

# Indium on Cu(100) from first principles: Energetics, complex formation, and diffusion of adsorbates and vacancies on terraces and at steps

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Indium (In) on the Cu (001) surface is a paradigmatic adsorption system exhibiting two important effects: first, In has been reported to foster the layer-by-layer growth of this surface; second, In diffuses anomalously and possibly in concert with surface vacancies, and has indeed been used as a tracer of vacancy surface diffusion. Detailed knowledge of the energetics and diffusion barriers of In on Cu (001), adsorbed, coadsorbed with Cu adatoms, or in the presence of surface vacancies, as can be extracted from first-principles calculations, is an important ingredient in the understanding of these effects. Surprisingly, only a very limited amount of theoretical work exists on this system, providing rather disparate results. Here we present *ab initio* calculations of the adsorption and clustering energetics, and diffusion and kinetic barriers for a large selection of possible systems and motions involving Cu vacancies and adatoms, In adsorbates, as well as clusters and complexes thereof. We address possible modes of vacancy creation and In incorporation involving kink sites at steps, as well as the interlayer diffusion of Cu with and without In at the step edge. Among the results shedding light on the diffusion mode of In:Cu(100) as well as on the surfactant action of In, we find that In diffuses via a concerted motion with vacancies, and that In at a step lowers drastically the exchange downstep diffusion barrier for Cu, thus favoring two-dimensional growth.

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## I. INTRODUCTION

The ability to predict the morphology of thin films during growth is of fundamental interest, as well of technological importance in the development of new materials and devices (e.g., in microelectronics), all the more so as the requirements for low defectivity<sup>1</sup> and smooth layers and thin films have grown more stringent. Fulfilling such requirements by tuning experimental growth parameters (pressure, temperature, deposition flux etc.) may be a less daunting endeavor when supported by detailed knowledge of surface processes on the atomic scale, such as e.g., adsorption and diffusion, which are notoriously difficult to access directly in experiment. Thus it is important to augment experiments with detailed, accurate first-principles calculations, which is the route followed here.

The energetics, clustering, and diffusion of atoms adsorbed on crystal surfaces play a crucial role in surface mass transport and growth, and is extensively studied.<sup>2,3</sup> The knowledge of the diffusion barriers of adsorbates and defects (for example, vacancies) responsible for on-surface mass transport is an essential step to understand the involved mechanisms. The Cu(100) surface contaminated with small amounts of adsorbed In (indium) atoms is a showcase of two important phenomena: first, In affects the growth mode, favoring the layer-by-layer self-growth at room temperature;<sup>4–6</sup> second, In atoms appear to diffuse on Cu(100) with unusually low frequencies and long jumps.<sup>7–12</sup> The mechanisms underlying these phenomena are not well understood, nor does a unified explanation exist. Furthermore, despite intense theoretical (almost exclusively<sup>12–20</sup> by semiempirical methods) and experimental<sup>4,12,21–23</sup> work over the years, even the details of simple adatom diffusion on Cu(100) are still not settled. Thus, systematic knowledge of diffusion barriers of In and Cu in the presence of vacancies (along with adsorp-

tion, binding and formation energies) is of obvious importance. The measurement of these quantities is difficult and indirect, so that their calculation via reliable, nonempirical, it *ab initio* techniques is a key part of the picture.

Here we first provide first-principles results on the adsorption or formation energies of adatoms, small clusters, and vacancies on the Cu(100) surface, and the binding energy of complexes thereof where applicable; we then determine the diffusion barriers for the same systems (In and Cu adsorbates, vacancies, small clusters). The two highlights of our results are: (a) surface-embedded In diffuses in the form of a vacancy-In complex, which performs a multistep concerted motion with maximum activation energy  $\sim 0.8$  eV in excellent agreement with experiment; (b) the presence of In at or near steps drastically eases exchange downstep Cu diffusion (the barrier decreases from 0.6 eV at the clean step to about 0.2 eV at the In-embedding step), thus fostering mass transport and two-dimensional (2D) growth.

## II. METHOD

Energies and forces are calculated from first-principles within density-functional theory in the generalized gradient approximation (GGA) for the exchange and correlation functional.<sup>24</sup> All calculations are done at zero temperature. In all cases, the symmetry is deliberately kept lower than the “natural” or expected one. We use the plane-wave ultrasoft pseudopotential<sup>25</sup> method as implemented in the VASP code.<sup>26</sup> The wave functions are expanded in plane waves with cutoff 205 eV.<sup>27</sup> All pseudopotential include nonlinear core corrections. We simulate the various surface configurations by slab-geometry periodic supercells five-layers-thick  $3 \times 3$  and  $5 \times 5$  slabs (45 and 125 atoms, respectively) with 8 Å vacuum spacing. To describe steps we use a different setting: for the [110]-oriented step, a three-layer slab with

TABLE I. Adsorption energies [in eV, see Eqs. (1) and (2)] of single In and Cu adatoms on Cu(001). The energy zero is the isolated In or Cu atom.  $E_{\text{ads}}$  is the adsorption energy,  $h$  is the vertical height of the adatom from the relaxed clean Cu(001) surface. In the case of an In substitutional atom, the Cu atom removed from the surface is assumed to migrate to a kink site, i.e., to gain the calculated Cu cohesive energy ( $-3.71$  eV).

Adatom	Adsorption site	$E_{\text{ads}}$ (eV)			$h$ (Å)
		This work	EAM <sup>a,b</sup>	LDA <sup>c</sup>	
Cu	Hollow	-3.09	-2.92		1.62
In	Hollow	-2.99	-2.94	-3.42	1.98
	Substitutional (surface)	-3.31	-3.37	>-3.20	0.53
	Substitutional (second layer)	-2.22	-2.71		
	Substitutional (third layer)	-2.33	-2.56		

<sup>a</sup>Reference 12.

<sup>b</sup>Reference 34.

<sup>c</sup>Reference 35.

two complete  $6 \times 6$  atom layers and the top one with three rows removed (90 atoms); for the [100]-oriented step, a three-layer slab with two complete  $5 \times 8$  layers and the outer one with four rows out of eight (100 atoms). The atoms in the bottom layer are kept clamped in all cases, while all others relax following quantum forces. Adsorption is effected on one side only (we verified that dipole effects are negligible in a set of test cases). All calculations are done at the Cu theoretical lattice parameter of  $3.64$  Å (less than 1% larger than the experimental value of  $3.61$  Å, consistently with other calculations<sup>14,28</sup> and the typical lattice-constant overestimation<sup>29</sup> in the GGA approximation). Brillouin-zone summations are done on Monkhorst-Pack<sup>30</sup>  $8 \times 8 \times 1$  grids and with the first-order Methfessel-Paxton method<sup>31</sup> with a smearing  $\sigma=0.2$  eV. We checked, by raising the cutoff to 230 eV, refining the mesh to  $12 \times 12 \times 2$  and varying the smearing, that the energies of interest (e.g., adsorption energies) are converged to within 30 meV, and differences thereof to about 10 meV with this setting. The error bar on the reported energies is therefore  $\pm 0.01$  eV.

Surface, adsorption, formation, and binding energies of the various systems in question are obtained as total energy differences. The chemical potentials for In and Cu are fixed at the total energy of the respective bulk phases referred to free spin-polarized atoms (i.e., the cohesive energy). For bulk Cu the cohesive energy per atom is 3.71 eV, about 6% larger than the experimental 3.49 eV and again similar to other calculations.<sup>14,32</sup> The calculated surface energy is of  $1.43$  J/m<sup>2</sup>. The relaxation of the clean Cu(001) slab amounts to a 3.4% contraction of the first layer spacing, whereas the second-to-third (and deeper) layer spacing relaxation is practically zero. These surface relaxation are in good agreement with those calculated in Ref. 14, although less so with experiments.<sup>33</sup>

### III. ENERGETICS: RESULTS AND DISCUSSION

The two main adsorption processes considered in this study are Cu or In atoms adsorbed on a (001) hollow site,

and an In atom substituting for a surface Cu(001) atom. In the former, the adsorption energy  $E_{\text{ads}}^{\text{hollow}}$  is calculated as

$$E_{\text{ads}}^{\text{hollow}} = E_{\text{slab+ad}} - E_{\text{slab}}, \quad (1)$$

where  $E_{\text{slab+ad}}$  is the total energy of the slab plus an adatom in a hollow site and  $E_{\text{slab}}$  is the total energy of the slab without adatom (the energy is taken to be zero in the case of a free atom). When an In atom adsorbs substituting a surface copper atom, the adsorption energy is

$$E_{\text{ads}}^{\text{subst}} = E_{\text{slab+subst}} + \mu_{\text{bulk}} - E_{\text{slab}}, \quad (2)$$

where  $E_{\text{slab+subst}}$  is the total energy of the slab with a substitutional In atom,  $E_{\text{slab}}$  is the total energy of the slab [not necessarily a perfect Cu(001) surface, but possibly with other impurities or defects present, as will be discussed in Secs. III B and III C], and  $\mu_{\text{bulk}}$  is the bulk energy of Cu, i.e., the removed surface Cu atom is supposed to be incorporated at a kink site. Adsorption and cohesive energies are referred conventionally to isolated atoms.

#### A. Adsorption of Cu and In on Cu(001)

The adsorption energies for In and Cu are reported in Table I along with those obtained in previous local-density-functional (LDA) (Refs. 35 and 36) and embedded-atom (EAM) (Refs. 12 and 34) calculations. The main result of this table is for the adsorption of In adatom. The favored configuration for an In adatom is substitutional for a Cu surface atom. Our result confirm the most credited interpretation of angular  $\gamma$ - $\gamma$  correlation<sup>4,37,38</sup> and more recent scanning tunneling microscopy (STM) experiments,<sup>12</sup> indicating the (nearly) substitutional terrace site as the lowest-energy adsorption site for In. The calculated height of the surface-embedded In over the Cu(001) surface plane is  $0.53$  Å, and agrees well with STM estimates<sup>12,39</sup> between  $0.4$  Å and  $0.6$  Å. LDA cluster calculations<sup>35</sup> report the hollow adsorption site as favored, probably due to their neglect of relaxations. Controversial results obtained with cluster methods were discussed earlier on.<sup>40-42</sup>

TABLE II. Adsorption [ $E_{\text{ads}}$ , see Eqs. (1) and (2)] and binding [ $E_{\text{bind}}$ , see Eq. (3)] energies in eV, of In and Cu atoms on Cu(001) at various distances from substitutional In. In adatoms are adsorbed on a hollow site (see Fig. 1) or substituted into a surface site (see Fig. 2). In both cases, their energy is taken to be zero when they are isolated. The ‘‘Adsorption site’’ column indicates the position of the adatom with respect to In substitutional.

Adatom	Adsorption site	$E_{\text{ads}}$ (eV)	$E_{\text{bind}}$ (eV)	
			This work	EAM
Cu	First-neighbor hollow	-3.01	0.08	0.21 <sup>a</sup>
	Second-neighbor hollow	-3.13	-0.04	0.20 <sup>a</sup>
	Isolated	-3.09		
In	First-neighbor hollow	-2.77	0.22	0.28 <sup>b</sup>
	Second-neighbor hollow	-2.99	0.00	0.01 <sup>b</sup>
	Isolated hollow	-2.99	0.00	
	First-neighbor substitutional	-3.18	0.13	0.26, <sup>b</sup> 0.15, <sup>c</sup>
	Second-neighbor substitutional	-3.34	-0.03	0.03, <sup>b</sup> -0.05 <sup>c</sup>
	Third-neighbor substitutional	-3.36	-0.05	
	Fourth-neighbor substitutional	-3.34	-0.03	
	Fifth-neighbor substitutional	-3.33	-0.02	
	Isolated substitutional	-3.31		

<sup>a</sup>Reference 12.

<sup>b</sup>Reference 34.

<sup>c</sup>Reference 44.

In Table I we also report the adsorption energies [calculated according to Eq. (2)] for In atoms substituted for Cu atoms in the second and third layer. At these bulklike sites, In is less stable than In substitutional in the surface layer by over 1 eV. This result is consistent with the negligible solubility of In in Cu at low temperature, and with the segregation of In during growth without appreciable loss.<sup>12</sup> A similar behavior was found for the analogous configuration of Sb on Ag(111) (see Ref. 43 and references therein).

### B. Adsorption on Cu(001) near substitutional In

In Table II we report the adsorption and binding energies for Cu and In atoms adsorbed on Cu(001) at various distances from an In atom substituted in a surface site (see Fig. 1). The case of an In atom adsorbed in a surface substitutional site at various distances from another substituted In atom (see Fig. 2) is also considered. The adsorption energies are calculated according to Eqs. (1) and (2), but in this case the slab contains a substitutional In atom. The binding energy is defined as

$$E_{\text{bind}} = E_{\text{slab+ad(subst)}} - E_{\text{slab}}, \quad (3)$$

where  $E_{\text{slab+ad(subst)}}$  is the energy of either a system with an adatom on a hollow site, or of a system with an additional substituted In adatom (two substituted In atoms present). The binding energy immediately shows the attractive or repulsive nature of the interaction of the surface-embedded In atom with adatoms on surface sites or other embedded-In atoms. The action of a substituted In is clearly repulsive at short range both for adatoms and other substitutional In atoms.

The larger size of In compared to Cu would suggest a repulsion mediated by the substrate and mainly of elastic origin.<sup>45,46</sup> A similar repulsive action on surface adatoms was

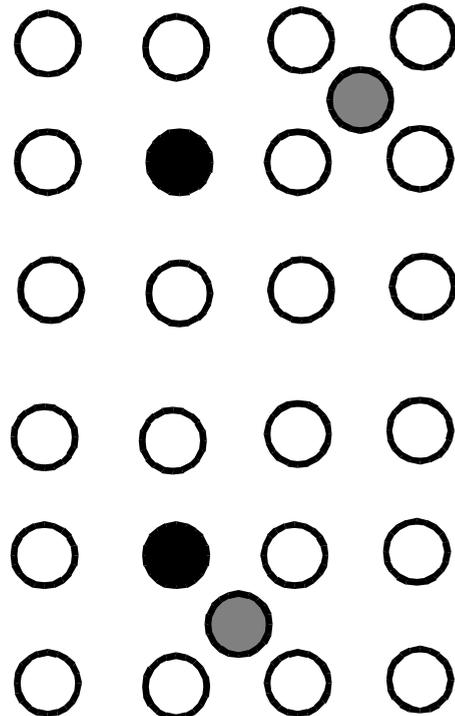


FIG. 1. Cu or In adatoms (gray circles) adsorbed on a first-neighbor hollow site (left) and on a second-neighbor hollow site (right) with respect to a substitutional In atom (black circles)

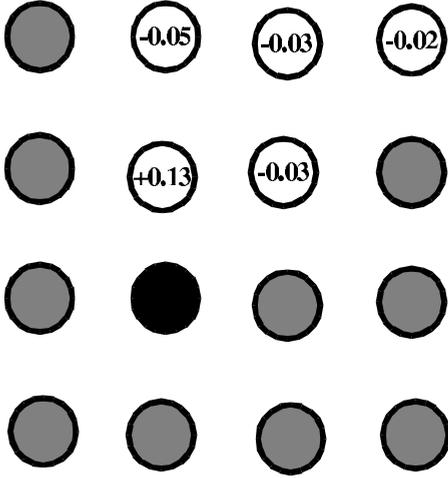


FIG. 2. In atoms (white circles) substituted at various distances from another substitutional In atom (black circle). The reported values inside the white circles are the binding energies,  $E_{\text{bind}}$  (eV), given in Table II. The gray circles are the Cu atoms of the substrate.

found theoretically for surface-substituted Sb on Ag(111),<sup>43</sup> and suggested<sup>43,47</sup> as the cause of the surfactant action of Sb on that system. However, for In incorporated in Cu(001) the repulsion is quite short range and much less intense. Thus, other effects are likely to concur to determine the surfactant action of In. We will elaborate this point further in Sec. IV.

Table II indicates that the interaction between substituted In atoms may be (slightly) attractive at distances larger than first neighbor. This result is consistent with STM (Refs. 12 and 39) and angular-correlation<sup>4,38</sup> experiments, which claim the observation of embedded-In clusters. These embedded-In islands should be randomly oriented, as all direction seems roughly equivalent from the calculations.

### C. Dimer and trimer adsorption on Cu(001)

The binding energies  $E_{\text{bind}}$  of an  $n$ -adatom clusters ( $n$ -mer) are calculated according to

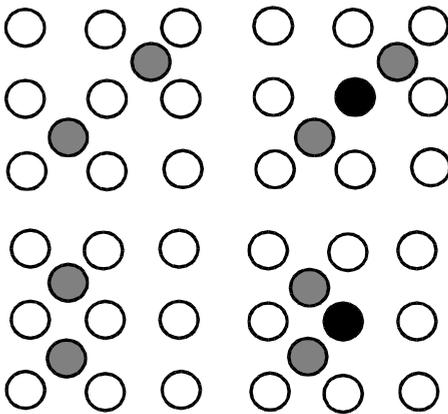


FIG. 3. The two considered dimers (gray circles) taken on a clean Cu(001) surface (top) and close (bottom) to a substitutional In atom at surface (black circle).

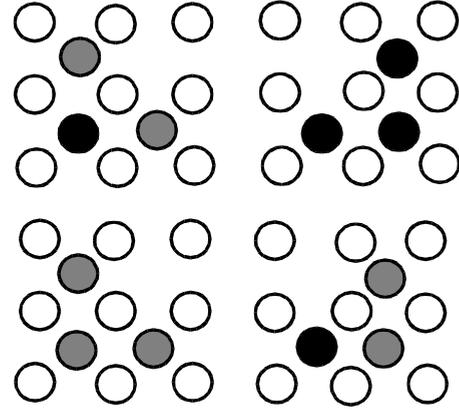


FIG. 4. The four considered (compact) trimers. The gray circles are Cu atoms while the black ones are In atoms.

$$E_{\text{bind}} = E_{\text{slab}+(n\text{-mer})} - nE_{\text{ads}}^{\text{hollow}} - E_{\text{slab}} \quad (4)$$

where  $E_{\text{slab}+(n\text{-mer})}$  is the energy of the system with the adsorbed and relaxed cluster,  $E_{\text{ads}}^{\text{hollow}}$  the adsorption energy of an isolated adatom [see Eq. (1)] and finally  $E_{\text{slab}}$  is the energy of either a clean Cu(001) slab or one with an embedded-In atom. Here we consider the dimers ( $n=2$ ) and trimers ( $n=3$ ) depicted, respectively, in Figs. 3 and 4. All geometries are of course fully relaxed.

The binding energies for various mixed dimers are reported in Table III. The binding energy for the homogeneous dimer Cu-Cu is negative, meaning attraction, and its value is in good agreement with previous EAM results.<sup>14,15,34,44</sup> The *ab initio* binding energy of  $-0.22$  eV given in Ref. 14 is also in a similar range. The agreement is poor with the  $-0.63$  eV obtained in Ref. 35, as well as for the two Cu-In and In-In dimers; as already mentioned, we presume this discrepancy may be due to an incomplete account of atomic relaxations in Ref. 35.

The Cu adatoms weakly attract each other also at second-neighbor distance (Fig. 3 dimer on the top-left). This is not obvious, as second-neighbor adatoms on other fcc (001)

TABLE III. Binding energies [see Eq. (4)] in eV for various In and Cu dimers on Cu(001), far from or near to embedded-In atoms. The considered dimers are those of Fig. 3.

Dimer	Component sites	$E_{\text{bind}}$ (eV)
Cu-Cu <sup>a</sup>	First-neighbor hollow	-0.36
Cu-Cu <sup>a</sup>	Second-neighbor hollow	-0.07
Cu-In <sup>a</sup>	First-neighbor hollow	-0.27
Cu-In <sup>a</sup>	Second-neighbor hollow	-0.09
In-In <sup>a</sup>	First-neighbor hollow	+0.03
In-In <sup>a</sup>	Second-neighbor hollow	-0.04
Cu-Cu <sup>b</sup>	First-neighbor hollow	-0.04
Cu-Cu <sup>b</sup>	Second-neighbor hollow	+0.27

<sup>a</sup>On a clean surface.

<sup>b</sup>On a surface with substitutional In.

TABLE IV. Binding energies [see Eq. (4)] in eV of various trimers on a clean Cu(001) surface. We consider the compact trimers of Fig. 4.

Trimer	$E_{\text{bind}}$ (eV)
Cu-Cu-Cu	-0.69
Cu-Cu-In	-0.60
Cu-In-Cu	-0.49
In-In-In	+0.02

faces have been reported to interact repulsively [*ab initio* results on Al (Ref. 48) and EAM on Ir and Pt (Refs. 49 and 50)] due to substrate mediation. Cu and In adatoms also bind to form a dimer, although less strongly; this suggests that any In adatom will function as nucleation-enhancing agent for deposited Cu adatoms, given its lower diffusion activation energy, and hence higher mobility (discussed in Sec. IV). Finally, a substitutional In atom acts as a destabilizing agent for Cu-Cu dimers next to it, although the effect is short range.

Due to its large size in comparison to Cu, In is not expected to cluster with another In at first-neighbor hollow sites, but possibly to bind weakly at second-neighbor sites. Indeed this is reflected by our results. In this regard, we disagree once more with cluster results,<sup>35</sup> and agree with EAM calculations.<sup>34</sup> Our finding of longer-range attraction may be compatible with STM experiments<sup>12,39</sup> suggesting the formation of on-terrace In clusters below 200 K.

Table IV reports binding energies for various trimers on the (001) surface. The results confirm those for dimers, with an attractive (except, as expected, for the all-indium trimer with atoms in first-neighbor hollow sites) interaction among adsorbates, stronger between Cu adatoms. Notice that the trimer binding energies are less than twice those of the corresponding dimers, hence the energy per bond is smaller in the trimer: this bond-energy saturation behavior is quite general, as shown for example in Refs. 15 or 51. The attraction between adsorbed In and Cu is consistent with the energy gain obtained by embedding In into a Cu layer, and suggests that when Cu islands are forced during growth to approach embedded-In atoms, the latter will exchange with a Cu adatom and segregate to the upper layer. Both the energetics of In already discussed, and the kinetics to be discussed in Sec. IV below, support this suggestion.

#### D. Vacancy formation on Cu(001)

The formation energy of a Cu vacancy is calculated as

$$E_{\text{vac}}^{\text{form}} = E_{\text{slab+vac}} + \mu_{\text{bulk}} - E_{\text{slab}}, \quad (5)$$

where  $E_{\text{slab+vac}}$  is the energy of a Cu slab with a vacancy,  $\mu_{\text{bulk}}$  is the bulk energy of Cu, and  $E_{\text{slab}}$  is the energy of an undefected Cu slab. The latter may be either clean or with a substitutional In atom. The value of the vacancy formation energy (Table V) on clean Cu(001) is 0.49 eV in our calculation. A similar *ab initio* result was obtained<sup>28</sup> using a

TABLE V. Formation energies (in eV, see Eq. (5)) of Cu vacancies on Cu(001). The configurations are shown in Fig. 5.

Vacant site	$E_{\text{vac}}^{\text{form}}$ (eV)
First neighbor to substitutional In	0.37
Second neighbor to substitutional In	0.50
Isolated	0.49

smaller supercell. The EAM formation energies are between 0.47 (Ref. 15) and 0.59 eV.<sup>13</sup> The few experimental values for the vacancy formation energy are in the range 0.45–0.57 eV.<sup>52,53</sup>

A key result is that a vacancy first neighbor to a substitutional In atom (see Fig. 5) has a formation energy 0.12 eV lower than a vacancy on a clean terrace, i.e., a vacancy tends to bind to substitutional In. Given its larger size compared to Cu, it is reasonable that an embedded In will exploit the extra room available near a vacancy; indeed, the formation energy for a vacancy second-neighbor to embedded In is essentially the same as for a vacancy on a clean terrace, indicating no In-vacancy interaction other than a pure size effect. The only (rather indirect and uncertain) experimental estimate of the interaction energy of a vacancy with an em-

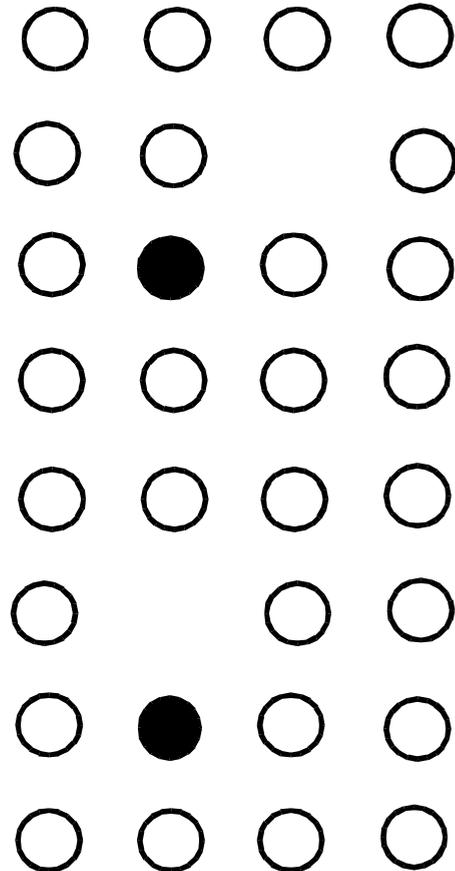


FIG. 5. Surface vacancies which are first neighbor (left) and second neighbor (right) with respect to an incorporated In atom (black circle) in the surface

TABLE VI. Adsorption energies (in eV, see Eq. (1)) of In and Cu adatoms on Cu(001) on hollow sites at various distances from a surface Cu vacancy (see Fig. 6).

Adatom	Spatial relationship between adatomic and vacancy site	$E_{\text{ads}}$ (eV)
Cu/Cu(001)	First neighbor (unstable)	-2.85
	Second neighbor	-3.07
	Isolated	-3.09
In/Cu(001)	First neighbor (unstable)	-2.90
	Second neighbor	-2.98
	Isolated	-2.99

bedded In is of about 0.25 eV,<sup>54-57</sup> somewhat higher than the calculated one.

As will be discussed in Sec. IV, the properties of this In-V complex are relevant to the interpretation of the diffusion of incorporated In on this surface. They indeed suggest the idea of In diffusion assisted by a vacancy, in close analogy with, for example, native-defect-assisted impurity diffusion in semiconductors.<sup>58</sup> This point will be discussed further in Sec. IV together with the question of how and where the vacancies are created. We will see that although the formation energy of a vacancy is modest, the activation energy necessary to create a vacancy by ejection of a Cu atom from the terrace is very large. Vacancies must be created elsewhere, and our calculations show that creation at kinks is efficient, and quite consistent with the experimental activation energy proposed for vacancy motion.<sup>12</sup>

Finally, we consider the vacancy interaction with Cu and In adatoms. The adsorption energies reported in Table VI clearly show that there is no sizable interaction between surface vacancies and adatoms. An exception is the nearest-neighbor site, whereby both Cu and In adatoms simply drop into the vacancy without kinetic hindrance.

#### IV. DIFFUSION: RESULTS AND DISCUSSION

As mentioned earlier on, systematic knowledge of diffusion barriers of In and Cu in the presence of vacancies (along with adsorption, binding and formation energies) is of obvious importance to the understanding of surfactant effects and anomalous diffusion. The measurement of these barriers is difficult and indirect, so that their calculation via reliable, nonempirical, *ab initio* techniques is a key part of the picture.

We obtain two main results: (a) surface-embedded In diffuses in the form of a vacancy-In complex, which performs a multistep concerted motion with maximum activation energy  $\sim 0.8$  eV in excellent agreement with experiment; (b) the presence of In at or near steps drastically eases exchange downstep Cu diffusion (the barrier decreases from 0.6 eV at the clean step to about 0.2 eV at the In-embedding step), thus fostering mass transport and 2D growth.

We calculate the diffusion barriers  $E_{\text{barrier}}$  appearing in the Boltzmann factor of the diffusion coefficient,

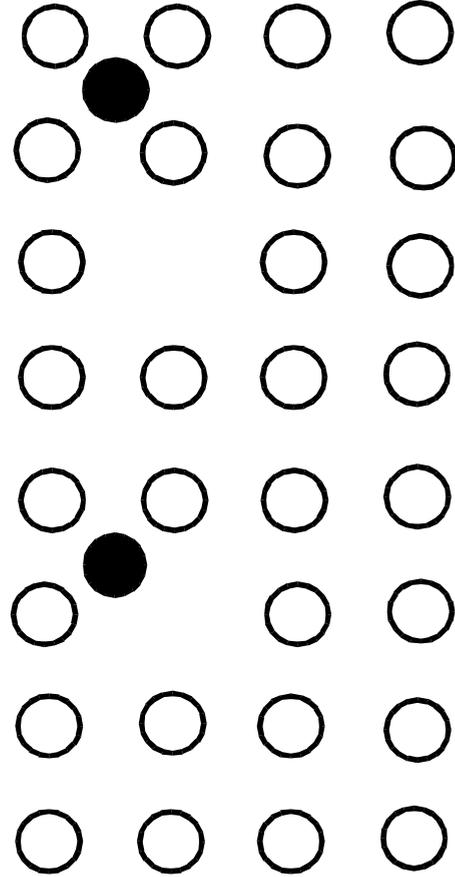


FIG. 6. The two considered configurations for adatoms (black circles) adsorbed in proximity of a surface vacancy (empty space)

$$D = D_0 e^{-E_{\text{barrier}}/k_B T}. \quad (6)$$

We do not address, instead, the prefactor  $D_0$ . The barriers are calculated according to

$$E_{\text{barrier}} = E_{\text{ads}}^{\text{ES}} - E_{\text{ads}}^{\text{TS}}, \quad (7)$$

where  $E_{\text{ads}}^{\text{ES}}$  is the energy of the considered adsorbate or defect (es. adatom, vacancy, dimer etc.) at its equilibrium site (ES), while  $E_{\text{ads}}^{\text{TS}}$  is the adsorption energy of the same adsorbate at the transition site (TS). The latter is determined by transition-state configurations identified with the nudged-elastic-band method.<sup>59</sup>

##### A. Diffusion of Cu and In on Cu(100)

Table VII reports the diffusion barriers for on-surface Cu and In adatoms. For Cu, we considered hopping or exchange on clean Cu(001), and exchange with a surface-embedded In adatom. This is because, as shown in Sec. III, the favored configuration for In on Cu (100) is surface substitutional. For In, we considered instead simple hopping, and exchange with a substrate (Cu) atom.

Despite its apparent simplicity, the favored migration mechanism for single adatoms diffusion on Cu(001)—single jump, exchange,<sup>60</sup> or alternative<sup>61,62</sup> mechanisms—has long been disputed. Especially the exchange diffusion barriers calculated with various semiempirical potentials are quite dis-

TABLE VII. Diffusion barriers [Eq. (7)] for of In and Cu adatoms ( $\text{In}_{\text{ads}}$  and  $\text{Cu}_{\text{ads}}$ ) on a Cu(100) surface for hopping and exchange as sketched in Fig. 7.

Adatom	Diffusion mechanism	$E_{\text{barrier}}$ (eV)
$\text{Cu}_{\text{ads}}$	Hopping	0.55
	$\text{Cu}_{\text{ads}}\text{-Cu}_{\text{surf}}$ exch	0.95
	$\text{Cu}_{\text{ads}}\text{-In}_{\text{subst}}$ exch	0.46
$\text{In}_{\text{ads}}$	Hopping	0.23
	$\text{In}_{\text{ads}}\text{-Cu}_{\text{surf}}$ exch	0.86

parate (see for example Refs. 12–20 and references therein). Experimentally, there exists just one STM direct observations of the adatom diffusion barrier and of the corresponding diffusion mechanism.<sup>12</sup> In all other experiments<sup>4,21–23</sup> the diffusion barriers were obtained indirectly. According to Ref. 12, the favored diffusion mechanism for Cu adatoms on Cu(100) is hopping, with an energy barrier of 0.36 eV.

Our calculations (Table VII) confirm that the hopping mechanism is favored over exchange. There remains a quantitative disagreement with experiment,<sup>4,12,21–23</sup> despite the high accuracy of our calculations. Our energy barriers are actually similar to those reported in Ref. 14, the only other GGA data point available,<sup>63</sup> although those calculations<sup>14</sup> were less accurate due to the computational limitations of the time (smaller supercell, relaxation of the first two layers only) and diffusion barriers were not evaluated by NEB. The disagreement of theory (the present calculations, and other first-principles<sup>14,64</sup> or EAM<sup>13–15,65</sup> studies) with STM experiment might be due to perturbations induced by the tip. It seems less likely for it to be an artifact due to the presence of vacancies: STM should readily observe any recombination of Cu adatoms with a mobile surface vacancy.<sup>66</sup> An influence of dimer mobility should be excluded as well, since dimers should also be distinguishable by STM. The possible problems with other experiments<sup>21–23</sup> are discussed in detail in Refs. 14 and 67. As also observed by Feibelman,<sup>68</sup> it is puzzling that all these experiments give similar barrier values, and consistently quite different from calculated values, especially those from first principles. It may be important to look to situations where the exchange mechanism can be relevant,

as seems to be the case for strained surfaces,<sup>69</sup> or when exchange process involves more than one substrate atom.<sup>61,62</sup> The latter, however, should be relevant only at high temperature. We note that a hopping-barrier lowering for Pt on Pt(100) from 0.56 to 0.36 eV (similar to the present discrepancy) has been reported in EAM calculations<sup>69</sup> upon enlarging the simulation cell from  $5 \times 5$  to  $10 \times 20$ . While EAM calculations also deviate appreciably from experiment for Cu, the observation of this effect for Pt (never investigated directly for Cu,) does hint at a possible size dependence beyond the scope of DFT calculations.

Table VII further lists the diffusion barriers of single In adatoms adsorbed on Cu(100), and of Cu adatoms involving one In atom at a surface substitutional site. Hopping is clearly favored also for In. The barrier is less than half that of Cu, similar to that obtained experimentally—although with reportedly low accuracy—by van Gastel,<sup>12</sup> and implies very fast In on-surface diffusion.

Two more important data in Table VII are the barriers for exchange of a Cu adatom with an surface-embedded In (line 3 of the Table), and for the reverse process of on-surface In exchanging with a surface Cu atom. The direct Cu-In exchange process has a barrier of 0.46 eV, which is lower than the hopping barrier of Cu, and in fact half the exchange barrier for Cu pairs. Thus Cu on surface will exchange easily with substitutional In: assuming a nonanomalous prefactor of order 10 THz, this mechanism activates around 200 K. The reverse process of In pushing out a Cu has almost twice as large a barrier, 0.86 eV, and activates at 500 K for the same prefactor. First, this indicates that In surface-substitutionals segregate efficiently<sup>8,12,34</sup> at room temperature when Cu is deposited. Second, the  $\text{Cu}_{\text{ad}}\text{-In}_{\text{sub}}$  easy exchange may suggest a pop up/travel/push back sequence of In in-surface diffusion, but the end event (In returning into substitutional position) is costly, and hence should be ruled out. Also, the rapidly diffusing on-surface In adatom would cover huge distances before exchanging back into the surface, which is not what experiments observe.<sup>7,8</sup> On the other hand, the idea<sup>7–10</sup> that In diffusion in the surface plane should be vacancy-assisted [as suggested also for the diffusion of Pd (Ref. 28) and Mn (Ref. 70) on this same surface] rather than adatom-assisted remains into play, and we will discuss it further in Sec. IV D.

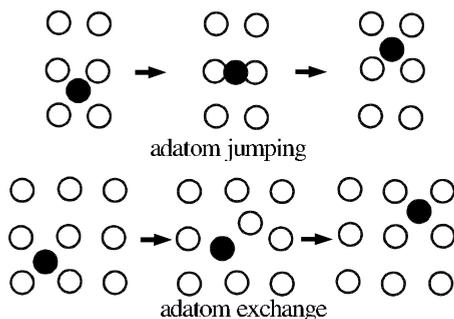


FIG. 7. Considered diffusion processes for an adatom (black circle) adsorbed on a Cu(100) surface (empty circles): simple jump (upper panel), adatom-substrate atom exchange (lower panel).

## B. Diffusion of Cu and In near a substitutional In

It has long been known<sup>5</sup> that surface-embedded In affects the self-growth of Cu low index surfaces. In particular it favors the layer-by-layer growth of both Cu(100) and Cu(111),<sup>71</sup> i.e., it acts as a surfactant for the homoepitaxy of Cu. A first step to understand the surfactant mechanism is looking at how the energetics and diffusion of on-surface Cu and In adatoms is modified by substitutional In. The results described in Sec. III abundantly confirm previous indications<sup>9,10,12,34,35</sup> that Cu and In adatoms are weakly repelled at short range by substitutional In. Here we analyze instead the effect of substitutional In on the diffusion barriers of adatoms. The global effect for Cu adatoms (see Fig. 8 and Table VIII) is (a) an effective weak (0.05 eV) energy reduc-

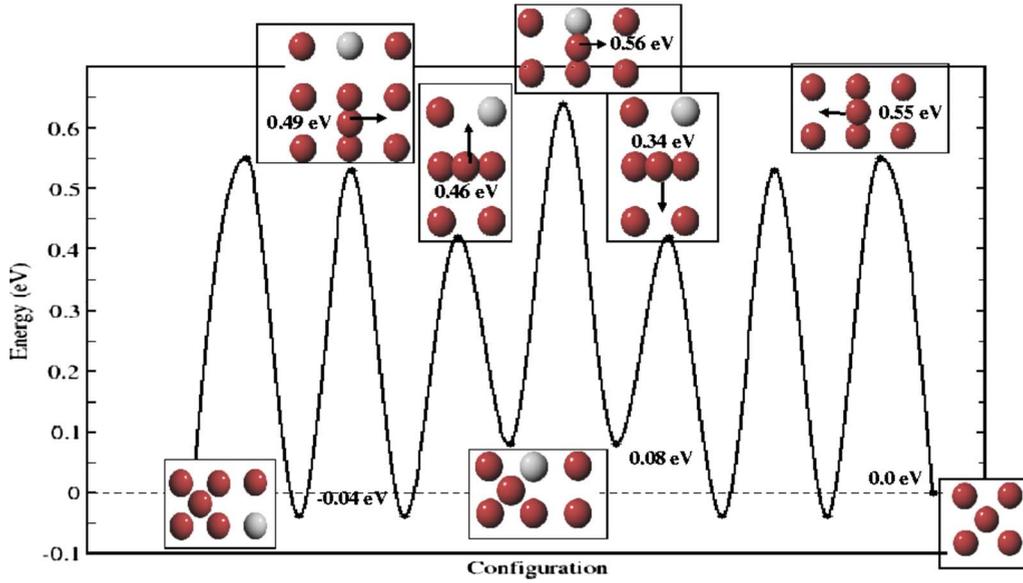


FIG. 8. (Color online) Pictorial illustration of Cu adatom interactions with a substitutional In. The energy zero is isolated substitutional In plus isolated Cu adatom. The diffusion barriers are listed in Table VIII.

tion (i.e., attraction) toward the vicinity of In, and (b) reduced diffusion barriers in the same region. So the net effect is a (weak) funneling of Cu toward the vicinity of substitutional In, whereby—based upon our calculated Cu-In exchange barrier—it will exchange with In.

The agreement with EAM (Ref. 12) calculations is not quantitative, and does not improve even comparing directly with nonrescaled EAM barriers (in Ref. 12 the barriers were divided<sup>4</sup> by 1.7 to match experimental adatom barriers). Unlike EAM, we find the reduction in the diffusion barriers of Cu near an incorporated In to be sizable (about 0.2 eV).

### C. Dimer and trimer diffusion

The calculated energy barriers for dimers and trimers are reported in Table IX. Only diffusion processes due to single

TABLE VIII. Diffusion barriers [Eq. (7)] for hopping of In and Cu adatoms ( $\text{In}_{\text{ads}}$  and  $\text{Cu}_{\text{ads}}$ ) in the vicinity of a substituted In atom. The processes are sketched in Fig. 8. Numbers in brackets refer to jumps between sites second-neighbor and first-neighbor to substitutional In. The EAM (Ref. 12) barriers in the second row are for a third-to-second-neighbor Cu jump. The EAM barriers are<sup>12</sup> rescaled by a factor 1.7 (see text).

Adatom	$E_{\text{barrier}}$ (eV)	
	This work	EAM <sup>a</sup>
$\text{Cu}_{\text{ads}}$	0.34(0.46)	0.23(0.33)
	0.56	0.35(0.35)
	0.49	
$\text{In}_{\text{ads}}$	0.15(0.23)	

<sup>a</sup>Reference 12.

atomic jumps have been considered in this study. These should be germane for diffusion at low temperatures: for dimers the relevant diffusion barriers are those to go from equilibrium to metastable states, i.e., from dimers with atoms adsorbed in first-neighbors hollow sites to dimers with atoms adsorbed in second-neighbors hollow sites (see Fig. 9), which are the rate-limiting processes. The diffusion barriers for the reverse processes cannot be but smaller, hence the corresponding processes are consequently much faster, and moreover they act against dissociation. The calculations clearly show that the diffusion barriers for all the dimers are comparable or even lower than those of single jumps of isolated Cu and In atoms. This means that the mass transport

TABLE IX. Single-atom hopping diffusion barriers from equilibrium to metastable states and vice versa (the latter are in brackets) in Cu-Cu, Cu-In, and In-In dimers and Cu-Cu-Cu, Cu-Cu-In, and Cu-In-Cu trimers adsorbed on Cu (100). Single-atom motions are considered only. For the Cu-In dimers, the two barriers refer to Cu adatom motion (first line) or In adatom motion (second line). See Figs. 9 and 10 for a sketch of the processes.

Dimer	$E_{\text{barrier}}$ (eV)
Cu-Cu	0.54(0.24)
Cu-In	0.48(0.31)
	0.17(-0.17)
In-In	0.23(0.16)
Trimer	$E_{\text{barrier}}$ (eV)
Cu-Cu-Cu	0.29
Cu-Cu-In	0.26
Cu-In-Cu	0.37(0.14)

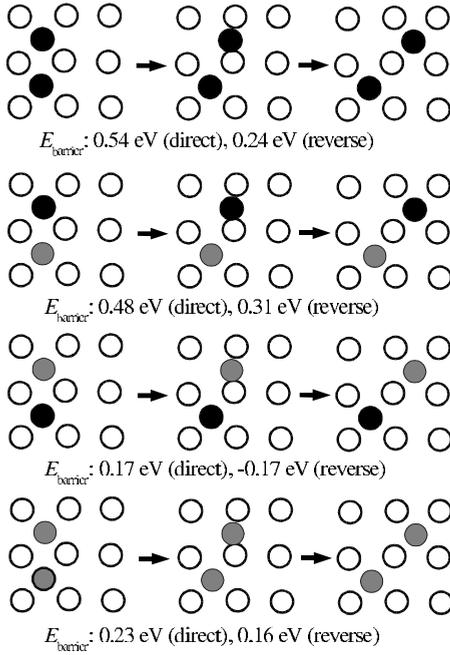


FIG. 9. Diffusion mechanisms and attendant energy barriers (see listing in Table IX) for dimers. Only single atom jumps have been considered. “Direct” indicates a jumps in the direction of dimer dissociation; “reverse” is the opposite motion. Black (white) circles denote Cu adatoms (terrace atoms); gray circles are In adatoms.

due to dimer diffusion can easily have same relevance as the adatomic mass transport. Moreover, the calculated barriers are expected to be smaller (possibly by up to 0.1 eV) in the case of a concerted jump, i.e., if we allowed the second atom of the dimer to follow the first during its motion. We also observe that, in the case of Cu-In dimers, In atoms do not experience a barrier, i.e., they flip into place seamlessly, when a dimer passes from a metastable to a stable state.

The above discussion suggests that dimers are mobile, and the smallest immobile clusters close to room tempera-

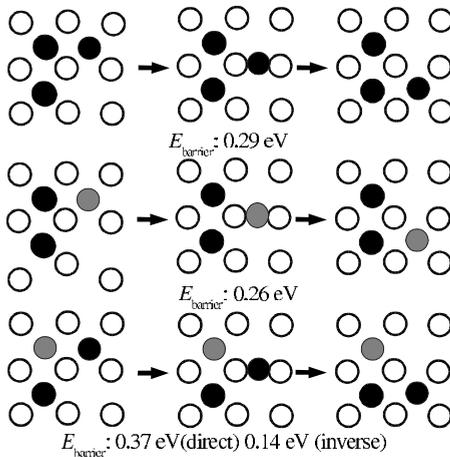


FIG. 10. Diffusion processes and attendant barriers (see also Table IX) for a Cu-Cu-Cu trimer (Cu adatom: black; substrate Cu: white) and two Cu-Cu-In trimers (black: Cu; gray: In). Only single atom jumps producing internal rearrangements have been considered.

TABLE X. Diffusion energy barriers for a vacancy on Cu(100) far from (see Fig. 11, upper panel) and in proximity of an embedded In (see Fig. 11, lower panel). Also reported the barriers for strained and compressed substrates. The two numbers for hopping near subst. In refer to motion toward and away from In, respectively.

Diffusion process	$E_{\text{barrier}}$ (eV)
Hopping	0.43
Hopping, strain: $-2.74\%$	0.28
Hopping, strain: $+2.74\%$	0.55
Hopping, near subst. In	0.28, 0.41
$V_{\text{Cu-In}_{\text{subst}}}$ exchange	0.07

tures must be trimers or larger. This should be accounted for in the rate-equation modeling of transport and island accretion on Cu (100). Our calculated barriers for trimers are also rather small, suggesting they may be mobile themselves. However, we cannot confirm this definitively based on our present data, since we only considered “in-place” motions that do not produce effective mass transport. Concerted multiatom motions would have to be simulated to conclusively decide this issue, but these are outside our present capabilities.

#### D. Vacancy diffusion and creation

Table X reports the calculated barriers for a surface vacancy on a flat Cu(100) terrace, both isolated and in the vicinity of a substituted In atom. For the isolated vacancy, the barriers have been calculated also under strain. The first physically relevant result is that the diffusion barrier for a vacancy in the unstrained system is lower than the diffusion barrier of a single Cu adatom. This result agrees a previous *ab initio* calculation,<sup>14</sup> and it can have important consequences for the surface mass transport in certain circumstances, such as Ostwald ripening.<sup>70,72</sup> The barrier is appreciably lower for a negative in-plane strain: for, e.g., epitaxial systems under negative strain the mass transport due to vacancies will probably be dominant (the barrier for adatom hop does not<sup>69,73</sup> change as drastically). The barrier at positive strain tells us that vacancy diffusion will not change appreciably at higher temperature because thermal lattice expansion is comparatively small on this strain scale.

The next important question is whether calculations support the view that vacancies assist<sup>7-10,28,70,74</sup> the diffusion of incorporated In atoms as well other embedded atoms on Cu(100) and Cu(111) surfaces, and in particular if In may be incorporated at steps and be slowly and homogeneously spread throughout the terrace by vacancy-assisted motion.<sup>7-10</sup> We defer the discussion of step incorporation to Sec. IV E and consider vacancy-assisted diffusion. Our calculations largely confirm this interpretation. We have shown in Sec. III that the energetic cost to form a vacancy besides an embedded In is significantly smaller than for a isolated vacancy (0.37 eV vs 0.49 eV). In other words, when a vacancy is close to an incorporated In at surface an In-vacancy complex is formed, and a correlated In-vacancy motion is

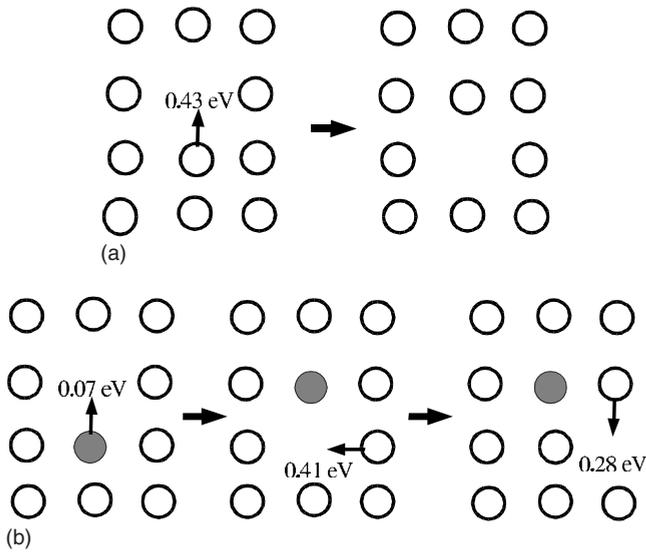


FIG. 11. Vacancy diffusion processes on clean Cu(100) (upper panel) and for a vacancy close to a substitutional In atom at surface (lower panel)

possible as that depicted in the lower panel of Fig. 11. The activation energy (formation plus diffusion) for this correlated motion, according to our calculation, is 0.78 eV: this is the sum of the vacancy formation energy near a substituted In (0.37 eV) and the largest of the diffusion barrier (0.41 eV) involved in the “slide-puzzle” correlated In-vacancy motion (Fig. 11, lower panel). This result is in good agreement with the experimental data in Refs. 7 and 8. This is analogous to the native-defect-assisted impurity diffusion in semiconductors.<sup>58</sup>

However, the activation energy is not the only relevant parameter to judge if the proposed mechanism is reasonable. It is important to check if the vacancy population is in thermodynamic equilibrium when the sample is imaged with STM, which happens hours after the sample is prepared.<sup>7,8</sup> This will only be true if none of the processes involved in vacancy *creation* is unreasonably costly; in other words, although vacancy formation is relatively inexpensive, its creation may still involve some huge barrier. Indeed, we calculated directly via NEB that the creation of a vacancy through the direct expulsion of an Cu atom from the terrace (the initial configuration is a flat surface, the final one a vacancy with a Cu adatom in a nearby hollow site) costs a huge 1.7 eV (a similar estimate was provided in Ref. 70). Thus a less costly mechanism of vacancy creation must be operative. A natural candidate event is vacancy creation at kink sites of surface steps, because Cu is naturally undercoordinated there, and also because vacancies can be formed without destructing the kink, i.e., the vacancy source itself.

We have then calculated via the NEB method the energy barriers for a vacancy to enter into a surface terrace from a kink site (or, more precisely, for a Cu atom to be detached from the kink) for both step orientations on Cu(100). These processes are depicted in Fig. 12 together with the calculated barriers. The respective barriers are 0.7 eV for a vacancy created at a kink site of [110]-oriented step, and 0.65 eV at a [100]-step. Both are somewhat smaller than the activation

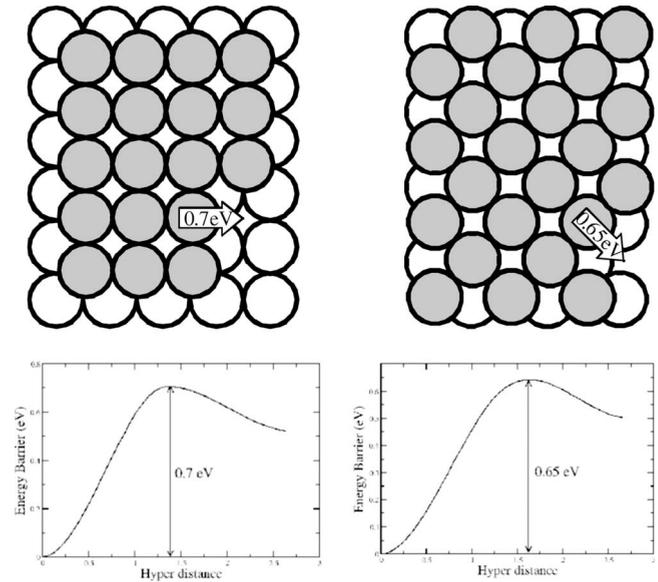


FIG. 12. Vacancy creation processes at kink sites and attendant activation energies calculated via NEB. Right panel: vacancy formation at kink on [100]-oriented step; left panel: same, along [110]-oriented step. White circles: Cu atoms on lower terrace; gray: Cu atoms on upper terrace.

energy of the vacancy estimated above. We conclude that vacancy creation at steps does not introduce a kinetic hindering, and that the activation energy is the rate-limiting factor (which is indeed consistent with observations).

### E. In incorporation and Cu migration at steps

As mentioned earlier, the most favored adsorption site for In on Cu(100) is surface substitutional. During Cu deposition, predeposited In will help nucleate Cu islands and will be embedded in them. If Cu is not deposited, however, on-surface In should exchange with a surface Cu. We have seen in Sec. IV A that this process is relatively expensive. Indeed, STM observations<sup>8,39</sup> suggest that In incorporation might occur at steps, and could be vacancy assisted. We performed calculations for an In adatom jumping into a pre-existing vacancy at a kink site, and found the barrier to be zero to computational accuracy (the barrier against vacancy formation is about 0.7 eV, as shown in Sec. IV D). Our calculations therefore support strongly the vacancy-assisted step-incorporation mechanism for In.

Steps are also thought<sup>5,35,75</sup> to play a role in the In surfactant action on Cu growth (although this viewpoint is not universally accepted<sup>12</sup>). We performed NEB calculations to evaluate the transition-state barriers of some interlayer diffusion processes for Cu, also involving In atoms in the vicinity of the steps. These calculations are quite expensive, so a selection of possible migration mechanisms have been investigated only for the [110]-oriented step. Given that no major island shape anisotropy is observed on this surface, we expect that such calculations should be broadly representative of the effect of In on downstep diffusion.

The Cu jump and push-out motions across the step edge have been investigated for the clean step (no In present) and

TABLE XI. Diffusion barriers (eV) for Cu downstep jump and exchange, for a clean step, an In-embedding step edge, and a step edge with In in the second upper-terrace row. “SEb” indicates the Schwöbel-Ehrlich additional barrier (the difference of the reported barrier to the lowest on-terrace diffusion barrier, i.e., that for a simple jump, 0.55 eV).

↓ Configuration; process →	Jump	SEb	Exchange	SEb
Clean step	0.76	0.21	0.64	0.09
In at step	0.67	0.12	0.20	-0.35

with In at the step edge (In is more stable by 0.22 eV when embedded at a step edge than when embedded in a terrace). From the calculated barriers, the Schwöbel-Ehrlich additional barrier for downstep motion is trivially extracted as the difference of each downstep barrier and the lowest on-terrace diffusion barrier. In the case of Cu, the latter is 0.55 eV for the jump process (Table VII). At a temperature such that homoatom motion is (just barely) activated on the terrace, an additional step-edge barrier will reflect the adatom away into the inner region of the upper terrace, thus hindering interlayer mass transport, and possibly leading to three-dimensional (3D) growth. If the additional barrier is negligible or negative, downstep diffusion would be unhindered and 2D growth would ensue.

The calculated barriers are reported in Table XI. At the clean step, we find a barrier of 0.76 eV for the jump, and 0.64 eV for the push out (at variance with semiempirical calculations<sup>35,75</sup> which found the opposite ordering). For In embedded at the step the barriers are 0.67 eV for the jump and 0.20 eV for the exchange Cu-In at the step. The Schwöbel-Ehrlich barrier is always smaller for the exchange processes than for any jump motion. In particular, in the presence of In at the step, the additional barrier becomes large and *negative*. Therefore, In facilitates the downstep exchange diffusion of Cu compared to the clean step case, thus enhancing interlayer mass transport and helping 2D growth. The rationale for the In-induced negative additional barrier is that Cu pushes In out onto the lower terrace more easily than it would another Cu, since embedded In is less bound to other terrace Cu’s than a Cu would be.

## V. SUMMARY

We have presented detailed first-principles calculations of adsorption and pairing of Cu and In adatoms, dimers, and trimers on Cu(001), as well as energies of formation and interaction of surface vacancies with adsorbates on this surface; also we studied the on-terrace diffusion barriers for Cu and In adatoms, dimers, trimers, and Cu vacancies, as well as

Cu adatoms at steps with or without In present. In all cases, we used large low-imposed-symmetry simulation slabs and allowed for multilayer relaxations in all cases. We summarize the main results.

In occupies preferentially a substitutional surface site. On-surface adsorption is disfavored by 0.3 eV, and subsurface sites are over 1 eV more costly, suggesting efficient surface segregation of In. Surface-embedded In is found to repel Cu adatoms at short-range. Surface-substitutional In and a Cu surface vacancy bind into a complex, which can diffuse with a lower effective barrier. We support the idea<sup>7</sup> that this is the main migration process involved in In diffusion on this surface. The creation of vacancies, on the other hand, occurs easily at kink site on steps. Similarly, In is very easily incorporated at steps.

The simple jump is favored over the exchange mechanism for single Cu adatoms, and is effectively their sole diffusion mechanism active at, e.g., room temperature. Even with our advanced computational settings, the quantitative disagreement with experimental barriers remains: the reasons for this are unclear at this time.

Cu adatoms are not the most mobile homoadsorbates on this surface. Most mixed dimers and trimers are clearly stable, and appear to have small diffusion barriers. Homodimers and, especially, surface vacancies have lower diffusion barriers than the adatom, and so should significantly influence mass transport on Cu(100). In fact, from our limited configuration sample, even trimers appear to be mobile, or at least not obviously immobile.

Substitutional In tends to weakly funnel Cu adatoms toward its own vicinity, but repels them at short range. Substitutional In will easily exchange with on-surface Cu, and segregate efficiently to the growing surface. These on-surface mechanisms may in principle be involved in surfactant action, but it is unclear that they are sufficient to cause it in practice. Given that In is easily incorporated at steps, interlayer barriers at steps may be more likely affected. We then studied interlayer Cu jump and push-out mechanisms at clean (no In involved) and In-contaminated steps. We found push outs be favored, with additional step barriers going to zero in two of the cases involving In at the step; thus In does indeed favor 2D growth by easing the interlayer mass transport of Cu, at least from the point of view of diffusion energetics.

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