pronounced in the initial time between  $1 \times 10^3$  and  $3 \times 10^3$  MCS where the permeability  $P_s$  strongly depends on the external field intensity.



**Figure 4.** Step permeability at constant temperature, 400 K, and variable external field imposed on adatoms. The field strength value  $E_e$  is related to  $E_{Cu-Cu}$  interaction energy in the TB SMA computational model. Its critical value for step transparency is evaluated to  $0.17E_{Cu-Cu}$ .



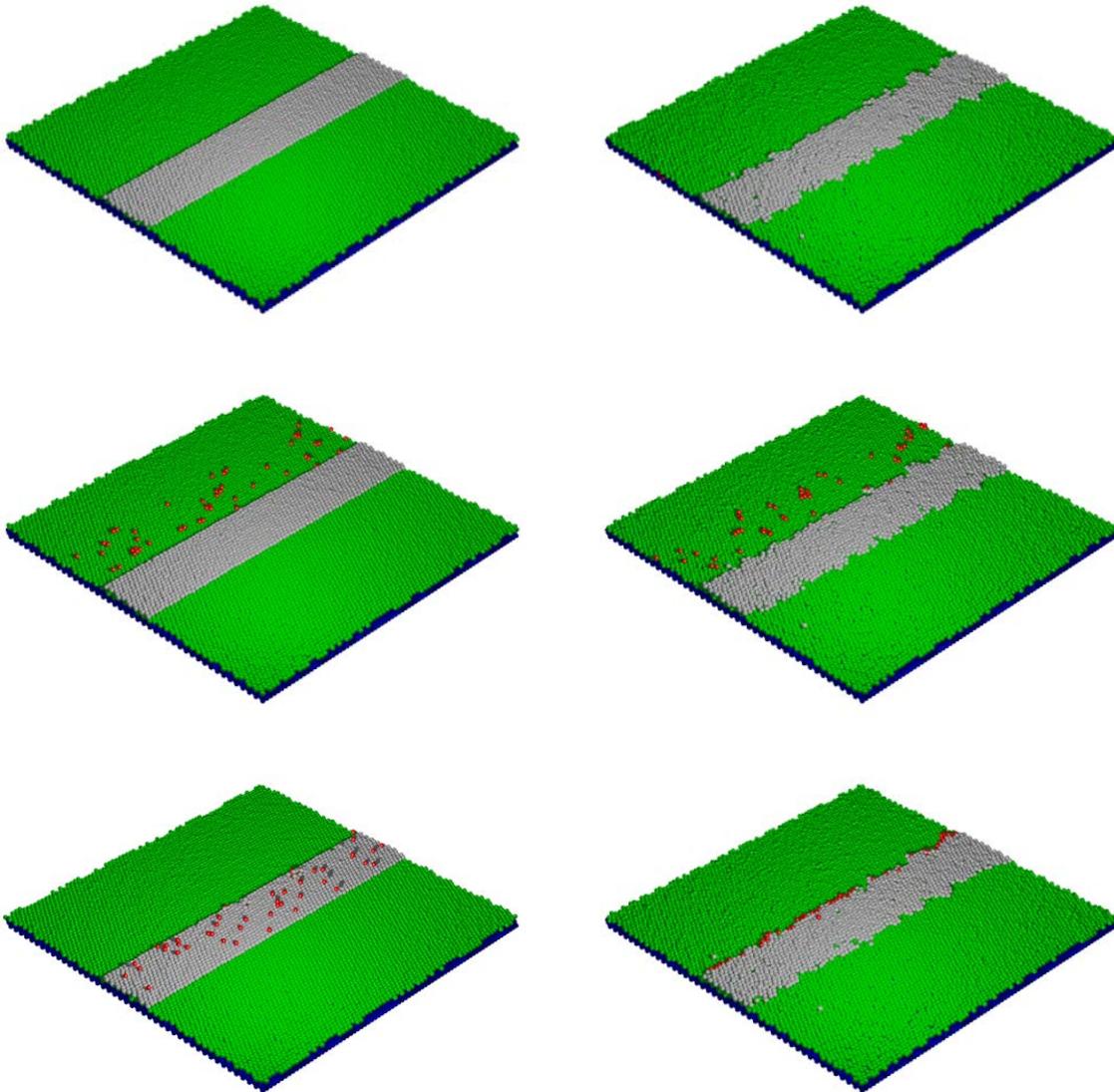
**Figure 5.** Average kink density of atomic B-step (see Ref. 1-3) of the terrace as a function of temperature. The step roughening transition takes place at about 700 K., see also figure 7. The inset arrows indicate I - flat step, II - kink site, III - atomic vacancy site.

It is essential to point out that step transparency was not observed at temperatures below 200 K despite the great strength of the external field which increases the adatom energy to  $E_a > E_s^d$ . This is due to the considerably weaker thermal fluctuations of adatoms and therefore lower probability for normal to the substrate displacements.

### 3.2. Step roughening impact on step permeability

The second problem of the present study deals with the dependence of step diffusion barriers on the fine atomic structure of steps. The adatoms can be attached to the terrace at energetically different places on the step and therefore the diffusion barrier on flat step could be significantly different from the diffusion barrier in a kink or step vacancy position, see figure 1 and figure 5 inset. This analysis requires detailed knowledge of the step morphology at the atomic scale including kink density and step vacancy distribution [13]. Being a temperature function, the equilibrium kink density defines also the step roughening transition at the point of annulling the step free energy. The impact of atomic step roughness on step permeability requires evaluation of the average kink density at fixed temperature. The equilibrium kink distribution between 200 and 750 K is shown in figure 5. Let us note that the symmetry of fcc(111) surface orientation provides two types, A- and B-steps on the terrace with different step free energies and therefore different densities of kinks and different step roughening temperatures [1-3]. In the present study we analyse kink density exclusively for B-steps for which the step transparency is under investigation. The kink density temperature dependence defines two different ranges of step permeability. The first,  $300 \text{ K} < T < 500 \text{ K}$ , relates to atomically smooth steps and the step transparency is controlled by the external field acting on adatoms. This diffusion scenario is shown in figure 6. The terrace being in thermodynamic equilibrium at 400 K has atomically smooth steps which are completely transparent for adatoms in overcritical external field. In contrast at high temperature the step morphology is atomically rough with a large number of energetically new adsorption sites, figure 7. These sites, having higher diffusion barriers compared to the adsorption sites on a flat step, completely block the adatoms and prevents their jumps on the upper terrace level. Hence, in the second temperature range,  $T$

> 700 K, the step permeability and corresponding diffusion kinetic are entirely controlled by the kinks density at the terrace edges.



**Figure 6.** Diffusion kinetics at atomically smooth terrace steps in equilibrium,  $T=400$  K. The step is entirely transparent for adatoms coming from the lower terrace level. The external field imposed on adatoms  $0.2E_{Cu-Cu}$  is overcritical for adsorption sites on flat step. Green balls – substrate atoms, gray balls – terrace atoms, red balls – adatoms.

**Figure 7.** Diffusion kinetics at atomically rough terrace steps in equilibrium,  $T=700$  K. The step permeability is tightly suppressed by the high density of kinks and vacancies on the step. The external field imposed on adatoms is  $0.2E_{Cu-Cu}$  same as those in figure 6. Green balls – substrate atoms, gray balls – terrace atoms, red balls – adatoms.

Increasing the system temperature above its critical value for step roughening transition, the adatom energy becomes again sufficiently high for the adatoms to overcome the step diffusion barriers at kink or step vacancy sites. As a result, the steps are again transparent for adatoms and step permeability

diffusion kinetics becomes operative again. Let us point out that the enhanced atomic scale surface dynamics originating from elevated system temperature also supports the mass transport via atomic exchange between different levels of terraces.

The present computational model reveals the temperature impact on the surface dynamics at the atomic scale. The temperature contributes to the adatom diffusion energy required for step permeability in a physically different way compared to the impact of the external field. The system temperature moulds simultaneously the surface structure and the surface dynamics of both steps and substrate atoms. Therefore, it shapes in a specific way the thermodynamic fluctuations of all atoms on the interface. In contrast, the external field impact is restricted only to the adatoms diffusing towards the terrace. Hence, in the adatom critical energy required for step permeability the contribution of the external field is not equivalent to those of the temperature. For instance, at low  $T$  the atomic step is expected to be non-permeable even for adatoms having overcritical diffusion energy for flat step. The reduced permeability is a result of low surface dynamics of atoms and therefore low thermodynamic fluctuations. Restricted fluctuations of atoms could decrease significantly the probability for atomic exchange at the terrace edges. In contrast, at high  $T$  and the same value of adatom diffusion energy (compensated by weak external field) the step will be transparent for diffusing adatoms because of the enhanced atomic surface dynamics.

#### 4. Conclusion

The present study provides atomistic insight into the step permeability diffusion kinetics of adatoms on crystalline vicinal surfaces. Based on detailed analysis of diffusion energy barriers at different sites of atomic steps (flat step area, kinks, and step vacancies) it reveals the step roughening impact on step permeability diffusion mechanism. On that physical background, the present model clearly defines three temperature-dependent diffusion scenarios of step permeability. The first scenario is realized at temperatures far below the critical temperature of step roughening transition,  $T_c$ . Here the atomic diffusion takes place on atomically smooth surface towards atomically smooth steps of the terrace. In this temperature region, depending on the strength of the external field imposed on adatoms, the step permeability could be entirely restricted or favoured. In this way, the resulting mass transfer between different levels of atomic terraces can be turned on or off. The second scenario operates at temperatures where the terrace steps are atomically rough. Because of the high density of kinks and step vacancies, the adatoms are blocked at the step edges and permeability collapses despite the enhanced value of the adatom thermal energy. The third scenario comes about at temperatures exceeding sufficiently  $T_c$ . In this case the adatom energy surpasses the diffusion energy barriers at kink sites and the step permeability diffusion kinetics comes again into play. Finally, the presented computational model opens a way to distinguish between the specific impacts of the thermal energy and the energy of the external field on the adatom diffusion on vicinal surfaces. While the variation of the system temperature influences the surface structure at the atomic scale by changing the energy barriers corresponding to smooth or rough interface, the external field only contributes to the adatom diffusion energy. The simulation results and the observed in the present study diffusion kinetics are in line with recent experimental findings of step bunching phenomena on Si surfaces.

#### Acknowledgment:

The authors acknowledge the financial help of Project BG051PO001-3.3.06-0038 funded by OP Human Resources Development 2007-2013 of EU Structural Funds.

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