EFFECTS OF ATOMIC INTERACTIONS IN TWO COMPONENT SUBMONOLAYER GROWTH

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Abstract. We discuss effects of the different chemical bondings on the island morphology and on the island density scaling in two-component submonolayer growth. Different regimes depending on the strength of the mutual interactions and on the relative mobility of species are described and studied by kinetic Monte Carlo simulations using a two-component solid-on-solid growth model. Results for the temperature and flux dependence of the island density as well as examples of the surface morphologies are presented.

1. Introduction

Recent progress in both experimental techniques and theoretical modeling of epitaxial growth allowed to improve our understanding of growth mechanisms on the atomic scale. In particular, a satisfactory understanding of growth in homoepitaxial systems is beginning to emerge. Many results were accumulated by basic material-oriented research as well as by general studies in the spirit of statistical mechanics. For example, the processes of nucleation and aggregation in single component submonolayer growth [1] are now well understood.

On the other hand, practically important materials prepared by growth contain several components or impurities. Our present understanding of the real microscopic processes going on in such systems is rather incomplete.
The investigation of multicomponent growth is more complicated not only because we have to consider more material parameters than in homoepitaxy, but because there are additional possible atomistic processes which have to be considered (inlayer or interlayer exchange, floating of adsorbates on the surface or the island edges, additional energy barriers due to island or step edge decoration etc.).

Multicomponent growth is controlled by the interactions between species. The interactions are determined by the chemical nature of components, as well as by the geometrical positions of the atoms. There are two basic features of submonolayer multicomponent growth which affect the surface morphology: effects of the strain due to atomic mismatch, and effects of the different chemical bondings between components of the system. Although it is broadly accepted that the presence of strain plays a crucial role in heteroepitaxy, in particular in the formation of ordered nanostructures, the different chemical bondings by themselves can result in interesting effects. As an example we may mention Hwang’s STM study of growth of Co on Ru(0001) with predeposited Ag [2]. He observed the formation of dendritic islands, despite the fact that neither of the two component metals exhibit this behavior. Hwang suggested that this can be explained by chemically induced step edge diffusion barriers between domains of different species, which should generally exist in multicomponent film growth. Another example are the effects of phase separation in multilayer molecular beam epitaxy [3].

In this paper, we concentrate on effects of the difference in chemical bondings between the atoms of a two-component system growing in the submonolayer regime. We discuss the effects on the resulting island morphology, and address the question of the modification of island density scaling.

We present some general considerations on different growth regimes in two component growth in Section 2. In the next Section 3, we describe a model for submonolayer two-component growth. Section 4 very briefly recalls the scaling law for the island density. In section 5, we discuss the case of a small concentration of one component. Section 6 contains results of kinetic Monte Carlo simulations of two component alloy growth. In particular, we show how the scaling of the island density is modified by the relative mobility of the components and interactions between them.

2. Different regimes of multicomponent growth

Growth in the presence of more than one type of particles is realized in various ways. The simplest scenario is the deposition of a certain type of particles on a substrate composed from a different material. This is usually
called heteroepitaxy. Interesting effects like growth-induced surface alloying of species which are immiscible in the bulk have been observed in such systems.

There are many experimental studies of growth in which two or more different components were deposited on a substrate consisting in general of a different material (see e.g. [4]). In the case of multicomponent growth, we need to distinguish different regimes of growth. The species can be either \textit{codeposited} simultaneously with generally different fluxes, or deposited sequentially, one of the species being \textit{predeposited}. We restrict ourselves in this paper to the simplest situation of two component growth. We call the components \textit{A} and \textit{B}, and we consider the situation where an alloy consisting of \textit{A} and \textit{B}, or a material (\textit{A}) in the presence of impurities (\textit{B}) grows on a certain substrate.

Important material parameters in submonolayer growth are the strengths of the interactions, both laterally and perpendicular to the surface. In comparison to homoepitaxy, two-component growth contains many more material parameters. However, within a certain temperature window only some of them may be important. The crucial parameter is the interaction between particles of different type. It can be both attractive or repulsive. We consider here the former. Depending on the relative strength of this interaction with respect to the interactions between particles of the same type, one can observe \textit{intermixing} (possibly leading to antiferromagnetic-like ordering) or \textit{phase separation}. The second important parameter is the relative mobility of the different species.

To simplify the classification, we fix one lateral interaction, let us say between \textit{A} and \textit{A}, and the mobility of one species, let us say of \textit{A}. The interaction between \textit{A} and \textit{B} and the interaction between \textit{B} and \textit{B} can be stronger or weaker than the interaction between \textit{A} and \textit{A}, and the mobility of \textit{B} can be higher or lower than the mobility of \textit{A}. This yields 12 qualitatively different situations of submonolayer growth in a bicomponent system. (In the case of the multilayer growth, such classification cannot be easily done due to the presence of additional interlayer processes.) It is important to note that the precise values of parameters needed to decide in which regime growth proceeds are often not well known. In this situation, it seems to be useful to explore different possible effects on a general level. We are not going to analyze all the situation here but we discuss some partial results.

3. Two-component submonolayer growth model

To carry out an effective analysis we need a reasonably simple, yet flexible model. Kinetic Monte Carlo (KMC) simulations proved to be a useful tool
for evaluating the importance of various microscopic processes. We use the variant of the solid-on-solid model with two surface species described in detail in [5]. The basic microscopic processes are random deposition and migration. Two types of particles are deposited with fluxes $F_A$ and $F_B$. In the case of codeposition the concentration of the two components is changed by the variation of the ratio $F_A/F_B$.

Diffusion is modeled by hopping to nearest-neighbor sites with the rate $R^X_D = k_0 \exp(-E^X_D/k_BT)$ for a particle of the type $X = A$ or $B$. The energy barrier $E^X_D = E^X_{\text{sub}} + \sum_{Y=A,B} n^{XY} E^{XY}_n$ depends on the interaction with the substrate (the first term) and on the lateral neighbors (the second term).

The interaction with the substrate is affected by the particle beneath the particle under consideration. It may be a substrate particle, which can be in general of a type different from $A$ or $B$ (let us call it $C$), or a previously deposited particle of type $A$ or $B$. We have in general six possibilities: $E^{AC}_{\text{sub}}$, $E^{BC}_{\text{sub}}$, $E^{AA}_{\text{sub}}$, $E^{BA}_{\text{sub}}$, $E^{AB}_{\text{sub}}$, $E^{BB}_{\text{sub}}$. However, in the situation of a low coverage and fast descent to the lower terrace one can suppose that only $E^{A}_{\text{sub}} = E^{AC}_{\text{sub}}$ and $E^{B}_{\text{sub}} = E^{BC}_{\text{sub}}$ are the relevant two parameters controlling the mobility of both particle types.

The interaction with the nearest-neighbors is controlled by bond counting, i.e. $n^{XY}$ is the number of nearest-neighbor $X-Y$ pairs and $E^{XY}_n$ the corresponding contribution to the barrier, with $E^{AB}_n = E^{BA}_n$. In all examples presented in this paper $E^{AA}_n = 0.3$ eV, $E^{A}_{\text{sub}} = 0.8$ eV and $k_0 = 10^{13}$ Hz.

4. Island density scaling

We call the island density $N$. In homoepitaxy, the scaling relation

$$N \sim (F/D)^{\chi}, \quad \chi = \frac{i^*}{i^* + 2} \quad (1)$$

between the deposition flux $F$ and the adatom diffusion coefficient $D$ has been well established theoretically [6–8] numerically [8–12] and experimentally [13]. In (1), $i^*$ denotes the size of the largest unstable cluster.

Little is known about the details of nucleation during submonolayer growth of two component systems. The presence of the second species affects the nucleation of the first one and vice versa. An obvious complication is that there are different types of islands. In principle, one can consider three island densities: $N_A$ ($N_B$) for islands composed only from $A$ ($B$), and $N$ for islands composed from both particle types. In the case of mixing, there is no problem, since $N$ is the relevant quantity. The situation is less clear in the presence of phase separation. Here islands composed only from one type of particles may exist for weak or repulsive $A-B$ interactions.
5. Effects of adsorbates

The situation is simpler if the coverage of one of the components is much smaller than the total coverage (let us say \( \theta_B \ll \theta \), then the \( B \)-component is an impurity), or if there is another mechanism like floating of one component (\( B \)) on the edges of the islands of the other component (\( A \)), since then \( N_A \approx N \).

Several microscopic mechanisms by which impurities could alter the relationship (1) were considered in the literature. First, impurities may act as nucleation centers, thus effectively decreasing \( i^* \) and therefore \( \chi \); in the extreme case of immobile adatom traps, the limit of spontaneous nucleation with \( i^* = \chi = 0 \) would be realized \([12, 14]\). Recently, we have shown that the predeposition of only a low concentration of impurities (\( \theta_B \) a few thousandth of ML) can lead to a severalfold increase of the island density \([15]\). However, the increase significantly depends on the mobility of the adsorbates. In the case of essentially immobile adsorbates (\( E_{B_{sub}} = 5 \) eV), a new feature in the flux dependence of the island density appears. Instead of a single power law relationship, there is a plateau where \( N \approx \theta_B \), reflecting the dominance of heterogeneous nucleation in a certain flux \([15]\) (temperature \([16]\)) interval. When its origin is not recognized, the evaluation of such a plateau within the usual analysis of island density scaling \([1]\) may lead to an anomalously low estimate of the adatom diffusion barrier, as well as to an anomalously small preexponential factor. This effect has been invoked \([17]\) to explain the extremely low diffusion prefactors reported recently for several metal surfaces \([18]\).

Second, impurities decorating the island edges may induce energy barriers to attachment. Kandel \([19]\) predicted using a rate equation theory that, provided these barriers are sufficiently strong, the exponent \( \chi \) in (1) is increased such that the above expression is replaced by \( \chi = 2i^*/(i^* + 3) \). Also this mechanisms implies an increase of the island density compared to the case of pure homoepitaxy. We found in KMC simulation that the key kinetic process for growth of decorated islands is the activated exchange of impurities and adatoms \([20]\). The rate of this process is taken as \( k_{ex} = k_0 \exp(-E_{ex}/k_BT) \), where \( E_{ex} \) is the corresponding activation barrier. In this simulation the barriers for exchange \( E_{ex} \) and for the \( B \)-mobility \( E_{sub} \) are fixed at \( E_{ex} = E_{B_{sub}} = 1 \) eV. We observed well decorated islands for both \( E_{AB_n} < E_{AA_n} \) and \( E_{AB_n} > E_{AA_n} \) (left panel of Fig. 1). We found that, in our case \([5]\), the floating mobile adsorbates indeed strongly increase the island density but without appreciably changing its power-law dependence on the flux (right panel of Fig. 1). The increase is stronger for larger \( E_{AB_n} \), and only slightly higher for predeposition than for codeposition. We also observed a stronger coverage dependence of the island density in comparison...
with homoepitaxy (right panel of Fig. 1). This was interpreted as a delay of the saturation regime, where the island density becomes independent of coverage. The coverage dependence is again more pronounced for strongly interacting adsorbates, but it is weaker in the case of predeposition than for codeposition.

Figure 1. Left panels: Examples of configurations obtained by codeposition with fluxes $F_A = F_B = 0.004$ ML/s at temperature $T = 500$ K using parameters: $E_{ex} = 1$ eV, and $E_{AB}^{n} = 0.4$ eV (upper subpanel), $E_{AB}^{n} = 0.2$ eV (lower subpanel). Closed (open) circles represent $A$ ($B$) atoms. Coverage $\theta = \theta_A + \theta_B = 0.2$ ML. We show only $50 \times 50$ sections of larger simulation boxes. Right panel: Averaged island density $N_A$ as a function of flux $F_A$ in codeposition with $F_B = F_A$ for several values of the total coverage $\theta$ and different energy barriers: $E_{AB}^{n} = 0.2$ eV - open symbols, $E_{AB}^{n} = 0.4$ eV - filled symbols. The exchange barrier $E_{ex} = 1$ eV. The behavior in homoepitaxy ($F_B = 0$) is shown for comparison.

Third, it has been argued on the basis of KMC simulations [21] that repulsive impurities can alter the exponent $\chi$ in (1) by rendering the diffusion of the adatoms anomalous, in the sense that their mean square displacement behaves as $\langle x^2 \rangle \sim t^\alpha$ with $\alpha < 1$. A scaling analysis for $t^\gamma = 1$ then predicts that $\chi = \alpha/(1+2\alpha) < 1/3$, i.e. the island density scaling exponent is predicted to decrease in this case.

6. Island density in binary alloy

In this section, we study nucleation in a situation where the concentration of both species is comparable. We shall discuss effects of the different mobility of both components and of the variation of the $A-B$ and $B-B$ interactions; as before, the mobility of $A$-atoms and $A-A$ interaction is fixed: $E_{sub}^A = 0.8$ eV, $E_{n}^{AA} = 0.3$ eV. We consider (i) the regime of phase separation, $E_{AB}^n =$
0.2 eV and $E_{n}^{BB} = 0.4$ eV, and (ii) the regime of the intermixing, $E_{n}^{AB} = 0.4$ eV and $E_{n}^{BB} = 0.2$ eV. In all simulations the particles are codeposited and the results are analyzed at the total coverage $\theta = 0.1$ ML.

In Fig. 2, we show the island density $N$ as a function of the inverse temperature for different mobilities of $B$-component in the regime of phase separation for codeposition with fluxes $F_A = F_B = 0.001$ ML/s (left panel) and $F_A = 0.001$ ML/s, $F_B = 0.0001$ ML/s (right panel). The behaviour in homoepitaxy, the case when there is no $B$-component, is shown for comparison. One can see that there is a substantial increase of the island density. Similar as for the case of immobile impurities, there is the indication of a plateau for the case of the lowest mobility of the $B$-component for both concentrations.

Hence, the mobility of the atoms of one component strongly influences the island density of the growing alloy even its concentration is small. Note that if the mobility of $B$ is higher than the mobility of $A$, then the island density is lower than in homoepitaxy for $F_A = F_B = 0.001$ ML/s, but not for $F_A = 0.001$ ML/s, $F_B = 0.0001$ ML/s. If one analyzes separately the density $N_A$ of islands composed only from $A$ (not shown) no clear picture appears.

The change of the island density with mobility is accompanied by a change of the island morphology. This is illustrated in the left column of Fig. 3 showing configurations at $T = 500$ K for different mobilities of $B$-atoms ($F_A = F_B = 0.001$ ML/s). We can see a transition from a situation in which $A$-islands are incorporated with comparably large $B$-islands into
Figure 3. Examples of configurations for different B-mobility from top to bottom: $E_{\text{sub}}^B = 0.6$ eV, $E_{\text{sub}}^B = 0.8$ eV, $E_{\text{sub}}^B = 1.0$ eV, $E_{\text{sub}}^B = 1.2$ eV and various regimes: phase separation with fluxes $F_A = F_B = 0.001$ ML/s (left column) and with fluxes $F_A = 0.001$ ML/s, $F_B = 0.0001$ ML/s (middle column), and intermixing with fluxes $F_A = 0.001$ ML/s, $F_B = 0.0001$ ML/s (right column). Closed (open) circles represent A (B) atoms. The total coverage $\theta = 0.1$ ML, temperature $T = 500$ K. We show only $50 \times 50$ sections of larger simulation boxes.
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Figure 4. Temperature (left panel) and coverage dependences (right panel) for codeposition with different fluxes $F_A = 0.001$ ML/s and $F_B = 0.0001$ ML/s. Left panel: density of islands $N$ as a function of the inverse temperature for low mobility of $B$ component, $E_{sub}^{B} = 1.2$ eV and different energy barriers $E_n^{BB}$ and $E_n^{AB}$, coverage is $\theta = 0.1$ ML. Right panel: density of islands $N$ (filled symbols) and free adatoms $n$ (open symbols) as a function of coverage $\theta$ for three different energy barriers $E_{sub}^{B} = 1.2$ eV (circles), $E_{sub}^{B} = 1.0$ eV (diamonds) and $E_{sub}^{B} = 0.8$ eV (squares), $E_n^{BB} = 0.4$ eV and $E_n^{AB} = 0.2$ eV, $T = 500$ K.

one island, to a situation in which there are $A$-islands attached to small $B$-islands. The second column corresponds to the right panel in Fig. 2. The effect of $B$-mobility on the island morphology (as well as on the island density cf. Fig. 2) is now weaker. The right column shows the situation in the intermixing regime.

The left panel of Fig. 4 compares island densities in the regimes of phase separation and intermixing for low $B$ mobility and two $B$-$B$ interaction strengths. We can see that in the intermixing regime the presence of a small fraction of a less mobile component increases the island density more than in the phase separation regime (cf. the middle and the right columns in Fig. 3). The increase of the strength of $B$-$B$ interaction has only a small effect, except for high temperatures in the phase separation regime.

In the right panel of Fig. 4 we display the coverage dependence of the island density and the density of free adatoms in the phase separation regime for different mobilities of the $B$-component. There is a delay of the saturation in the island density and of decrease of the free adatoms density. The effect is stronger for lower $B$-mobility. It can be explained by the continuous creation of centers for heterogeneous nucleation.

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