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A theoretical study of surfactant action in the layer-by-layer homoepitaxial growth of metals: the case of In on Cu(111)

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Abstract

A surfactant-mediated homoepitaxial metal system, Cu/In/Cu(111), is studied by using first-principles calculations and the kinetic Monte Carlo method. A new repulsion model is proposed for the Cu/In/Cu(111) system where surface-substitutional In atoms repel diffusing Cu adatoms and build a repulsion network. This repulsion network results in an average increase of terrace barriers for adatoms Cu and enhanced island density. The layer-by-layer growth for the Cu/In/Cu(111) system is achieved with a repulsion model in a kinetic Monte Carlo simulation. The importance of the additional barrier ΔE is confirmed in determining film morphology. © 1998 Elsevier Science B.V.

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1. Introduction

Over the last few years, many experiments have shown that the shape of a film grown on a solid surface can be appreciably altered by the presence of small amounts of surfactants [1–7]. Smooth Ge film can be grown on a Si(100) surface preadsorbed by a monolayer of As, Sb, or Te [1–4] while films grown on a clean surface are rough. It has also been observed that the presence of Sb on Ag, O on Pt, or In on Cu can induce layer-by-layer homoepitaxial growth under conditions typical for island growth in these systems [5–7]. In these studies, the term “surfactant” refers to a monolayer or a submonolayer of foreign atoms on the surface. The classical definition of surfactant is “a substance that lowers surface tension, thereby increasing spreading and wetting properties” [8]. Currently a surfactant is accepted to be a generic agent promoting

two-dimensional (2D) layer-by-layer (LBL) growth as opposed to three-dimensional (3D) island growth for a special crystal face [9].

A detailed understanding of the mechanisms involved in the surfactant-mediated growth for both semiconductor and metal systems in heteroepitaxy and homoepitaxy is not only of fundamental interest, but also has technological importance. The growth of thick, low-defect films with abrupt interfaces and smooth layers is an essential requirement for many modern electronic device applications.

In the present study we restrict our discussion to metal-on-metal homoepitaxial growth. Zhang and Lagally suggested a general model (ZL model) for metal systems [8]. The ZL model is based on the inequality $V_{A-A} > V_{A-S} \gg V_{S-S}$ connecting the adatom–adatom, adatom–surfactant and surfactant–surfactant bond strengths (A = adatom, S = surfactant). In this

Letter, one typical surfactant-mediated layer-by-layer homoepitaxial metal system, Cu/In/Cu(111), is studied by using first-principles calculations and the kinetic Monte Carlo method. Our results show that ZL's assumption is not satisfied in the Cu/In/Cu(111) homoepitaxial system. A repulsion model based on first-principles calculations is proposed where surface-substitutional surfactant In atoms repel deposited Cu atoms and affect their migrations and nucleations. Kinetic Monte Carlo simulation results are in good agreement with experiments. These results confirm the importance of the additional barrier ΔE in determining film morphology.

This Letter is organized as follows. Section 2 contains a brief description of first-principles calculations, our repulsion model and the simulation method used. In Section 3 we present calculated results and detailed discussions and we conclude in Section 4.

2. Model and method

2.1. Calculation of binding energies and diffusion barriers

In this Letter, a discrete variational X_α (DV- X_α) method is used in the calculation of various binding energies and diffusion barriers in the Cu/In/Cu(111) system. The DV- X_α method we used is a first-principles molecular cluster approach based on the local-density-functional (LDF) theory. The matrix elements of the Hamiltonian and overlapping are evaluated by a numerical integration technique on a grid of about 1200 points per atom. In DV the atomic wave functions ϕ are generated numerically from the same LDF solutions as for the free atoms and are used as basis functions. The molecular wave functions and eigenvalues are determined using the self-consistent charge to the potential. More details of this method have been given in Refs. [10–13]. The frozen-core approximation is used for Cu, In except that the Cu 3d, In 4d electrons are treated fully in the self-consistent iterations. Hedin–Lundqvist exchange-correlation terms are adopted in the potential. This cluster approach has been proved to be a very good one in studying adsorption on a transition metal surface [11–13].

The diffusion barriers are given by the difference

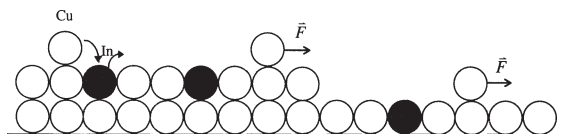


Fig. 1. Schematic picture of our repulsion model for the Cu/In/Cu(111) system. The force \vec{F} is the repulsive interaction between surface-substitutional In and Cu adatoms. In atoms segregate by the Cu–In exchange process. Open circles represent adatoms Cu and filled circles represent surfactants In. For details see the text.

between the highest energy obtained in a saddle-point configuration and the energy in the initial situation. For the calculation of Cu–In exchange barriers we use Feibelman's method where a Cu adatom replaces a substrate In atom, as the latter becomes an adatom in a nearest-neighbor fcc site [14].

In the present calculations, the flat (111) surface of Cu is simulated by the model cluster Cu_{24} ; and we adopt the Cu_{33} cluster to simulate a stepped Cu(111) surface in the calculation of those barriers concerning steps.

2.2. Our repulsion model for the Cu/In/Cu(111) system

Our calculated results show that ZL's basic assumption is not satisfied in the Cu/In/Cu(111) system ($V_{\text{Cu-Cu}} < V_{\text{Cu-In}}$). Thus a new model is needed for the Cu/In/Cu(111) system. According to our results, In atoms preferably stay at surface-substitutional sites, and surface-substitutional In atoms repel diffusing Cu adatoms. We propose a repulsion model for the Cu/In/Cu(111) system. In our repulsion model, the Cu–In exchange process and the repulsive interaction between surface-substitutional In atoms and deposited Cu atoms are the main action mechanisms of surfactants In. They are shown in Fig. 1. The Cu–In exchange process is a necessary condition for surfactant-mediated LBL growth, which is confirmed from our calculated results below.

For the unannealed surface, most preadsorbed In atoms occupy on-surface sites at the beginning of deposition. Due to $V_{\text{Cu-In}} > V_{\text{Cu-Cu}}$, after Cu atoms are deposited, In atoms will be centers of nucleation of deposited atoms. After small islands centering about In atoms are formed, the repulsion effect of surface-substitutional In atoms begins to be put into action.

The Cu atoms landing on small islands will diffuse to the edges of the islands and step down rapidly due to the repulsion. Thus a smooth first layer is grown and an almost uniformly distributed repulsion network of surface-substitutional In atoms is formed. From the second layer on, the repulsion network starts to take effect. For the annealed surface, preadsorbed In atoms occupy surface-substitutional sites and build a repulsion network at the beginning of deposition.

When a deposited Cu atom enters this network, it will be repelled by In atoms around it. In a given time, the distance traveled by the Cu walker is diminished greatly, that is to say, the terrace diffusion barrier E_{surf} is increased on average. It is a repulsive interaction and a network that lead to an increase of E_{surf} on average and an enhanced island density. Our simulated results also show that the growth mode of Cu/In/Cu(111) depends on In coverage, this proves that an increase of E_{surf} is a global effect of the surfactant network. For the interacting system, there are many microscopic diffusion barriers, the value of the measured diffusion barrier E_{surf} must result from some complex average of all of them, and does not refer to any microscopic process in particular [15]. In our present model, we focus on the qualitative property of E_{surf} .

We use the repulsion mechanism during the whole surfactant-mediated growth (up to about 10 ML thick). For the Cu/In/Cu(111) system, the adatom-surfactant interaction energy is approximately equal to $(0.18/\rho)$ eV, where ρ is the distance between the adatom Cu and the surface-substitutional surfactant In (at most three lattice sites away) based on our calculated results. The difference $E_f - E_i$ is calculated where E_i (E_f) is the interaction energy of an adatom Cu with all the surface-substitutional surfactants In nearby when an adatom Cu is at its location before (after) a jump. So in the presence of the surfactants In, the energy barrier ϵ for an adatom Cu diffusing on terraces, which is calculated from the intersection point between harmonic potential well centers on adjacent sites, is defined as [16]

$$\epsilon = \epsilon_0 + (E_f - E_i)/2 + (E_f - E_i)^2/16\epsilon_0, \quad (1)$$

where ϵ_0 is the energy barrier for an adatom Cu diffusing on terraces without surfactants In.

2.3. Simulation method

We consider a solid-on-solid model growing on an L one-dimensional substrate with periodic boundary conditions. The $h(x, t)$ represents the height of the surface at the one-dimensional substrate at position x and t . Surfactants are precovered over the substrate with a uniform random distribution. Atoms are deposited randomly on the surface at a constant rate and deposition of a single atom at position x increments the height by unity. In a single time step, a small number of atoms are deposited randomly on the surface, and all the atoms including surfactants on the surface are allowed to hop to nearest-neighbor empty sites.

Here we use the time-dependent Monte Carlo method (TDMC) [16] to simulate growth processes. Because an atom hops in each time-dependent Monte Carlo cycle, TDMC can overcome the “rare event problem”.

If there are N atoms in the system and the total number of possible transitions is M , for each transition type, the transition rate is ω_i ($i = 1, 2, \dots, M$), where $\omega_i = \nu \exp(-\epsilon_{bi}/KT)$, ϵ_{bi} is the energy barrier for the i th transition type. We assume that there are N_{bi} transitions of the i th transition type, so a chosen transition type j has a relative rate R_j ,

$$R_j = \frac{N_{bj} \exp(-\epsilon_j/KT)}{\sum_i^M N_{bi} \exp(-\epsilon_{bi}/KT)}. \quad (2)$$

At first the computer searches for all possible transitions in the system and calculates the corresponding R by means of (2), and then generates a random number α between zero and one. According to α and R , the energy barrier for the jump to be chosen will be determined. Then another random number β can determine the jump in this transition type. That is to say, two random numbers determine a particular jump.

It is important to calculate the real time for studying the dynamical behavior in the Monte Carlo simulation. If we denote by L the number of sites on the one-dimensional lattice, the mean time between the deposition of two atoms in our simulation is $T_d = T_0/L$, where T_0 is the time needed to grow a monolayer. A new method to calculate the real time was developed recently [17], in which a real time interval Δt_i for one particular jump is related to the total number of possible transition types M ,

$$\Delta t_i = \frac{\exp(\epsilon_{bi}/KT)}{\nu M}, \quad (3)$$

$$T_d = \sum_{i=1}^n \Delta t_i, \quad (4)$$

where n is the total number of jumps in the time interval T_d .

In order to assess the relative importance of different processes in influencing the growth morphology, we have done various model simulations. For the Cu/In/Cu(111) system, the deposition rate is 0.01 monolayer per second (ML/s), the typical coverage of surfactants In is 0.08. These parameters conform with the experiment [7]. The surface temperature is 225 K in all model simulations. For the Cu/In/Cu(111) system, LBL growth can be induced at 225 K [7]. Since the interlayer mass transport will be enhanced as the growth temperature is increased, we choose the lowest temperature 225 K as the typical simulation temperature to test the various models. The vibrational frequency ν depends on the adatom mass and the interatomic force constant. According to our calculated results, we choose 10^{12} s^{-1} for Cu atoms (on the Cu(111) face) and 10^{12} s^{-1} for In atoms (on the Cu(111) face) in our simulations, respectively.

To characterize the quality of the growing surface, we measure the interface width $W(L, t)$,

$$W(L, t) = \sqrt{\langle h^2(x, t) \rangle - \langle h(x, t) \rangle^2}.$$

So the relationship of $W(L, t) \sim t$ can show the variation of surface flatness with the time t , which can indicate the growth mode.

Simulations have been carried out for $L = 600$ with various models and parameters. Multiple growth runs have been made for the same parameters but with different random number sequences, and results have been averaged together to reduce statistical fluctuations.

3. Results and discussion

3.1. Binding energies and diffusion barriers

Our first-principles calculations show that the binding energies of Cu–Cu and Cu–In dimers which are at nearest neighboring fcc sites on the Cu(111) sur-

face are 0.25 eV and 0.42 eV, respectively. Therefore, In atoms preferably stay among Cu islands and the assumption of the ZL model is not satisfied in the Cu/In/Cu(111) system. There is a large repulsive force between the two In atoms at nearest neighboring fcc sites, and the repulsive energy is 0.61 eV, which results in a uniform distribution of In atoms over the Cu(111) surface.

The adsorption energy of In at a surface-substitutional site is 3.4 eV, and the adsorption energy of In at an on-surface fcc hollow site is 2.84 eV, thus In atoms favor surface-substitutional sites.

The various calculated migration barriers for Cu and In atoms on the Cu(111) surface are summarized in Table 1, which are used in our kinetic simulations. The terrace barriers for Cu adatoms and In surfactants on the Cu(111) surface are 0.12 eV and 0.03 eV, respectively, which are consistent with other calculations [18,19]. The terrace barriers for a Cu adatom having one nearest neighbor, Cu and In, are 0.42 eV and 0.47 eV, respectively. The energy barrier for the Cu–In exchange process is 0.55 eV, and it is small enough to ensure the segregation of In surfactants.

3.2. Kinetic Monte Carlo simulation results

The simulation results for the Cu/In/Cu(111) system with our repulsion model are shown in Fig. 2, where we plot the interface width $W(L, t)$ as a function of the deposition time t . The surface temperature is 225 K and an annealed surface is chosen as the starting surface [7].

Curve (a) is for pure Cu-on-Cu(111) growth. The interface becomes increasingly rough as growth proceeds.

In curve (b), the preadsorbed In atoms have a coverage $\theta_{\text{In}} = 0.08$, the Cu–In exchange process is turned off but repulsion between Cu and surface-substitutional In atoms is allowed. The interface becomes increasingly rough as growth proceeds. Only the first layer is smooth. All surfactant In atoms have been buried within the first layer. Similar results are obtained if none of the two processes are turned on.

In curve (c), the Cu–In exchange process is turned on but repulsion is not allowed. It is clear that the interface width is also increasing from layer to layer. Compared with curve (b), the interface width increases slowly, but shows no clear oscillation.

Table 1

Energy barriers for the Cu/In/Cu(111) system used in the model simulations. $N_i(N_f)$ is the number of in-layer nearest neighbors in the initial (final) state. Refer to Fig. 1 for the Cu–In exchange process

Diffusion type	Intralayer diffusion		Energy barrier (eV)	
	N_i	N_f	Cu/Cu(111)	In/Cu(111)
diffusion on terrace	0	0	0.12	0.03
	1 (Cu atom)	0	0.42	0.27
	1 (In atom)	0	0.47	0.01
diffusion to step			0.12	0.03
dissociation from step			0.67	0.53
	Interlayer diffusion			
Cu–In exchange process			0.55	
cross step directly			0.26 ^a	0.30

^aAlso see Ref. [21]

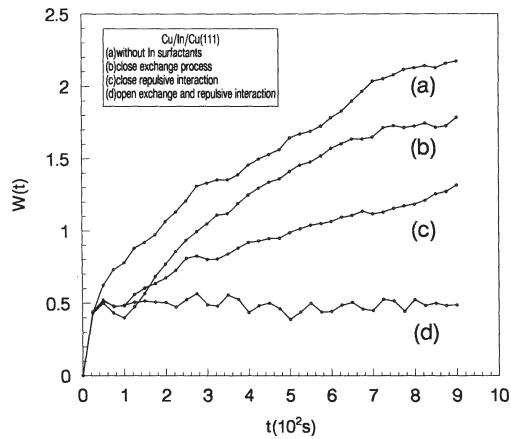


Fig. 2. The interface width $W(t)$ as a function of the deposition time t for the Cu/In/Cu(111) system under different conditions. For every case, the surface temperature is 225 K. For (b)–(d), the In coverage is $\theta_{\text{In}} = 0.08$, the deposition rate is 0.01 ML/s and $L = 600$. For details see the text.

In curve (d), the interface width $W(t)$ displays perfect oscillations indicating LBL growth where both Cu–In exchange process and repulsive interaction are turned on. After 10 layers are grown, about 68% of preadsorbed In atoms have been buried in lower layers.

From the above results, it is obviously seen that our repulsion model can apply to the Cu/In/Cu(111) system. Surfactant In atoms induce LBL growth through segregation and repulsive interaction mechanisms. Comparing curves (b), (c), (d), we know that neither of the two mechanisms can induce LBL growth alone. In the Cu/In/Cu(111) system, the re-

pulsion network constructed by surface-substitutional In atoms results in an increase of terrace barriers for Cu adatoms on average, so island density is enhanced. Enhanced Cu island density has been observed in the experiment [7]. This can increase interlayer mass transport and induce LBL growth. The segregation process ensures that In atoms can continue to influence the growth mode of successive layers. If the segregation process is turned off, only one smooth layer (first layer) is obtained (see curve (b) in Fig. 2.).

We have also investigated the effect of surfactant coverage for the Cu/In/Cu(111) system. The simulated results show that the roughness of the interface will increase rapidly at $\theta_{\text{In}} = 0.01$ and $\theta_{\text{In}} = 0.03$. Clearly, if the surfactant coverage is too low, an average increase in the terrace barriers for Cu adatoms is very small, island density can be enhanced only a little. So, LBL growth can not be induced.

3.3. Additional barrier ΔE and surfactant mechanism

Now let us discuss the effects of surfactants in the above metal system, Cu/In/Cu(111). A necessary condition for LBL growth is rapid interlayer mass transport. It is imaginable that surfactants must have enhanced interlayer mass transport in some way. In order to assess the interlayer mass transport during the growth quantitatively, Meyer et al. introduced a ratio factor $R_{0,C}/R_{1,C}$ [20],

$$\left(\frac{R_{0,C}}{R_{1,C}}\right) = \left(\frac{h_0}{h_1} + \frac{2 \exp(\Delta E/KT)}{R_{1,C}}\right)^{1/2}, \quad (5)$$

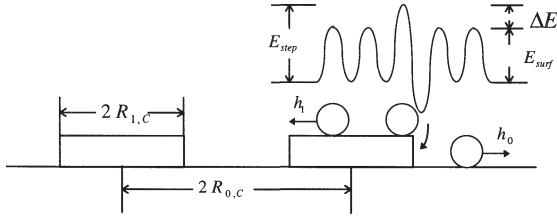


Fig. 3. Schematic diagram for Meyer's ratio factor $R_{0,C}/R_{1,C}$ and potential diagram for adatoms. $R_{1,C}$ is the critical radius of the first-layer island; $R_{0,C}$ is the measure of the spacing between the center of first-layer island. ΔE is the difference between the terrace barrier E_{surf} and the step-edge barrier E_{step} . For details see the text.

where $R_{1,C}$ is the critical radius of the first-layer island (the radius of the first-layer island at the onset of second-layer nucleation), $R_{0,C}$ is the measure of the spacing between the centers of first-layer islands, h_0 and h_1 are the hopping probabilities on the substrate and the first-layer island, respectively, and the additional barrier ΔE is the difference between the hopping barriers on the terrace and step edges, $\Delta E = E_{step} - E_{surf}$ (see Fig. 3). The ratio $R_{0,C}/R_{1,C}$ is close to 1 for smooth growth and larger than roughly 1.5 for 3D island growth.

It is clear from Eq. (5) that there exist multiple possibilities to decrease the value of $R_{0,C}/R_{1,C}$. In a pure system, $h_0 = h_1$, thus, the most efficient way to decrease the value of $R_{0,C}/R_{1,C}$ is to increase the growth temperature. Because low-temperature layer-by-layer growth is often desired, the next choice is to reduce ΔE . There exist two ways to reduce ΔE . One way is to reduce the step-edge barrier E_{step} , the other is to increase the terrace barrier E_{surf} . An increase of the terrace barrier E_{surf} will induce enhanced island density. Apparently, either a reduced E_{step} or an enhanced island density can enhance interlayer mass transport. In the Cu/In/Cu(111) system, surfactants In atoms preferably stay at a surface-substitutional site and repel Cu atoms approaching them. It is the repulsion network that leads to an increase of the average diffusion barriers for Cu atoms on terraces E_{surf} and enhanced island density.

Our (1 + 1)-dimensional model is simple but enough for qualitative descriptions. For the unannealed surface, due to $V_{Cu-Cu} < V_{Cu-In}$, many small islands centering about In atoms are formed in the early stage of growth in two dimensions. This phenomenon occurs in one dimension as well, the only

difference is the dimensionality of the island. From the second layer on, the repulsion network starts to take into effect. For two dimensions, after the deposited Cu atoms enter the repulsive network, they tend to avoid those repulsive centers In and aggregate to small islands between those In atoms. As in two dimensions, many small islands are formed between the surface-substitutional In atoms in (1 + 1)-dimensional simulations. The island density N satisfies the scaling relation: $N \sim r^\lambda \exp(\lambda\beta E_{surf})$, r is the deposition rate. In two dimensions, $\lambda = \frac{1}{3}$, and in one dimension $\lambda = \frac{1}{4}$ [22]. Therefore, an increase of N implies an increase of the diffusion barrier E_{surf} under the same growth conditions. It is the repulsion network that leads to an increase of E_{surf} on average. Our simulated results show that the growth mode of Cu/In/Cu(111) also depends on In coverage, this proves that an increase of E_{surf} is a global effect of surfactant network. Based on the above analysis, we can conclude that the (1 + 1)-dimensional model we used conforms with the real growth process in a qualitative manner but quantitative descriptions are different apparently.

4. Summary and conclusion

We have studied a surfactant-mediated homoepitaxial metal system, Cu/In/Cu(111), using first-principles calculations and kinetic Monte Carlo simulations. Our results show that the repulsion model is suited to the Cu/In/Cu(111) system.

For the Cu/In/Cu(111) system, surfactants In increase the terrace barrier E_{surf} by a repulsive interaction network. In this metal system, surfactants In can segregate effectively, which is a necessary condition for surfactants.

Our calculated results also show that the additional barrier ΔE is an essential physical quantity in determining film growth mode. Only if ΔE become smaller, will smooth growth be induced. Increasing E_{surf} is proved to be an effective way.

It is noteworthy that (1 + 1)-dimensional simulation is relatively simple but is enough for qualitative analysis. At present, we are performing (2 + 1)-dimensional simulations in order to get a deeper insight into the surfactant mechanisms.

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References

- [1] M. Copel, M.C. Reuter, E. Kaxiras, R.M. Tromp, *Phys. Rev. Lett.* 63 (1989) 632.
- [2] D.J. Eaglesham, F.C. Unterwald, D.C. Jacobson, *Phys. Rev. Lett.* 70 (1993) 966.
- [3] R.M. Tromp, M.C. Reuter, *Phys. Rev. Lett.* 68 (1992) 954.
- [4] H.J. Osten, J. Klatt, G. Lippert, E. Bugiel, S. Higuchi, *J. Appl. Phys.* 74 (1993) 2507.
- [5] H.A. van der Vegt, H.M. van Pinxteren, M. Lohmeier, E. Vlieg, *Phys. Rev. Lett.* 68 (1992) 3335.
- [6] S. Esch, M. Hohage, T. Michely, G. Comsa, *Phys. Rev. Lett.* 72 (1994) 518.
- [7] H.A. van der Vegt, J. Alvarez, X. Torrelles, S. Ferrer, E. Vlieg, *Phys. Rev. B* 52 (1995) 17443.
- [8] Zhenyu Zhang, M.G. Lagally, *Phys. Rev. Lett.* 72 (1994) 693.
- [9] V. Fiorentini, S. Oppo, M. Scheffler, *Appl. Phys. A* 60 (1995) 399.
- [10] D.E. Ellis, G.S. Painter, *Phys. Rev. B* 2 (1970) 2887.
- [11] Pei-Lin Cao, D.E. Ellis, A.J. Freeman, *Phys. Rev. B* 25 (1982) 2124.
- [12] Pei-lin Cao, D.E. Ellis, A.J. Freeman, Q.Q. Zheng, S.D. Bader, *Phys. Rev. B* 30 (1984) 4146.
- [13] Wu Yue, Pei-lin Cao, *Surf. Sci.* 179, L26.
- [14] P.J. Feibelman, *Phys. Rev. Lett.* 65 (1990) 729.
- [15] R. Gomer, *Rep. Pro. Phys.* 53 (1990) 917.
- [16] A.M. Bowler, E.S. Hood, *J. Chem. Phys.* 94 (1991) 5162.
- [17] Pei-Lin Cao, *Phys. Rev. Lett.* 73 (1994) 2595.
- [18] L. Hansen, P. Stoltze, K.W. Jacobson, J.K. Norskov, *Phys. Rev. B* 44 (1991) 6523.
- [19] C.D. Van Siclen, *Phys. Rev. B* 51 (1995) 7796.
- [20] J.A. Meyer, J. Vrijmoeth, H.A. van der Vegt, E. Vlieg, R.J. Behm, *Phys. Rev. B* 51 (1995) 14790.
- [21] M. Breeman, G.T. Barkema, M.H. Langelaar, D.O. Boerma, *Thin Solid Film* 272 (1996) 195.
- [22] M. Bartelt, J.W. Evans, *Phys. Rev. B* 46 (1992) 12675.