

Interaction between Cu atoms and isolated ^{111}In probe atoms on a Cu(100) surface

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Perturbed angular correlation spectroscopy offers a detailed picture of the sites and mobility of individual ^{111}In probe atoms deposited under various conditions onto Cu(100) surfaces. Generally four sites can be distinguished: the adatomic terrace and step sites, plus the substitutional terrace and step sites. After investigating the behavior of In on flat Cu(100) surfaces we address some specific issues: the interaction between In adatoms and Cu islands, the surface segregation of In after deposition of extra Cu layers, and the interaction between substitutional In terrace atoms with Cu adatoms. We conclude that In atoms strongly prefer substitutional terrace sites; they try to keep this environment during subsequent Cu deposition. Our measurements do not support the proposed surfactant mechanism of In on Cu(100), in which Cu adatoms reach a lower terrace by pushing out an In atom at a step edge.

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I. INTRODUCTION

The first successful application of surfactants in the epitaxial growth of metals was reported by van der Vegt *et al.*¹ They observed that evaporation of submonolayer coverages of Sb on Ag(111) changes the growth of Ag from a rough two-dimensional to a smooth layer-by-layer mode. Later, various other metal-surfactant combinations were found. For example, submonolayer coverages of In act as a surfactant during the growth of Cu(100) and Cu(111) at 225 and 300 K.² This effect was also theoretically predicted by Breeman and Boerma.³ For the case of Cu(100) they concluded from atom-embedding calculations that In atoms present at or in step edges lower the energy barriers for Cu interlayer diffusion and promote smooth layer-by-layer growth of Cu. On the basis of these calculations, van der Vegt *et al.* interpreted their results in terms of In-induced lowering of this so-called Schwoebel barrier. We note that they implicitly assumed that segregation of In towards the surface occurs.

Lately, the Cu/In/Cu(100) system was the subject of another theoretical investigation. Jiang *et al.*⁴ determined the interaction potentials from first-principles calculations and performed dynamic Monte Carlo simulations of the Cu growth process at 225 K in the presence of In as a surfactant. Layer-by-layer growth occurred only when two “surfactant mechanisms” were active: the In-Cu exchange (which leads to the segregation of the surfactant atoms towards the surface) and the push-out mechanism already described by Breeman and Boerma.³ The latter mechanism consists of the following stages: (a) an In atom is situated at or in an island edge, while a Cu adatom, on top of the same island, reaches the edge at the place where the surfactant resides, and (b) the Cu atom “steps down” by pushing away the surfactant atom. In this way the interlayer diffusion of Cu is enhanced, while the surfactant atoms remain at or in island edges.

The perturbed angular correlation (PAC) technique makes it possible to monitor the sites of probe atoms, in our case ^{111}In , on a substrate.⁵ In this way we can obtain information on the interaction, on an atomic scale, between an In (surfactant) atom and Cu atoms. The probe atoms are deposited by the soft-landing technique,^{6,7} i.e., the radioactive ions are

separated by mass and decelerated to an energy of roughly 5 eV before they land on the surface. This energy is sufficiently low to prevent the formation of surface vacancies. Our initial experiments start with the simple situation in which the probe atoms are deposited at low temperature as immobile adatoms onto well-prepared Cu(100) surfaces. After annealing we study the PAC signals associated with the migration of In atoms to other sites. These signals are then used to characterize the environment of the In probe atoms in other circumstances, for instance when they are incorporated into the terraces and interact with deposited Cu adatoms. In this way we directly investigate the role of In “surfactant” atoms in the epitaxial growth of Cu on Cu(100).

II. EXPERIMENT

A. PAC spectroscopy

The PAC technique measures the hyperfine interaction in an intermediate nuclear state, in this case the 245 keV, $I = 5/2$ intermediate state of the isotope ^{111}Cd .⁸ This is done in the time domain, by monitoring the time dependence of the angular correlation of the 171–245 keV γ -ray cascade populated in the decay of ^{111}In to ^{111}Cd . For the measurements presented here, the relevant hyperfine interaction is the quadrupole interaction, i.e., the coupling between the nuclear quadrupole moment tensor of the intermediate state and the electric field gradient (EFG) tensor set up by all electrons at the position of the nucleus. The quadrupole interaction splits the $I = 5/2$ state into three doubly degenerate sublevels. For each environment of the probe atom the PAC signal contains three frequencies, corresponding to the energy differences between these three sublevels. The quadrupole frequency $\nu_Q \equiv eQV_{zz}/h$ and the asymmetry parameter $\eta \equiv (V_{xx} - V_{yy})/V_{zz}$ are obtained from the measured PAC frequencies by diagonalizing the quadrupole interaction Hamiltonian.⁹ Here, V_{xx} , V_{yy} , and V_{zz} are the elements of the diagonalized EFG tensor, ordered in such a way that $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$. One can easily show⁹ that for $\eta = 0$ the frequencies are in the ratio 1:2:3, while for $\eta = 1$ they are in the ratio 1:1:2.

The time-dependent angular correlation was measured in a standard fast-slow coincidence setup, with the four detec-

tors in the horizontal plane, making angles of 45° and 135° with the normal to the vertical sample plane. The experimental ratio $R(t)$ is given by $R(t) \equiv \frac{2}{3}(1 + \kappa)(C_{180} - C_{90}) / (C_{180} + \kappa C_{90})$, where C_{180} and C_{90} are the averaged and background corrected count rates for the various 180° and 90° detector combinations. The value of κ is chosen in such a way that in the denominator of this expression the oscillations approximately cancel.

A least-square fit of the experimental ratio $R(t)$ is made using a function $F(t) \equiv A_{eff} \sum_i f_i G_i(t)$, where $G_i(t)$ is the perturbation function for a certain environment (site) i , f_i the fraction of probe atoms in this site, and A_{eff} the effective anisotropy of the γ cascade. The perturbation factor $G_i(t)$ has the form $G_i(t) = \sum_{n=0}^3 S_{ni} \cos(\omega_{ni} t)$, where ω_{ni} ($n = 1, 2, 3$) are the angular PAC frequencies for site i and $\omega_{0i} = 0$. The constant $A_{eff} S_{0i}$ is called the ‘‘hard core’’ value for site i . The coefficients S_{ni} depend on the orientation of the principal axes of the EFG tensor relative to the detectors. Because for all observed sites the z axis of the EFG is the normal to the sample plane, while the x axis is lying both in the sample plane and in the detector plane, it turns out that $S_{3i} = 0$ for our geometry, so that we generally observe only two frequencies per site, and these coincide if $\eta = 1$.

When fitting the data in this way, one normally observes that the sum of the contributions of the various sites to the total anisotropy is smaller than expected. This is a common feature of PAC spectroscopy on surfaces. The missing anisotropy is lost in the first few nanoseconds, where the fit is not reliable due to the finite time resolution and the uncertainties in the zero of the time scale for the various detector combinations. The fast damping is associated with a wide distribution of quadrupole frequencies, due to probe atoms trapped in various sites associated with impurities and defects at the surface. We call this the ‘‘invisible fraction,’’ in contrast to the fractions accounted for in the fit.

After annealing above 300 K we normally observe a unique site that accounts for about 80% of the expected anisotropy. Unless stated otherwise, the quoted fractions f_i are normalized with respect to the anisotropy of this site.

B. Experimental details

A Cu single crystal was mechanically polished parallel to the (100) plane with an accuracy of better than 0.1° and subsequently etched in a solution of H_3PO_4 , CH_3COOH , and H_2O . The crystal was cleaned *in situ* by a few cycles of sputtering with 1 keV Ar^+ followed by annealing at 600 K for up to 2 h. No contamination was detected by Auger electron spectroscopy. The low-energy electron diffraction (LEED) pattern showed sharp spots, a low background, and the expected fourfold symmetry.

After preparation, radioactive ^{111}In probes were deposited during periods varying between 30 and 45 min. The total deposition dose was always below 10^{12} atoms/cm 2 , i.e., less than 10^{-3} of a monolayer (ML). A typical dose was 10^{-4} ML. The nominal energy of 5 eV can be considered as a rough upper limit for the energy of the ions that reach the surface. During deposition, the pressure in the soft-landing chamber remained below 5×10^{-11} mbar.

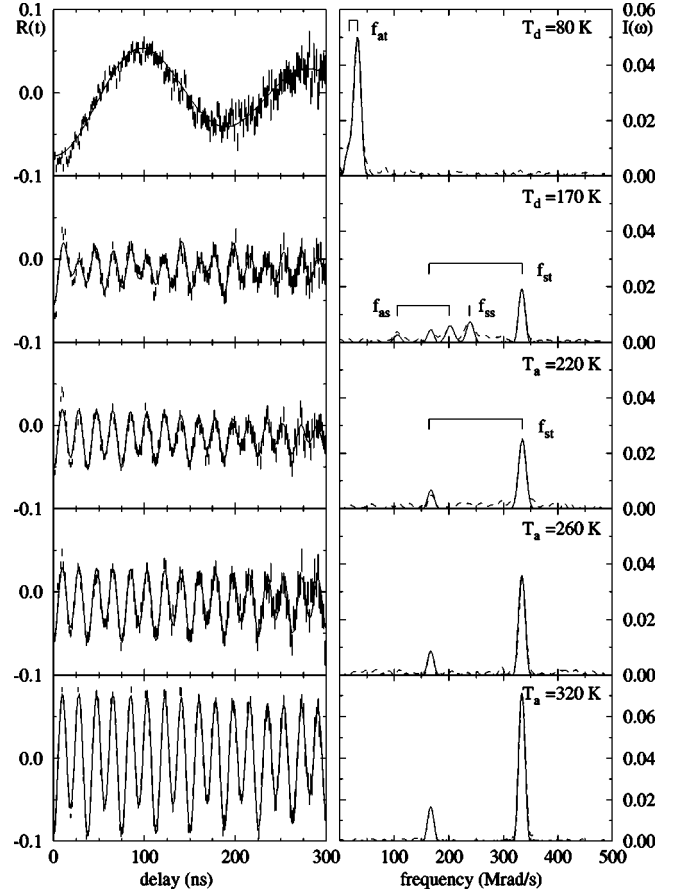


FIG. 1. PAC spectra and their Fourier transforms obtained after deposition of ^{111}In with an energy of 5 eV on a Cu(100) surface at a substrate temperature of 80 K (top) and 170 K (second), and subsequent annealing for 15 min at 220, 260, and 320 K. All measurements were performed at 80 K.

After each deposition, a PAC spectrum was taken to characterize the initial situation. In most cases, after the first measurement Cu was deposited on the surface at different substrate temperatures and concentrations, and new PAC spectra were subsequently accumulated. A typical PAC measurement took approximately 3 h. All measurements were performed at 80 K in order to rule out temperature-dependent frequency shifts and to facilitate comparison between the different observed hyperfine interaction frequencies.

III. RESULTS AND DISCUSSION

A. Sites and mobility of isolated ^{111}In atoms on Cu(100)

After surface preparation, radioactive ^{111}In atoms with an energy of 5 eV were deposited on the surface at 80 K. Thermal diffusion of Cu adatoms is inhibited at this temperature. 3,10,11 The sample was annealed for 15 min at various temperatures. Typical PAC spectra and their Fourier transforms are shown in Fig. 1. The solid lines in the experimental spectra and in the Fourier transforms represent the fit. The peaks that belong together and the site to which they belong are indicated in the Fourier transforms.

In total, four sites are observed: the adatomic terrace site (f_{at}), the adatomic step site (f_{as}), the substitutional step site

TABLE I. Hyperfine interaction parameters for ^{111}In on (vicinal) Cu(100) deposited by evaporation (left column) and by soft-landing ion deposition. All data were measured at a substrate temperature of 80 K.

Site	Cu(100) ^a		Cu(17 1 1) ^b		Cu(100) ^c	
	ν_Q (MHz)	η	ν_Q (MHz)	η	ν_Q (MHz)	η
f_{at}	16.0(3)	0.0(1)	17.1(2)	0.0(5)	17.5(2)	0.0(5)
f_{as}	110(1)	0.16(2)	108(1)	0.12(2)	109(1)	0.18(3)
f_{ss}	161(1)	0.81(2)	144(1)	1.00(5)	148(3)	1.0(1)
f_{st}	181(1)	0.05(5)	184(1)	0.00(5)	178(1)	0.00(5)

^aReferences 14 and 15.

^bReferences 6 and 17.

^cThis work.

(f_{ss}) and the substitutional terrace site (f_{st}). This is the same notation as used in earlier work.^{6,12,13} Table I summarizes the measured hyperfine interaction parameters for ^{111}In on Cu(100). For comparison, the parameters reported by Klas *et al.*,¹⁴ by Fink *et al.*,^{15,16} and by Laurens and co-workers^{6,17} are also given. The data of Laurens and co-workers are obtained on vicinal (17 1 1) surfaces with relatively short (100) terraces.

From the data presented in Table I one observes some differences concerning the substitutional step (f_{ss}) and the substitutional terrace site (f_{st}). The deviating interaction frequency for the f_{ss} site measured by Fink *et al.* is related to a small and statistically insignificant extra frequency component in the data of these authors. If we ignore this component, the data of Fink *et al.* lead to $\eta=1$ and $\nu_Q = 146$ MHz, in good agreement with the other data.

The largest difference in interaction frequencies (3.4%) occurs for ^{111}In incorporated in the relatively short terraces on Cu(17 1 1) (average width 8.5 interatomic distances) and the much broader terraces on Cu(100). We note that this difference is not caused by different measurement temperatures: both spectra were measured at 80 K. The difference in frequencies suggests that sites close to step edges experience a slightly larger EFG.

Figure 2 gives information about the diffusion behavior and the resulting atomic sites of isolated ^{111}In atoms on the Cu(100) surface, compared with our earlier work on the vicinal (17 1 1) surface.^{13,17} There are clear differences in behavior, which we will now discuss.

The (17 1 1) data show that part of the deposited In atoms reside at steps already at 50 K and that thermal mobility sets in just above 80 K. The step density on a (100) surface is much lower than that on a (17 1 1) surface, and, as a consequence, no In atoms reside at steps immediately after deposition at 80 K. The fraction in adatomic terrace sites amounts to approximately 70%.

After annealing at 120 K no well-defined sites are observed. The PAC signal is strongly damped, most probably due to a distribution of static electric field gradients. Based on the activation energy for hopping derived from the (17 1 1) data, $E_a=0.22(3)$ eV, we estimate that the In adatoms can make 10^5 – 10^6 jumps during the anneal at 120 K. Presumably the In probe atoms are trapped by structural defects and/or impurities during their random walk on the terrace.

This effect is not observed on the (17 1 1) surface at this temperature, because there the steps are the dominant traps for the diffusing In atoms.

Three different sites are visible after an ^{111}In deposition at a substrate temperature of 170 K (see Fig. 1, second from top): the adatomic step site f_{as} (11%), the substitutional step site f_{ss} (9%), and the substitutional terrace site f_{st} (26%). We note here that the ‘‘adatomic step site’’ is probably an In atom at a kink in the step.¹⁷ The low occupation of the adatomic step f_{as} and the substitutional step f_{ss} sites is consistent with the low step density on a (100) surface. The total visible fraction (46%) is rather small; presumably some In

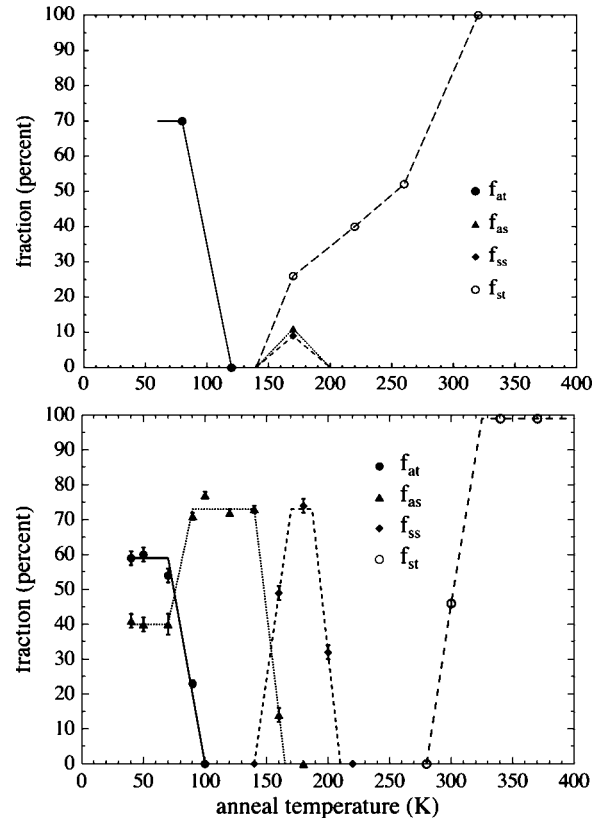


FIG. 2. Fractions of ^{111}In atoms at various sites as a function of anneal or deposition temperature, after deposition on Cu(100) (top, this work) and on Cu(17 1 1) (bottom, Refs. 6 and 17).

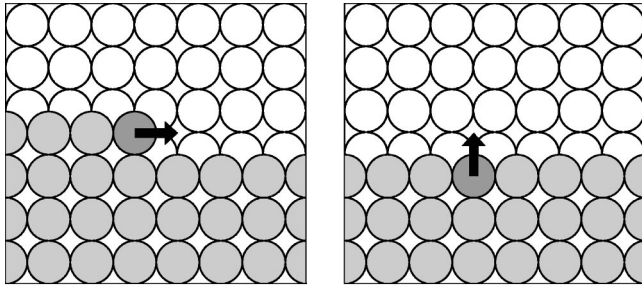


FIG. 3. Two mechanisms that lead to a vacancy in a Cu step edge. Left, a Cu atom moves from a kink position to an at-step position, right, a Cu atom moves from an in-step position to an adatomic position.

adatoms are trapped at surface imperfections even at this temperature.

Annealing at 220 K and higher results in the disappearance of the step-correlated sites and a gradual increase of the substitutional terrace fraction. The preference for substitutional terrace sites after annealing at temperatures above 260 K is in perfect agreement with the prediction³ that this is energetically the most stable configuration. However, on Cu(100) the incorporation in terrace sites starts much earlier than on Cu(111), where the In probe atoms start to occupy terrace sites only above 280 K. In the following we will discuss the mechanism of the incorporation of In atoms into terraces and explain this difference in behavior.

An ¹¹¹In atom can penetrate into the relatively long and straight steps on a Cu (111) surface only if the step contains vacancies. There are two different processes that lead to vacancy creation in the steps (see Fig. 3): (1) a Cu atom leaves a kink and moves to an adatomic step site, and (2) a Cu atom leaves a substitutional step site and moves to an adatomic step site. The first process has the smallest activation energy,^{3,18} which is only slightly larger than the activation energy needed for adatom diffusion on the terrace. Experimentally determined adatom diffusion barriers^{19–21} indicate that Cu adatoms become mobile at approximately 140 K. This implies that step vacancies are formed between 150 and 160 K. These are indeed the temperatures at which isolated ¹¹¹In atoms occupy substitutional step sites on a Cu(111) surface. We conclude that the number of created vacancies is proportional to the number of kinks present along a step.

At the temperatures at which Cu adatoms are mobile and form islands on the (100) surface, the island edges are not straight, but irregular. Thus, the kink concentration and the adatom concentration along the perimeter of an island are larger than those in the case of the relatively straight step on a vicinal surface. This makes the incorporation of In atoms in steps more effective. Moreover, after the In atom has been incorporated in a step, it may trap Cu atoms moving along the steps. This eventually yields the observed substitutional terrace site.

B. Interaction between isolated ¹¹¹In adatoms and Cu islands

In order to obtain a more detailed picture of the interaction between In atoms and Cu islands on a Cu(100) surface,

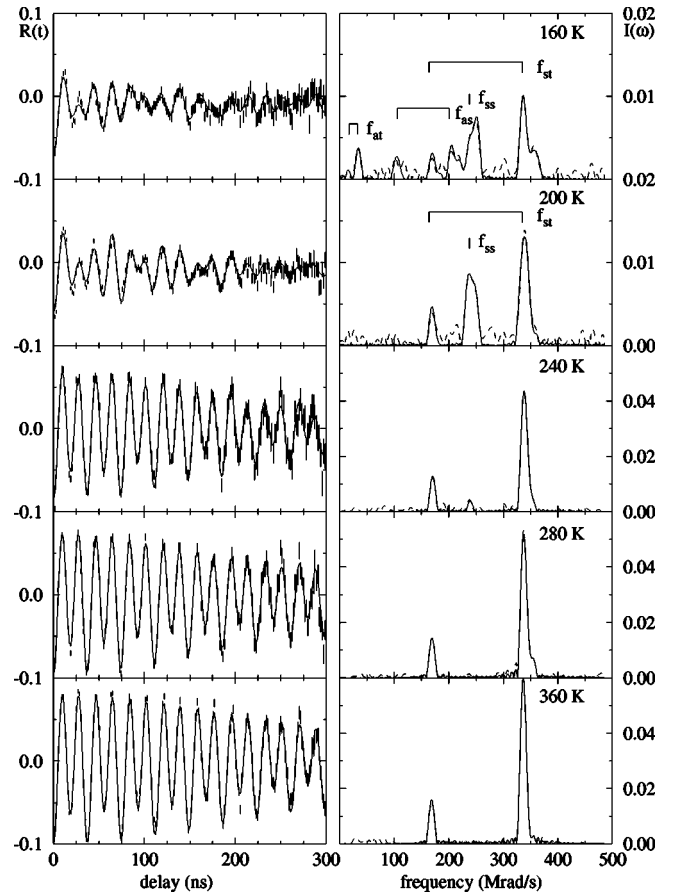


FIG. 4. PAC spectra and their Fourier transforms obtained after deposition of 0.2 ML of Cu on a Cu(100) surface, at a substrate temperature of 300 K, and additional deposition of ¹¹¹In probe atoms at 160 K. The sample was subsequently annealed for 15 min. at the indicated temperatures. All PAC measurements were performed at 80 K.

the following experiments were performed. Cu islands were produced by depositing 0.2 ML of Cu atoms, with an energy of 5 eV, on a freshly prepared Cu(100) surface at a substrate temperature of 300 K. Based on Monte Carlo simulations, we expect the Cu islands to consist of more than 50 atoms and to have irregular edges. Radioactive ¹¹¹In atoms were deposited with the same energy, at a substrate temperature of 160 K. At this temperature not only In and Cu adatoms but also Cu atoms at island edges are mobile. After the In deposition, the crystal was annealed at stepwise increasing temperatures. Figure 4 shows the PAC spectra together with their Fourier transforms. The frequencies of the four In sites measured for the case of isolated ¹¹¹In atoms deposited on Cu(100) (shown in Fig. 1) are visible in the Fourier transforms. However, it is obvious from Fig. 4 that additional sites are present. For instance, in the case of f_{ss} and f_{st} the Fourier lines are broadened, indicating extra sites with slightly higher interaction frequencies.

Figure 4 shows that some deposited ¹¹¹In atoms occupy adatomic terrace sites after deposition at 160 K. This is remarkable because In adatoms usually reach steps or are trapped at surface defects already at temperatures of 120 K. Moreover, in the presence of copper islands, the step density

TABLE II. Hyperfine interaction parameters for ^{111}In on Cu(17 1 1), on Cu(100), and on Cu(100) decorated with various amounts of Cu. In the latter case, the frequencies were obtained from a Fourier analysis with enhanced resolution. All data were measured at a substrate temperature of 80 K.

Site	Cu(100) ^a		Cu(100)+extra Cu ^b	
	ν_Q (MHz)	η	ν_Q (MHz)	η
f_{at}	17.5(2)	0.0(5)	18.0(2)	0.0(5)
f_{as}	109(1)	0.18(3)	106(1)	0.12(2)
$f_{\text{as-like}}$	–	–	117(1)	0.23(6)
f_{ss}	148(3)	1.0(1)	149(1)	1.00(5)
$f_{\text{ss-like}}$	–	–	156(1)	1.00(5)
f_{st}	178(1)	0.00(5)	178(1)	0.00(5)
$f_{\text{st-like}}$	–	–	182(1)	0.00(5)
$f_{\text{st-like}}$	–	–	185(1)	0.00(5)
$f_{\text{st-like}}$	–	–	192(1)	0.00(5)

^aThis work, data from Fig. 1.

^bThis work, data from Figs. 3, 6, 7, 9, and 10.

is higher than that in the case of a clean Cu(100) surface, and so is the probability for the indium atoms to reach a step. The low-frequency component observed at 160 K nevertheless suggests that In atoms are trapped in an adatomlike configuration. A plausible explanation is that In atoms are trapped *on top* of Cu islands and that they cannot step down at 160 K, whereas they do so at 200 K. Taking the prefactor of this process as $10^{12\pm 1} \text{ s}^{-1}$, we calculate a diffusion barrier of 0.53(6) eV. This compares well with the calculations of van Siclen,²² who obtained barriers of 0.57 and 0.65 eV for jump and exchange processes across the step.

A new feature is that sites with slightly larger hyperfine interaction parameters appear when Cu islands are present on the surface. In Fig. 4 this is best visible as an asymmetric broadening of the second angular frequency of the f_{st} at about 350 Mrad/s. This implies a corresponding asymmetric distribution in the values of the static electric field gradients. The frequency variations within a certain family of sites amount to only a few percent. This is due to the fact that the main component of the electric field gradient tensor, V_{zz} , is still perpendicular to the surface, which makes it hardly sensitive to in-plane changes caused by more distant neighbors of the probe atoms. This might seem a disadvantage, but it makes it possible to group the new sites into already known categories: the adatomic step (kink) site (two Cu neighbors in the surface layer), the substitutional step site (three Cu neighbors in this layer), and the substitutional terrace site (four Cu neighbors). In Table II we list the results of the fits of these quadrupole distributions in terms of such categories. Due to the limited spectral resolution of the PAC technique, it is impossible to make a detailed interpretation of these components. Nevertheless it seems reasonable to associate the shift to higher frequencies with the presence of Cu vacancies in the surface layer close to the probe atom but not as nearest neighbor. Such a situation occurs, for instance, if the probe atom is close to an island edge.

In Fig. 5 the different site fractions of ^{111}In on an island-decorated Cu(100) surface are plotted as a function of the

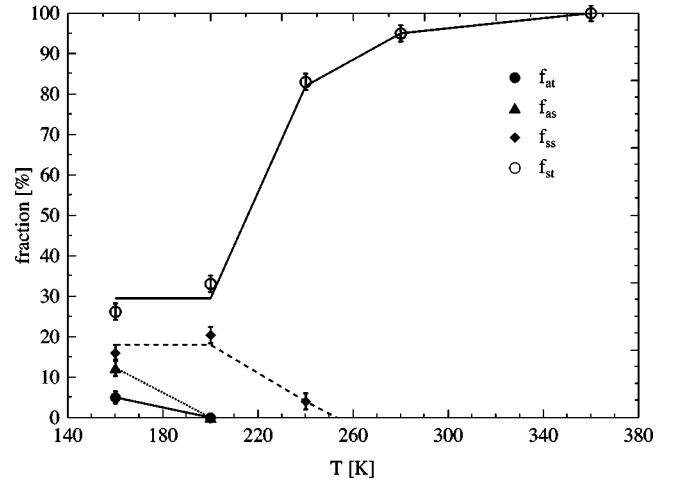


FIG. 5. Atomic site fractions of ^{111}In on an island-decorated Cu(100) surface as a function of anneal temperature. The lines are drawn to guide the eye.

annealing temperature. For the sake of presentation, all similar sites are grouped under a generic name such as f_{as} , f_{ss} , or f_{st} . The most significant difference with the case of isolated ^{111}In deposited on Cu(100) (see Fig. 2) is that on the island-decorated surface the f_{ss} site remains populated up to somewhat higher temperatures. Given the large amount of available edge sites, this is not surprising. However, after annealing at 240 K, the population of the substitutional step sites is already marginally small (4%), while 83% of the In atoms reside in two different substitutional terracelike sites.

The fact that we do not observe In atoms in or at steps above 240 K is in contradiction with the interpretation of the experiments of van der Vegt *et al.*,² who observed the influence of In atoms on the growth of a Cu(100) layer in the temperature interval from 225 K to 300 K. We will return to this point later.

C. Interaction between ^{111}In atoms in the surface and isolated Cu adatoms

Although we observe a fine structure in the signal associated with terracelike environments of In atoms, we cannot identify precisely the configurations of the new f_{st} -like sites. Although we consider it unlikely, we cannot exclude the possibility that one of the new sites can be assigned to a cluster of a substitutional terrace ^{111}In atom and one or more Cu adatoms. In order to address this issue, we produced Cu adatoms in two different ways. In the first method, radioactive ^{111}In atoms were deposited with an energy larger than 10 eV on a Cu(100) surface at 80 K. In this way, the impinging In atoms are able to create a surface vacancy and immediately occupy it, while the generated Cu adatoms reside in the first- and/or the second-neighbor shell and are not mobile at 80 K.¹⁷ In the second method, In probe atoms were incorporated in the terraces, after which Cu adatoms were deposited on the surface at a temperature at which they are immobile.

Method I. We deposited 25 eV ^{111}In probe atoms on Cu(100) surface, at 80 K. Figure 6 illustrates the PAC spec-

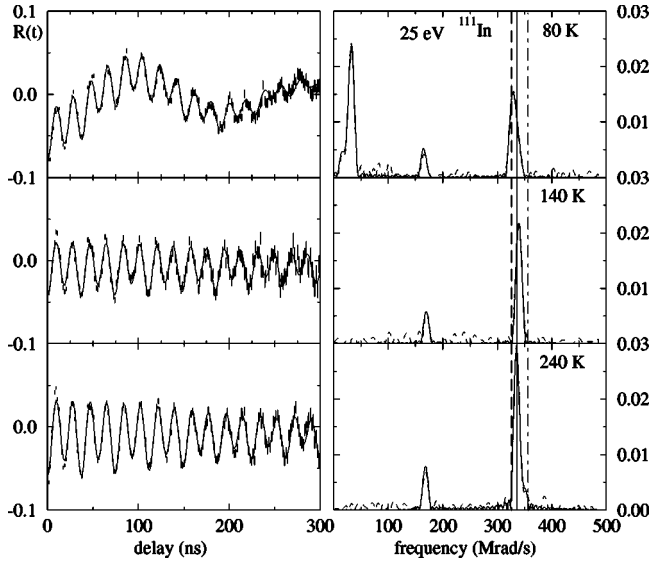


FIG. 6. PAC spectra and their Fourier transforms obtained after deposition of ^{111}In with an energy of 25 eV on a Cu(100) surface at a substrate temperature of 80 K. All measurements were performed at 80 K. The solid line in the Fourier transform marks the value of the second angular frequency of the substitutional terrace site. The dashed line indicates a frequency shift of -2% , and the dashed-dotted line a shift of $+4\%$.

tra together with their Fourier transforms, obtained after the deposition and after annealing at 140 and 240 K. Immediately after the deposition, the In probes occupy adatomic terrace sites (up to a fraction of 46%) and two different substitutional terrace sites (together accounting for 41%). No step-correlated sites appear in the spectrum, as expected for a Cu(100) surface with broad terraces. In the Fourier transform the value of the second angular frequency of the original substitutional terrace site is indicated with a solid line. The dashed line indicates the frequency of the new f_{st} -like site, which is 2% smaller than the frequency of the f_{st} site. The value of the new frequency was obtained from a Fourier analysis with enhanced resolution. The populations of the two terrace sites are approximately equal.

Annealing of the sample at 140 K causes the disappearance of both the adatomic terrace and the new f_{st} -like site. We recall that Cu adatoms become mobile on a terrace at approximately 140 K.^{19–21} The disappearance of the f_{st} -like site is a strong indication that this site consists of a substitutional terrace ^{111}In atom, decorated with one Cu adatom. We conjecture that isolated Cu adatoms are *not* strongly bound to In atoms residing in a terrace. Furthermore, we conclude that the presence of one Cu adatom in the neighborhood of an ^{111}In atom in the terrace does not lead to an exchange process, which would turn the In probe into an adatom. This holds at least for the temperature interval between 80 and 140 K. Finally we note that the presence of a Cu adatom leads to a *decrease* of the terrace frequency.

After annealing at 240 K, the fraction of In atoms in the terrace has slightly increased and another f_{st} -like site, with a 4% larger frequency, appears in the PAC spectrum (see dash-dotted line in Fig. 6). This frequency is the same as observed

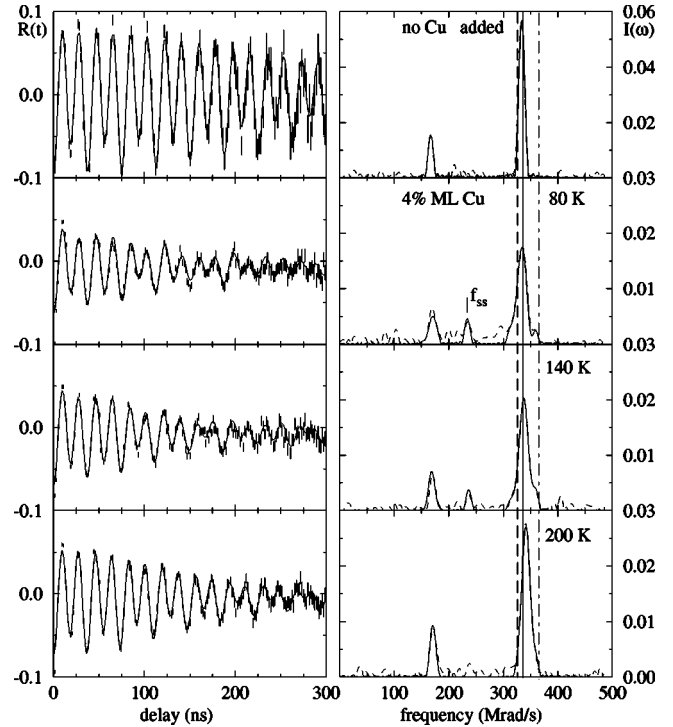


FIG. 7. PAC spectra and their Fourier transforms obtained after deposition of ^{111}In on a Cu(100) surface at a substrate temperature of 360 K, after deposition of an additional 0.04 ML of 5 eV Cu at 80 K, and after subsequent annealing for 15 min at the indicated temperatures. All measurements were performed at 80 K.

in the case of ^{111}In atoms residing in the short (100) terraces of vicinal Cu(17 1 1) (see Table I). The corresponding fraction, amounting to 12%, is assigned to In atoms that have diffused via a step into a terrace and still reside in the immediate neighborhood of the step. This is a plausible assignment for the following reason. The mobility of In atoms in the Cu(100) terrace has been directly observed near room temperature with scanning tunneling microscopy (STM).²³ Based on this work we estimate the In jump rate caused by thermally activated vacancies at 240 K as 10^{-5} s^{-1} . So, if an In atom has reached a substitutional terrace site via a step edge, we do not expect it to move during an anneal treatment of 15 min at 240 K. We recall that similar sites were observed when In was deposited on a Cu surface decorated with Cu islands and annealed above 200 K (see Fig. 4 and Table II).

Method II. First, radioactive ^{111}In atoms were deposited on the Cu surface at a substrate temperature of 360 K. In the top part of Fig. 7 the PAC spectrum and its Fourier transform obtained after the In deposition are plotted. All In atoms occupy substitutional terrace sites. The vertical solid line in the Fourier transform indicates the second angular frequency of the f_{st} -site. After this preparative step, 0.04 ML of 5 eV Cu was deposited at 80 K, a temperature at which Cu adatoms cannot move across the terrace. Figure 8 indicates the expected Cu adatom distribution as calculated by a dynamical Monte Carlo method based on potentials described by Breeman and co-workers (see Refs. 3 and 24 for details). The simulated lattice contained 100×100 atoms. Although we

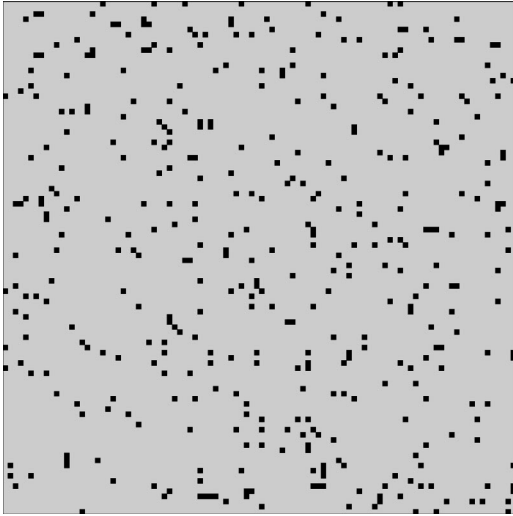


FIG. 8. The Cu adatom distribution after deposition of 0.04 ML of Cu on a Cu(100) surface at 80 K.

should be careful concerning the quantitative aspects of this calculation, we can state that the clustering process is still in its starting phase.

After Cu deposition we observe a broad frequency distribution in the interval 200–300 Mrad/s, but on top of that we can discern some clear signals. 31% of the initial fraction of the In atoms still occupy the substitutional terrace site. Additional peaks appear on both sides of the angular frequency of the f_{st} site. The -2% site, which we identified as ^{111}In atoms in the terrace with a Cu adatom as nearest or next-nearest neighbor, represents 13% of the initial visible fraction. There is also spectral weight in the interval just below this frequency, possibly correlated with In atoms in the terrace that have more than one Cu adatom as neighbor. The presence of copper dimers and trimers on the surface, predicted by our Monte Carlo simulation, supports this assumption.

In addition, an f_{st} -like site with a 6% larger frequency occurs after the Cu deposition. The corresponding fraction is 4% of the fraction visible after the In deposition. Earlier we argued that f_{st} -like sites that give rise to frequencies larger than that of the substitutional terrace site are likely to correspond with ^{111}In atoms close to a step-down edge. This will happen if they are incorporated in small islands. If this site assignment holds, it implies that In atoms that occupy this $+6\%$ site *already* exchanged places with a Cu adatom and reside within a small cluster containing at least 8 Cu atoms. This plausible scenario is in agreement with the occurrence of the substitutional step site (5.5% fraction) visible at 238 Mrad/s. This signal must be due to In atoms that, after having moved into the top layer, end up at the periphery of the small islands. The broad frequency distribution in the interval 200–300 Mrad/s is probably associated with a variety of In-Cu adatomic clusters of smaller size. In total, approximately 15% of the ^{111}In atoms in the terrace exchange places with the deposited Cu adatoms, at a temperature as low as 80 K. Because we do not observe individual In adatoms after the Cu deposition, we draw the conclusion that the exchange

TABLE III. Fractions of individual f_{st} -like sites. Data from Fig. 7.

$T(K)$	Fractions (%)			Sum
	-2%	f_{st}	$+6\%$	
80	21	31	4	56
140	20	20	24	64
200	13	35	30	78

process needs more than one Cu adatom in the neighborhood of an In terrace atom. This is in agreement with the result of method I.

At this point it is interesting to follow the annealing behavior of this system. The frequency distribution between 200 and 300 Mrad/s disappears at 140 K, the temperature at which Cu adatoms become mobile. The clusters that gave rise to this frequency distribution either break up or diffuse towards other clusters and coalesce. The substitutional step site (f_{ss}) is stable up to a temperature of at least 140 K.

Table III summarizes the fractions of all f_{st} -like sites immediately after Cu deposition at 80 K, and after annealing at 140 and 200 K. One observes that the sum of the f_{st} -like fractions gradually increases, as does the average frequency. This indicates a depletion of Cu-decorated terrace sites and an increasing number of In atoms residing in small islands.

D. ^{111}In segregation at 80 K

An essential property of a surfactant is that it can easily segregate towards the surface during growth. This was indeed the case in the experiment described by van der Vegt:² after deposition of 11 ML of Cu at room temperature the intensity of the In Auger peak had not changed within the experimental errors. The PAC technique is useful to investigate the segregation process and to determine which factors inhibit or enhance it.

The experiments were performed as follows. After surface preparation, radioactive ^{111}In atoms were deposited on the surface at a temperature of 360 K. After the deposition the sample was cooled down to 80 K and an initial PAC spectrum was recorded. Subsequently, various amounts of 5 eV Cu were deposited at a substrate temperature of 80 K, each time on a freshly prepared surface. Although adatom diffusion is inhibited at this temperature, Cu(100) grows nevertheless in a quasi-layer-by-layer mode. This has been attributed to the *funneling* mechanism: Cu atoms landing in a site that is not fourfold coordinated will immediately jump downwards and occupy the vacancy in the underlying layer.²⁴ Although this process is effective in limiting the number of monolayers growing simultaneously, it cannot prevent the incorporation of vacancies in the growing film.

All probe atoms occupy substitutional terrace sites, f_{st} immediately after their deposition (Fig. 9, top). The well-defined environment gives rise to almost no damping of the spectrum. After deposition of 1 ML of Cu at 80 K, the damping is significantly stronger and more frequencies appear in the Fourier transform of the PAC spectrum, in particular be-

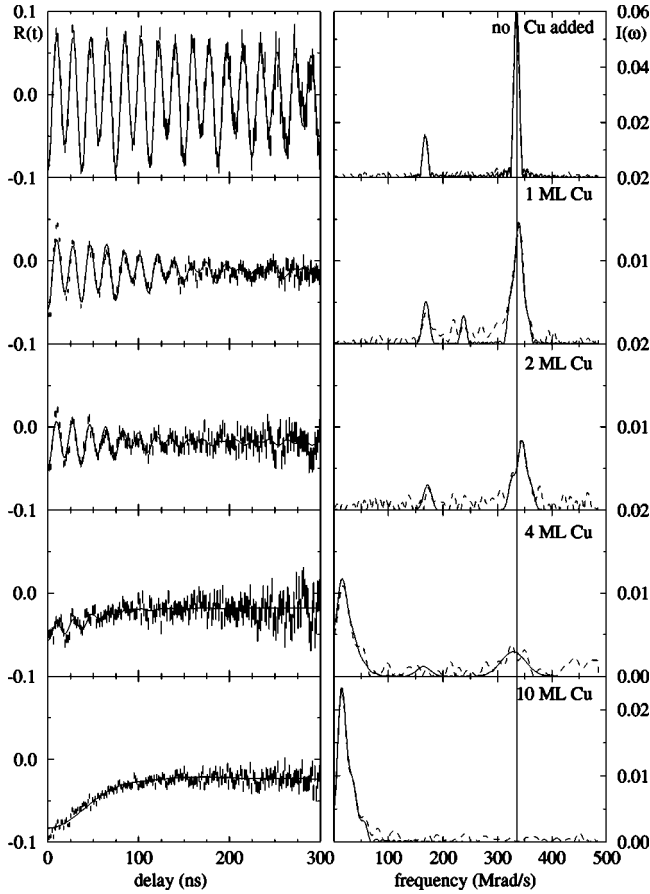


FIG. 9. PAC spectra and their Fourier transforms obtained after deposition of ^{111}In on a Cu(100) surface at a substrate temperature of 360 K, and after subsequent depositions of 5 eV Cu atoms at 80 K to the indicated amount. All measurements were performed at 80 K. The vertical solid line indicates the angular frequency of the original substitutional terrace site for isolated ^{111}In on Cu(100).

tween 200 and 300 Mrad/s. This may be due to In atoms that occupy island-edge correlated sites, as in Fig. 4 at 160 and 200 K. Not surprisingly, we observe also a distribution of f_{st} -like sites. If In atoms were buried under the extra Cu layer, they would experience only a weak electric field gradient. There is no sign of such a signal; apparently the large majority of the In atoms is able to move into the evaporated Cu layer, which is defective because the deposition is performed at 80 K.

Deposition of 2 ML of Cu at 80 K results in a stronger damping of the PAC signal. This is due to the fact that the disorder in the top Cu layer increases. We also observed an increase in the time-independent part of the angular correlation function (the so-called hard core). This is due to In atoms that are buried under the Cu layer and experience a cubic environment.

Increasing the coverage results in a gradual increase of the intensity of this component and the appearance of a new component with a low frequency. Similar to the fraction in cubic sites, we attribute this component to ^{111}In atoms that are caught within the grown layers, and experience a small EFG caused by the presence of point defects, most likely vacancies, in more distant neighbor shells. Whereas we still

TABLE IV. Fractions of individual f_{st} -like sites after deposition of ^{111}In on a Cu(100) surface at 360 K, after deposition of an additional 1 ML of 5 eV Cu at 80 K, and after subsequent annealing at the indicated temperatures.

T(K)	Fractions (%)				Sum
	-2%	f_{st}	+4%	+6%	
80	20	18	10	0	48
180	0	31	24	10	65
240	0	81	0	8	89
300	0	84	13	0	97

observe a fraction of In atoms at the surface after deposition of 4 ML of Cu, this component has completely vanished after deposition of 10 ML. From our data we draw the conclusion that In shows surfactant behavior even at 80 K: each time a Cu layer is deposited, approximately 70% of the top-layer ^{111}In atoms pop up to the new surface.

E. ^{111}In segregation as a function of temperature

In the previous section we have seen that In atoms show a clear tendency to segregate towards the surface even after deposition of Cu at a substrate temperature of 80 K. In order to determine the temperature dependence of the segregation process we deposited radioactive ^{111}In atoms at a substrate temperature of 360 K, followed by 1 ML of 5 eV of Cu at 80 K, and took PAC spectra after subsequent annealing at 180, 240, and 300 K.

Table IV summarizes the measured fractions of the f_{st} -like sites. The sum of the fractions is gradually restored to the value after deposition of In at 360 K. This sum is a lower limit for the fraction of In atoms at the surface because, particularly at 80 K, we lose some intensity in a broad frequency distribution.

We conclude that at a temperature of 240 K and higher, In atoms are able to segregate towards the surface with an efficiency of 90% or better. In line with this, the component due to the buried ^{111}In atoms decreases to zero. A very similar behavior was observed after deposition of 2 ML of Cu at 80 K and subsequent annealing. These results are in excellent agreement with those of van der Vegt.²

F. ^{111}In segregation during submonolayer Cu growth

To follow the ^{111}In surfactant atoms during the growth of an additional Cu layer, we performed the following experiments. ^{111}In atoms were deposited at 360 K in order to ensure that all In atoms occupied substitutional terrace sites. Next, 5 eV Cu atoms were deposited in different submonolayer concentrations, at a temperature of 200 K. In Sec. III E it was shown that at this temperature the large majority of the indium atoms segregate towards the surface. The obtained PAC spectra and their Fourier transforms are shown in Fig. 10. This figure shows that most of the In probe atoms occupy sites where the interaction strength is larger than that at the f_{st} site. In Sec. III B we correlated these terracelike sites with In in Cu islands. This scenario is plausible: deposition of Cu

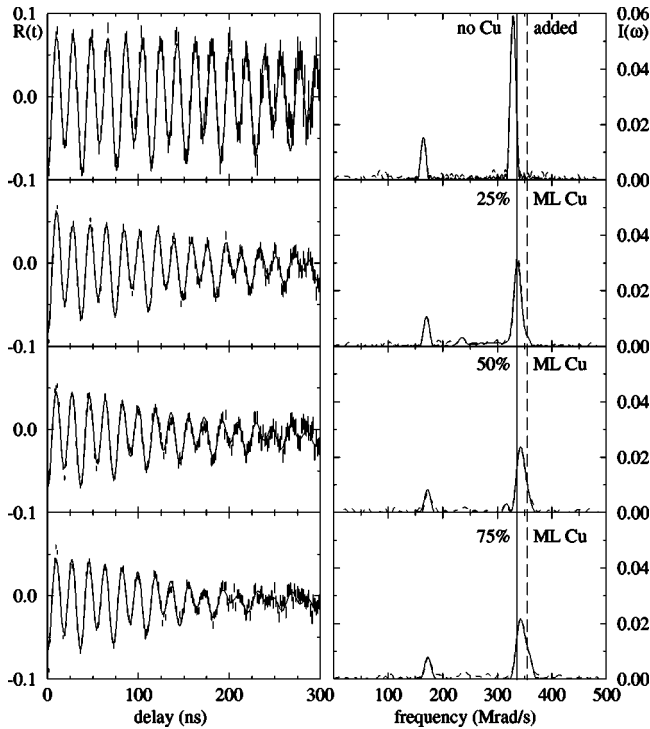


FIG. 10. PAC spectra and their Fourier transforms obtained after deposition of ^{111}In on a Cu(100) surface at a substrate temperature of 360 K, and after subsequent deposition of 5 eV Cu at 200 K, to the indicated amount. In the top panel, the deviation of the second frequency of the substitutional terrace site from its regular value (solid vertical line) is due to the fact that the first measurement was performed while cooling the sample from 360 to 200 K. All other measurements were performed at 80 K.

at a substrate temperature of 200 K leads to the formation of Cu islands and, at the same time, enhances the probability of In segregation and incorporation of In in these islands. The frequency distribution extends over a region up to 8% higher than the original terrace frequency. The corresponding sites are stable at a substrate temperature of 200 K and account for approximately 65% of the visible In atoms. The appreciable frequency shifts suggest that these In atoms are close to island edges. However, they still have four Cu neighbors because we do not observe In atoms in substitutional step sites.

Sites with frequencies slightly smaller than that of the substitutional terrace site do occur for Cu coverages of 25% and 50%, but the corresponding fractions are smaller than 6%. In Sec. III C, PAC signals with such frequencies were correlated with ^{111}In atoms in terrace sites with one or more Cu adatoms as neighbors, i.e., with In atoms that have not yet moved into the upper layer. The small intensity of this component demonstrates the effectiveness of the segregation process for these Cu adatom coverages.

Additionally, for a coverage of 25% Cu we have evidence for a continuous frequency distribution between 200 and 300 Mrad/s. The corresponding fraction is about 10%. As in Sec. III C we assign this fraction to In atoms that have exchanged places with Cu adatoms and reside in various In-Cu adatomic clusters (small islands). This assignment is also plausible in

this case, because at 200 K the clustering of mobile Cu adatoms leads to a large distribution of island sizes.

IV. CONCLUSIONS

We investigated site occupation and diffusion of isolated ^{111}In atoms on a Cu(100) surface and observed the same four sites as measured for ^{111}In on vicinal Cu(100).^{6,13,17} the adatomic terrace site (f_{at}), adatomic step site (f_{as}), substitutional step site (f_{ss}), and substitutional terrace site (f_{st}). The interaction frequency measured for the substitutional terrace site is approximately 3% smaller than the value known from experiments performed on vicinal Cu(100). This difference is attributed to the presence of steps in the neighborhood of the probe atoms incorporated in a vicinal surface.

The diffusion behavior of In on Cu(100) follows, generally, the same trend as in the case of Cu(111): when the deposition or anneal temperature is increased the deposited In adatoms first move to adatomic step sites, then become incorporated into the steps and finally into the terraces. There is, however, a difference: probe atoms occupy substitutional terrace sites on a Cu(100) surface already at 170 K, while in the case of ^{111}In on vicinal surfaces the f_{st} site occurs only above 280 K, after a drastic drop in the visible fraction in the temperature interval between 220 and 280 K. Apparently, the incorporation of In in a Cu(100) surface proceeds much more effectively, probably due to the presence of islands with irregular edges (high concentration of kinks, vacancies, and adatoms).

We also studied the interaction between isolated ^{111}In adatoms and Cu islands on Cu(100). In this case, more than the four known sites appear in the PAC spectra. However, the new sites resemble the f_{at} , f_{ss} , and f_{st} sites and have only slightly different interaction frequencies. Their occurrence is a consequence of the diversity in shape of Cu islands, compared with the relatively straight steps on a vicinal surface.

Upon annealing the In atoms get incorporated in Cu islands and occupy substitutional terracelike sites. This is in agreement with earlier calculations^{3,24} that predict that the substitutional terrace site is the most stable site for In deposited on a Cu(100) surface. At this point, we mention that the majority of the In atoms resides within the Cu islands already at 220 K. The frequencies for these terracelike sites are generally larger than that of the pure substitutional terrace site. No ^{111}In atoms are found in adatomic steplike sites at this temperature, while the fraction of the ^{111}In atoms in substitutional step sites amounts to only 10%.

As to the segregation of In during and after Cu deposition at 80 K, our experiments show that for every deposited Cu layer about 70% of the In atoms, initially in terraces, segregate towards the surface. Increasing the number of deposited layers results in the incorporation of larger fractions of the In atoms in the grown layers. After deposition of 10 ML of Cu at 80 K, all In atoms are buried.

We demonstrated that annealing after Cu deposition has a positive effect on the segregation process. During annealing at temperatures higher than 200 K the fraction of the In atoms that segregate towards the surface increases to approxi-

mately 90%. While these observations are in perfect agreement with the findings reported by van der Vegt,² they do not support the mechanism of surfactant action suggested by these authors and supported by embedded-atom³ and *ab initio*⁴ calculations. According to the proposed “push-out” mechanism, the In atoms have to reside in or at the step edges, where they facilitate Cu interlayer diffusion. However, we did not observe any In atoms at or in step edges after deposition of Cu on top of In probe atoms at 200 K, although there are indications that they are near such edges. Consequently, the push-out mechanism cannot be responsible for the surfactant action of the In atoms. The same conclusion follows from the observation that after deposition of In atoms on already existing Cu islands the population of the substitutional step site is small up to 240 K and zero above this temperature. Since the surfactant behavior exists both at 225 K and 300 K, another mechanism than push-out has to be invoked.

Our study of the interaction between Cu adatoms and

¹¹¹In in substitutional terrace sites shows that a single Cu adatom is not strongly bound to an In atom in the surface and that its presence *does not* lead to site exchange. However, the presence of a Cu adatomic cluster in the vicinity of an In atom in the terrace drives this In atom into an adatomic site at temperatures as low as 80 K, and finally to incorporation into the Cu cluster. This implies that the activation energy for this process is smaller than 0.25 eV.

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