

# Film–substrate interface mixing in the energetic deposition of Ag on Cu(001)

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## Abstract

Molecular dynamics simulations are performed to investigate the interface mixing between the growing film and the substrate during energetic (3–9 eV) deposition of Ag on Cu(001). The statistics of single Ag atom impacts on a Cu(001) surface are presented with respect to the impact energy, substrate temperature, and different angles of incidence. It is shown that the probability of exchange is at its highest in the vicinity of a bridge position between two surface atoms. Furthermore, it is shown that incidence at certain directions leads to great intermixing. In addition, the direct simulations of the deposition process of Ag atoms on Cu(001) are performed, and the growth of a film and the creation of a metastable alloy near the interface are monitored as a function of time. The concentration profiles are then investigated with a simple model based on the probability of a single exchange event. © 1999 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

In recent years the use of layered structures in different technological applications has increased because multilayer systems have many interesting physical properties. For instance, by using layered heterostructures in compound semiconductors one can change the electronic band structure of a semiconductor to make the technology of blue–green lasers possible [1]. With multilayer structures in metallic systems one can change the magnetic properties of these systems which can make the technology of high-density information storage

devices possible [2]. In particular, it is quite difficult to obtain high-quality layers with sharp interfaces in multilayer metallic systems. On the other hand, in some cases, like in catalytic systems, the formation of a surface alloy in an ultrathin film on a substrate might be the desired property [3]. Experimental studies [4] have shown that interface mixing may have quite a strong influence on the electronic and magnetic properties of different systems. Thus, it is of interest to know how to control interface mixing between the growing film and the substrate during a growth process.

The manufacture of layered systems can be done e.g. by using molecular beam epitaxy (MBE). However, it requires considerable heating of the substrate during the growth process. High temper-

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ature processing leads to inevitable interlayer and bulk diffusion, which leads to undesirable properties in some multilayered systems. Thus, the lowering of temperature during epitaxial growth is of great importance for modern microelectronics technology [5]. However, due to the presence of the Ehrlich–Schwoebel barrier near the step edge, the mobility of adatoms on a surface at low temperature is not sufficient to promote layer-by-layer growth [6,25], but instead it leads to the three-dimensional growth of a film. One way to promote layer-by-layer growth is to enhance adatom mobility through energy transfer from energetic particles to the adatoms, e.g. as in ion beam-assisted deposition [7]. Recently, direct experimental evidence of adatom mobility enhancement due to ion bombardment using ion energies of 15–65 eV has been reported [8]. However, the ion bombardment has some drawbacks, e.g. defect and impurity formation in a growing film and/or substrate sputtering.

Another way to provide enhanced adatom mobility at low temperatures is energetic deposition, e.g. laser ablation deposition [9] and ion plasma sputter deposition (IPSD) [10]. The major difference between IPSD and MBE processes is the energy of depositing particles. Since in an IPSD process the depositing particles are sputtered from a target by ion beams, they have a considerably large energy of 2–30 eV [10]. Thus, in IPSD processes the adatoms of a growing film deposit on a surface with sufficient kinetic energy which then enhances the lateral atomic motion of adatoms on the surface. However, too high energies of adatoms lead to defect formation and substrate sputtering, as mentioned above. There are some numerical simulations that indicate surface sputtering and deep damage at impact energies of 80–100 eV for Cu/Cu systems [11,12] and 50 eV for a Co/Cu system [13]. Therefore, we restrict our present investigation to energies less than 10 eV.

There are some numerical studies on heterostructural films grown under deposition processes [14–16]. In these studies the depositing adatoms with kinetic energy higher than 3 eV produced impact-exchange events between adatoms and atoms in the film and substrate. Thus, the different atomic species intermix with each other near the

interface, forming a surface alloy. This mechanism is particularly important in the low temperature region, where other mechanisms for intermixing have been suppressed. In spite of the fact that some systematic simulations of heteroepitaxy have already been done, there are still some open questions about the effect of different physical conditions on the growth of a film, such as the incident angle of an adatom and the local environment of the surface of a substrate.

In this study, we investigate film–substrate interface mixing in the system of Ag on Cu(001) using semi-empirical molecular dynamics (MD). Under normal conditions Ag has limited solubility in bulk Cu, but there is some experimental evidence on the formation of Ag–Cu alloys on a Cu(001) surface [17]. This system was also studied earlier with computational methods [14,15,18–20], but only the adatom and monolayer systems and the structure and stability of the surface alloy formed. In this work, we make MD simulations in order to get detailed microscopic knowledge on the exchange processes of single atoms and the growth of a film on a substrate. We investigated the probability of exchange as a function of impact energy, arrival angle of an adatom and substrate temperature. From these results we can make a systematic analysis of how the growth conditions should be chosen to get a film with the desired properties. We also construct a simple model which can be used to predict e.g. the exchange probability from the concentration profile of substrate atoms in a film.

The paper is organised as follows. Section 2 contains a description of the method used in the calculations as well as a simple model for predicting exchange probabilities from concentration profiles. We present the results and a discussion in Section 3. Finally, a summary is given in Section 4.

## 2. Models used in calculations

### 2.1. Simulation model

The molecular dynamics simulations are made with finite atomic slabs with two atomic layers fixed on the bottom, the other layers being free,

Table 1

Characteristic energies for Ag adatom on Cu(001) surface compared with the values of other calculations based on the molecular dynamics/Monte Carlo corrected effective medium theory [19]. All data are given in electronvolts

	This work	Ref. [19]
Binding energy	−2.61	−2.66
Activation energy, jump diffusion	0.40	0.48
Activation energy, exchange diffusion	0.98	0.91

and periodic boundary conditions in the directions [100] and [010] parallel to the surface. We use the classical *NVE* ensemble. The equations of motion are solved using a leap-frog algorithm with a time step of  $10^{-15}$  s. A conventional spherical cutoff and a minimum image technique are used in the numerical simulations. We use an interaction potential of the embedded atom method (EAM) in our MD simulations [21]. For this potential the cutoff radius used is 5 Å.

There are, however, some open questions about the validity of the potential used in these calculations. First, we use interatomic potentials fitted to the equilibrium properties of corresponding crystals in the energy range 0.1–1 eV, while the energy range of our calculations is 3–9 eV. Our tests show that the short-range part of the EAM interaction potential for Ag–Cu dimers agrees well with that of the sputtering potential of Molier for Cu–Cu dimers in the energy range 3–10 eV [22]. This means that the repulsive part of the EAM potential is described with sufficient accuracy for the present calculations. Second, one does not know how well the mixed interaction of Ag–Cu is described in the EAM potentials. To check the validity of the Ag–Cu interaction model used in this work we performed calculations of energy barriers for surface diffusion of a single Ag atom on a flat Cu(001) surface. Table 1 shows the results together with the results of another computational method [19]. One can see that there is a good agreement between these two models, supporting the reliability of the potential parameters used in this work.

### 2.2. Probability model for layer-by-layer growth

We estimate the probability of a single exchange event between an adatom and a substrate atom as

a ratio of the number of exchange events ( $N_{\text{ex}}$ ) to the total number of impacts of single adsorbate atoms ( $N_{\text{tot}}$ ):

$$p = \frac{N_{\text{ex}}}{N_{\text{tot}}}. \quad (1)$$

One can derive (see Appendix A) an equation for the concentration profile of the substrate atoms in the deposited film:

$$P(m) = \left(1 - \frac{p}{2}\right) \left(\frac{p}{2}\right)^m, \quad 0 \leq m < l, \quad (2)$$

where  $l$  is the topmost layer of the film and  $p$  is the exchange probability. With this formula one can calculate the concentration of substrate atoms in a certain layer ( $m$ ) of a film if the exchange probability is known, or vice versa.

## 3. Results and discussion

### 3.1. Single exchange processes

At first we investigate the energetic impacts of a single Ag atom on the Cu(001) substrate using EAM MD. The slab representing the Cu substrate is 11 layers thick with 128 atoms per layer. The task is to estimate the probability of an exchange event for an atom falling on the substrate at a random position. However, the introduction of atoms on the whole surface area by using a random number generator is too time-consuming a procedure. Therefore, we use geometrical probabilities to handle the problem (see Fig. 1). The initial positions of Ag atoms are set in a plane, which is parallel to the surface and outside the range of interatomic interactions from the surface, forming a grid that covers half of the surface unit cell with a small step. This region is sufficient for most of the cases. Before the impact of an adatom, the atoms of the substrate receive random velocities corresponding to a Maxwellian distribution and the system is equilibrated at a given temperature during 10 000 time steps. Thus every run (landing of an atom on the substrate) starts from a statistically independent state of the substrate. The total number of attempts for each initial condition is

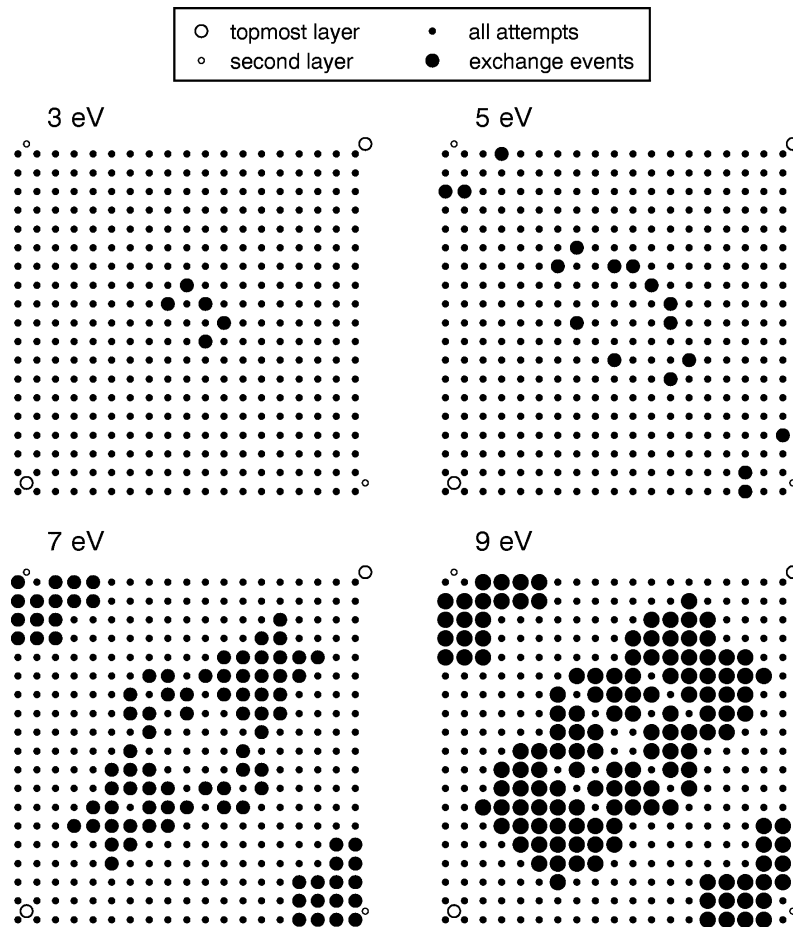


Fig. 1. Spatial distribution of exchange events on the surface for different values of kinetic energy of an adatom at normal incidence and temperature of the substrate  $T=0$  K. Large and small open circles represent the topmost and second atomic layer of the Cu substrate, respectively. Filled circles correspond to all the attempts for atom impacts and larger filled circles correspond to positions of successful exchange events. Horizontal direction is [100] and vertical direction [010]. The diagonal of the square corresponds to the Cu–Cu nearest-neighbour distance (2.55 Å).

361, corresponding to the different initial positions of the grid.

At the beginning of each run an Ag atom receives an initial momentum directed towards the surface. Atoms are deposited with impact energies in the range 3–9 eV, which corresponds to energies in sputtering deposition [10]. We observed that adatoms rapidly (during 2000 MD steps) lose their energy as they interact with the substrate. Large vertical shifts of the substrate atoms take place immediately after the impact. However, these disturbances quickly relax and the crystal order is recovered. Fig. 1 presents the region of exchange

for the different values of arrival energy at incidences normal to the surface and at zero substrate temperature. Although the zero temperature case is out of the validity range of the classical MD, we expect that our simulation allows a correct qualitative description of the influence of different factors on the exchange at low temperatures. Thus, we have not tried to investigate any quantum effects, but tried to omit the effect of lattice vibrations on the conclusion drawn from the behaviour of the system under different conditions. For impact energies larger than a definite threshold value (about 3 eV) the exchange events are

Table 2

Single exchange probabilities ( $p$ ) for Ag on Cu(001) as a function of the impact energy ( $E_{\text{kin}}$ ), temperature of the substrate ( $T$ ), and azimuthal angle ( $\phi$ ). The left part of the table shows the values of the different quantities (including the polar angle  $\theta$ ) during simulations

$E_{\text{kin}}$ (eV)	$T$ (K)	$\theta$ (°)	$\phi$ (°)	Quantities	Data				
3.0–9.0	0	0	0	$E_{\text{kin}}$ (eV)		3.0	5.0	7.0	9.0
				$p(E_{\text{kin}})$		0.014	0.047	0.258	0.396
5.0	0–300	0	0	$T$ (K)		0	100	200	300
				$p(T)$		0.047	0.166	0.194	0.252
7.0	0	35	0–45	$\phi$ (°)	–45	–30	0	30	45
				$p(\phi)$	0.116	0.152	0.360	0.349	0.374

observed. Fig. 1 also shows that the positions of the exchange events tend to locate slightly off of the centre of the line joining the nearest-neighbour surface atoms. While the impact energy is increased the exchange events also occur between second nearest neighbours similarly. Here we should also mention that for incidences normal to the surface an even smaller area of the surface unit cell could be used due to an additional symmetry axis, as can be seen in Fig. 1. The region of the exchange grows with increasing impact energy (see also Table 2). similar effects are observed when raising the temperature of the substrate (see Table 2). This is not surprising since the thermal motion of the substrate atoms enhances the mobility of the surface atoms and thus the exchange probability. Therefore, the higher the temperature of the substrate, the higher the probability of the exchange process.

We have also performed simulations with different angles of incidence. There are two angles to characterise the direction: a polar angle  $\theta$  which is the angle between the direction of an impact and the normal [001] of the surface, and an azimuthal angle  $\phi$  which is the angle on the plane of the surface, between the direction of an impact and the crystallographic direction [100] (a positive angle corresponds to a clockwise rotation). We have tested different values for the polar angle  $\theta$  while keeping the other parameters fixed (see Fig. 2). Our simulations show that the impacts with energy 7 eV and polar angle  $\theta$  greater than  $45^\circ$  do not produce any exchange events at all. This is because the adatom comes from too gentle an angle to the surface, and thus it considers the

substrate a mirror. At an angle of  $45^\circ$ , which corresponds to the direction [101], the adatoms do not see the second (or deeper) layer atoms at all. But as soon as the angle decreases below that value adatoms, while penetrating into the substrate, can bounce from second layer atoms to first layer atoms producing exchange events. The fit presented in Fig. 2 through the data points has nothing to do with reflecting planes but rather tells us about the open channels for adatoms to penetrate through the first atomic layer and to hit atoms in the second or third layer of the substrate.

To check the influence of the azimuthal angle  $\phi$  on the probability of the exchange events, we fixed the polar angle  $\theta = 35^\circ$  and varied the azimuthal angle in the range from  $-45^\circ$  to  $45^\circ$  (see Table 2).

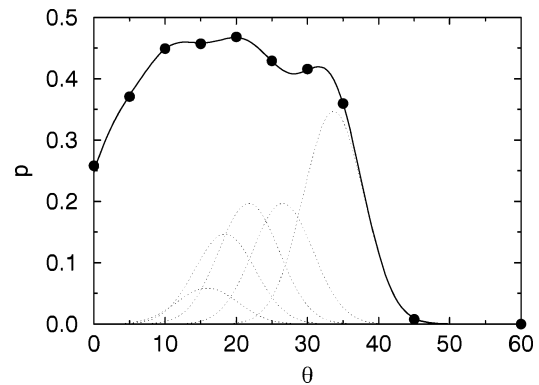


Fig. 2. The probability of exchange as a function of the polar angle  $\theta$  represented by filled circles ( $T=0$  K,  $\phi=0^\circ$ ,  $E_{\text{kin}}=7$  eV). The solid curve has been fitted to the data points by adding Gaussians located at the angles corresponding to the lattice directions  $[20k]$ ,  $k \geq 3$ . The first five Gaussian functions are presented with dotted curves.

If we only took the positive angles into consideration with the region used in simulations (see also Fig. 1) we would miss the generality of the behaviour of the system under the azimuthal angle. This is because in the general case we need the whole surface unit cell to be considered. The same effect as taking into account the whole surface unit cell is to consider the corresponding negative angles. Thus, for the general result of the azimuthal angles one should take an average of the exchange values with the angles  $\phi$  and  $-\phi$ . On the other hand, for instance, the azimuthal angles  $30^\circ$  and  $60^\circ$  give the same exchange probability because of symmetries. In this respect there is no meaningful dependence of the probability on the azimuthal angle, whereas there are some local regions that give larger exchange probabilities than others. In conclusion, there is a maximum at angles  $0^\circ$ ,  $90^\circ$  and so on, and an almost equal reduction in exchange probability between these angles. This behaviour may change if the temperature of the substrate is taken into account, because of different vibrational modes on surfaces. However, this is not investigated here any further.

### 3.2. Simulation of a growing film

Next we investigate the influence of exchange effect on the thin film growth by performing direct simulation of the deposition process. The process of thin film deposition is simulated by a flux of Ag atoms to the Cu substrate. In the simulation of a growing film the slab contains six layers of substrate with 450 Cu atoms in each layer. One bottom layer of the substrate is fixed to keep the centre of mass immobile. At the beginning of each simulation the substrate atoms have Maxwellian velocity distribution corresponding to a given temperature (300 K). After the equilibrium of the substrate is reached the growth process is started. One Ag adatom at a time is set at a randomly chosen position in a plane located outside the range of interaction above the surface. After that the atom is allowed to impact the surface with kinetic energy 7 eV, polar angle  $\theta = 35^\circ$  and zero azimuthal angle. Those atoms that drift back into the source direction by collisions with the beam or substrate atoms are deleted as they reach the

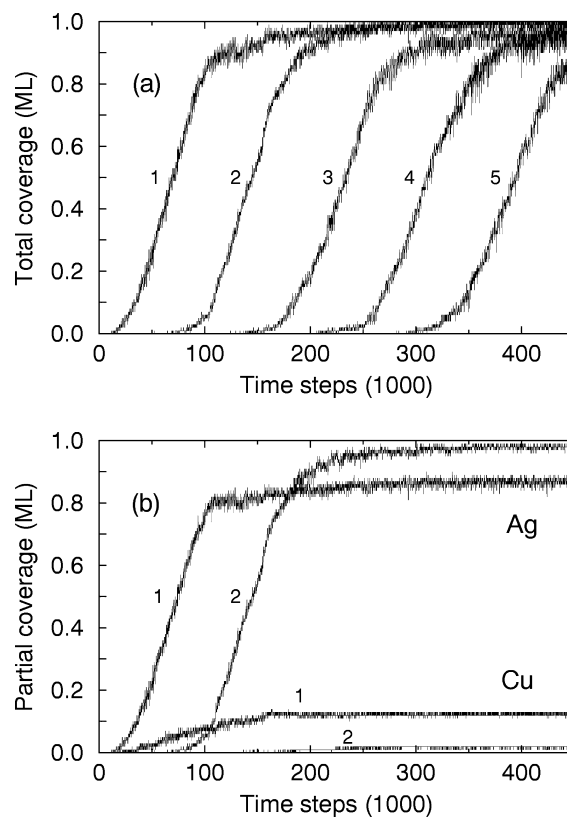


Fig. 3. (a) Total coverage for the growth of the first five Ag layers (1–5) on Cu(001) as a function of time steps ( $E_{\text{kin}} = 7$  eV,  $T = 300$  K,  $\theta = 35^\circ$ ,  $\phi = 0^\circ$ ) presented as monolayers. (b) Partial coverage of Ag and Cu for the first two grown layers (1–2) on Cu(001). For clarity, the coverages from the third layer and further are not presented in this picture.

upper plane of the simulation cell. The temperature is controlled by scaling the velocities of the substrate particles. A new atom is released into the system after each 200 time steps. After finishing the deposition of adatoms the system is equilibrated during an additional 10 000 steps. In such a way 4–5 monolayers (ML) of Ag are grown on a Cu(001) substrate. The choice of different parameters has been made to get the best possible statistics for calculations and to simulate similar conditions as used in the experiments [17].

To characterise the growth process we plotted a total and partial coverage in the film layers (Fig. 3). We can observe a well-ordered growth of an Ag film on the Cu(001) substrate, close to

Table 3

The number of different species ( $n$ ) in a certain layer, nearest-neighbour distances ( $d_{nn}$ ) in a layer, and interlayer spacing ( $d_{ll}$ ) between successive layers near the interface. The interlayer spacing is the distance between a layer and the one just below it. Nearest-neighbour distances and interlayer spacing are given in Ångströms

	$n(\text{Ag})$	$n(\text{Cu})$	$d_{nn}(\text{Ag-Ag})$	$d_{nn}(\text{Cu-Cu})$	$d_{ll}$
Third layer of the film	389	1	2.90	—	2.38
Second layer of the film	383	7	2.90	—	2.32
First layer of the film	358	52	2.82	—	2.18
First layer of the substrate	60	390	2.72	2.50	1.88
Second layer of the substrate	0	450	—	2.55	1.82

layer-by-layer mode (Fig. 3a). There is already about 0.6 ML coverage when the second layer begins to grow. Detailed information on the process of intermixing can be obtained by analysing partial coverages and the structure in the layers of the film. The intermixing of species in the interface layers of the film is represented in Fig. 3b. The penetration depth of Ag atoms into the substrate is only one layer, which indicates that, in this case, there are effectively no other exchange processes except for those between the surface and impacting atoms (see also Table 3).

The concentration of Cu atoms in the layers of the film decreases with increasing thickness of the film. This is not surprising since exchanges only take place on the surface. Even if the exchange probability was equal to 1, the behaviour would be qualitatively the same (see also Fig. 5). Fig. 3b shows that the content of Cu in the first Ag layer increases with increasing Ag coverage and reaches a maximum when there is about 0.95 ML and 0.8 ML total coverage in the first and second layer, respectively. Exchange processes between the adatoms and the first layer lead to a situation in which the partial coverage of Cu in the first layer does not increase any more, while it increases in the second layer. There is about 13% Cu in the first layer of the film when the second layer is complete. Similar processes are obtained for the growth of the second layer, but the maximum Cu content is only about 3%. The partial coverages of Ag for the third layers and so on are almost those of the total coverages in Fig. 3a and the partial coverage of Cu for the third layer is almost an order of magnitude smaller than that for the second layer (see also Fig. 5). As a result of exchange events

there is about 13% Ag in the first layer of the substrate (see Table 3). Thus it seems that only one or two layers of a surface alloy can be formed in this way. One can see from Table 3 that there are 450 atoms per layer in the Cu substrate, but as the Ag film starts to grow the number of atoms per layer decreases and reaches a value of 390. This is because of lattice mismatch between Ag (4.09 Å) and Cu (3.62 Å) [17]. The structure analysis of an Ag monolayer on Cu(001) has already been done by others [18,20] and these computational results are in good agreement with experiments [17]. Especially, Christensen et al. [20] have made a thorough analysis of the phase diagrams for surface alloys. For Ag/Cu(001) they concluded that the deposited material stays in the surface layer and does not penetrate the substrate, and that surface alloying, stable or metastable, occurs. The present results are thus in good agreement with the findings by Christensen et al. [20]. Thus, there is no need for a wide discussion about that in this paper. We only mention some data about our calculations and represent them in Table 3 and Fig. 4.

We have gathered the nearest-neighbour and interlayer distances in Table 3. One can see that the nearest-neighbour distance between Ag atoms in the growing film increases with increasing thickness of the film and then saturates to a value of 2.90 Å while the Cu–Cu distance in the substrate layers is 2.55 Å. The structure of the growing Ag film also changes from that of fcc(001) to fcc(111), which can already be seen in the pair correlation data for the first layer of the film (Fig. 4). This behaviour is due to the lattice mismatch between Ag and Cu as mentioned above. Thus, the Ag film

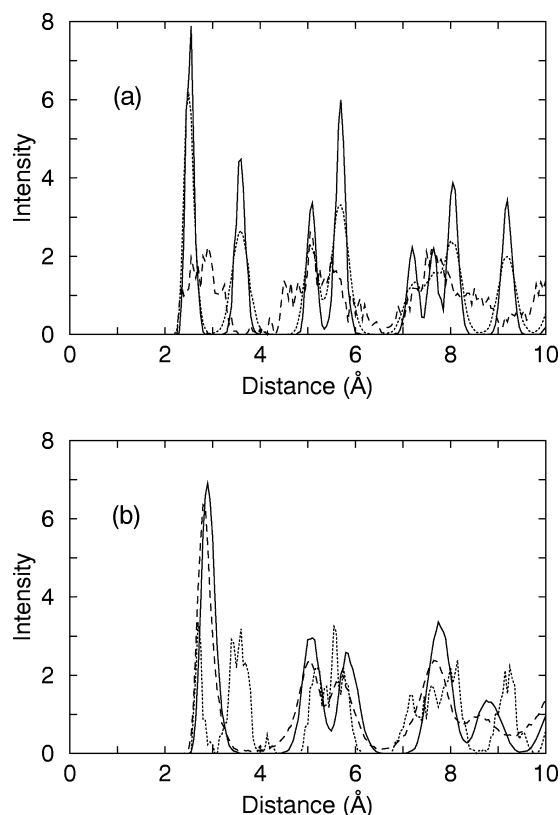


Fig. 4. Pair correlation functions in specific layers: (a) for Cu–Cu — the second layer (solid line) and first layer (dotted line) of the substrate, and the first layer (dashed line) of the film; and (b) for Ag–Ag — the first layer (dotted line) of the substrate, and the first layer (dashed line) and second layer (solid line) of the film.

grows as an fcc(111) structure on the Cu(001) substrate. Cu atoms have been distributed more or less randomly in the first layer of the films. The situation is not so clear in the case of the first layer of the substrate. The structure of this layer is fcc(001) and Ag atoms replace Cu atoms in fcc(001) surface sites. However, it seems that Ag atoms like to form small groups, two to three atoms in size, forming a web shape structure. The pair correlation function also indicates some kind of short-range structure for Ag–Ag. However, the time scales of these calculations might be too short for the Ag-c(10×2) or pseudo-Ag(111) structures seen by the experimentalists [17], and the structure

of the first layer of the substrate has been frozen to that existing when the other layers start to grow.

Our results seem to be at least in qualitative agreement with experiments. Here we give a short overview of the experimental results available [17]. Experiments show that at temperatures of 225 K and below there exists no surface alloy formation, while at temperatures of 300 K and above surface alloy is formed with a low coverage region, up to 0.13 ML of Ag on Cu(001), but only within the surface layer of the Cu substrate. The average distance between Ag atoms along the direction [110] on Cu(001) is 2.85 Å, while the bulk nearest-neighbour distance is 2.89 Å. The height of the Ag-c(10×2) island is 2.25 Å, while the Ag(111) step height on the Ag(111) surface is 2.36 Å. At medium coverage (0.13–0.7 ML) it has been found that Ag segregates on the surface. This is natural since the surface tension of Ag is considerably smaller than that of Cu [23]. At higher coverages, a rough growth morphology and 3D Ag(111) growth have been observed.

The concentration profile of Cu atoms in the deposited Ag film obtained from our simulation can be compared with that calculated using the probability model presented earlier in this paper, provided that the probability for a single exchange process is known. Fig. 5 represents the simulated and theoretical values of the concentration of Cu atoms in the Ag film as a function of the number of the atomic layer in the film. Theoretical estimates have been calculated using the value of the probability of exchange events equal to 0.396 obtained from MD simulations of single Ag atom impacts on a Cu(001) surface under the same conditions as the growth simulation. In Fig. 5 we have also presented the values of the theoretical maximum for the exchange, i.e.  $p=1.0$ .

There is a least-squares fit to the simulation data points in Fig. 5. The line corresponds to a probability of 0.288 based on the probability model. The discrepancy between the results (0.288 and 0.396) may be explained by different factors: insufficient statistics in MD simulations, too high flux of adatoms, neglecting the effects of local environment on the exchange probability between single adatoms and substrate atoms, and surface diffusion. The growth of the film is not exactly

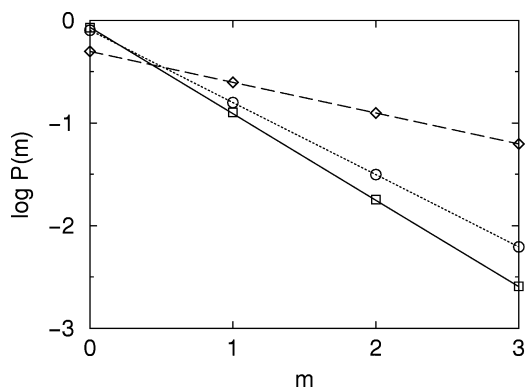


Fig. 5. The logarithmic profiles of Cu atoms in the growing film for the single exchange probabilities of 1.0 (diamonds and dashed line) and 0.396 (circles and dotted line) based on the present model and given as a function of the number of the layer in the film ( $m=0$  is the first layer of the substrate,  $m=1$  is the first layer of the film and so on). Squares represent the results of the MD simulation of the growing film ( $E_{\text{kin}}=7$  eV,  $T=300$  K,  $\theta=35^\circ$ ,  $\phi=0^\circ$ ). The solid line is the least-squares fit to the data points and corresponds to a probability of 0.288 based on the present model.

layer-by-layer. Exchanged Ag atoms near Cu atoms in the surface layer and the diffusion of exchanged Cu atoms on the surface change the exchange probability. Also, as the film is growing there are islands of different sizes forming edges and kinks on the surface. The characters of Ag and Cu atom diffusion on the film formed on the substrate differ from each other. This situation is changing all the time during the growth of the first few layers in the film. Thus, the different types of atom can migrate from a topmost layer to a lower terrace with different probabilities due to the different energy barriers near to an edge of a growing island. Thus, the effective exchange probability is not the same as that between a single adatom and the substrate. The agreement between simulation and theory could be improved by taking into account these effects in the probability model. This may lead to a method of analysing separately the effects of different factors on the growth process of a film in more detail in the future. In addition, the comparison between computational results and experiments is not so straightforward because of different time and length scales. In our calculations, for example, the time scale is too short to investigate interlayer diffusion or segre-

gation during the growth process. However, these things are not so important at low temperatures. In future, it may be possible to investigate such dynamic phenomena by increasing time scales [24].

#### 4. Summary

In this work we have studied film–substrate interface mixing due to the energetic impact of Ag adatoms on a Cu(001) surface with MD simulations. It was shown that for impact energies higher than the threshold of 3 eV exchange events between adatoms and substrate atoms take place. The probability of an exchange process rises with increasing impact energy and substrate temperature. The regions of exchange events are located between the surface atoms of the substrate. An incidence with polar angle of  $45^\circ$  and less provides exchange processes. This means that sharp interfaces and high-quality ultrathin films could be fabricated by deposition at large angles to the surface normal. On the other hand, one could be interested in a surface alloy formation. One can thus adjust the probability of exchange by changing the energy of arriving atoms and the substrate temperature to activate the formation of a surface alloy.

A direct simulation of a deposition process showed the mixing of substrate atoms in the film. We saw that the concentration profile of Cu atoms in the Ag film can be approximated by a simple power law. By using a more sophisticated probability model for the deposition process in future, it would be possible to analyse the interatomic potential between the substrate and adsorbate atoms by considering the concentration profile of the substrate atoms in the deposited film. However, only a few layers of a surface alloy can be made in this way. But this is often just what is needed for catalytic systems. On the other hand, if we want to grow layered structures on a substrate the interface mixing will be restricted near the interface for the case of Ag film growth on Cu(001). Furthermore, the results showed that the Ag film grows on Cu(001) with an fcc(111) structure, which is in accordance with experimental findings.

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## Appendix A

Assuming now that a film grows layer-by-layer, the probability that an impacting and a substrate atom change place is  $p$ , and there are  $n$  possible sites on a surface. The concentration profile of substrate atoms in the growing film can be derived in the following way. The probability that the first hit of an adatom on the surface removes an atom from the substrate, introduces it to the growing film and replaces the substrate atom with the adatom is  $p$ . For the second hit there are two possibilities: the impacting atom hits (i) the substrate or (ii) the first growing layer. The probability for the second hit to pick a substrate atom to the first layer through case (i) and (ii) is  $(n-1/n)p$  and 0, respectively. This is because in the second case the impacting atom goes to the first layer either by exchange or by diffusion, since layer-by-layer growth is assumed (i.e. we take a large enough time between consecutive impacts). For the third hit there are again two possibilities. The first case leads to the probability  $(n-2/n)p$  for the exchange and the second one to the probability zero as above.

After the first layer of the film has been completed the probability for an arbitrary first layer atom to be a substrate atom [ $P^t(1)$ ] can be obtained by summing the probabilities of the individual hits and then dividing the sum by  $n$ :

$$P^t(1) = \frac{1}{n} \sum_{k=1}^n \frac{n-k+1}{n} p = \frac{n+1}{2n} p.$$

The superscript  $t$  refers to the topmost layer of the film. Now for the first layer of the substrate we have:

$$P(0) = P^t(0) - P^t(1) = 1 - \frac{n+1}{2n} p,$$

where  $P^t(0)$  is the probability of finding a substrate atom in the surface layer of the clean substrate.

The growth of the second layer of the film is similar to that of the first layer provided the probability of the exchange process is changed from  $p$  to  $P^t(1)p$  because the exchange is assumed to occur between an adatom and the topmost layer only, and thus the probability of an adatom hitting a substrate atom in the first layer of the film is reduced by a factor of  $P^t(1)$ . The procedure above can be generalised for an  $l$ -layer film, leading to the probability of finding a substrate atom in the topmost layer:

$$P^t(l) = \left( \frac{n+1}{2n} p \right)^l,$$

and the probability of finding a substrate atom in the  $m$ th layer of the  $l$ -layer film:

$$P(m) = P^t(m) - P^t(m+1) = \left( 1 - \frac{n+1}{2n} p \right) \left( \frac{n+1}{2n} p \right)^m,$$

$$0 \leq m < l.$$

If the area of the surface tends to infinity ( $n \rightarrow \infty$ ) we finally get the probabilities:

$$P^t(l) = \left( \frac{p}{2} \right)^l,$$

$$P(m) = \left( 1 - \frac{p}{2} \right) \left( \frac{p}{2} \right)^m, \quad 0 \leq m < l$$

for the  $l$ -layer film. The formulae above can be used to calculate the concentration profile (normalised to unity) of the substrate atoms in the deposited film provided the exchange probability  $p$  is known.

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