Formation and Diffusion of S-Decorated Cu Clusters on Cu(111)

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S-decorated Cu trimers are a likely agent of S-enhanced Cu transport between islands on Cu(111). According to *ab initio* calculations, excellent S bonding to trimer-Cu dangling valence results in an ad-Cu_3S_3 formation energy of only ~0.28 eV, compared to 0.79 eV for a self-adsorbed Cu atom, and a diffusion barrier ≤0.35 eV.

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The power of low concentrations of foreign atoms to affect growth morphology has persuaded surface scientists to devote a decade's work to "surfactant-directed" self-assembly of ultrathin films [1]. But effects of impurities *not deposited purposely* may be as important as effects of surfactants and also merit serious study.

Time-resolved scanning-tunneling microscopy (STM) reveals, e.g., that monolayer-high Cu islands on thick Cu(111) films ripen ~3–4 orders of magnitude faster when S, a common impurity, is adsorbed [2]. To understand how S acts, I ask what Cu_nS_m clusters form more readily on Cu(111) than a Cu adatom, and diffuse easily. A systematic *ab initio* search reveals that the smallest such cluster is ad-Cu_3S_3 (see Fig. 1). Its formation energy is ~0.5 eV lower than a Cu adatom's, and, corresponding to tight internal bonding, its diffusion barrier is ≤0.35 eV.

This means that S can act as a "skyhook," weakening the bonds of a Cu adatom cluster to the substrate and promoting its transport. Such an effect has been proposed for H on metals (M), through formation of HM dimers [3], but how *divalent* S might act as a skyhook has not been known till now.

Because close packing means better coordinated first-layer atoms, self-adsorption costs more energy on closer-packed surfaces. Cu/Cu(111) obeys this rule. The present density functional theory (DFT) [4] calculations, based on the generalized gradient approximation (GGA) [5], say that 0.79 eV is needed to form a Cu adatom on Cu(111). The same logic that predicts this large E_{form}(ad-Cu) suggests that the self-diffusion barrier on Cu(111), E_{diff}(ad-Cu), should be small. The present finding $E_{\mathrm{diff}}(\text{ad-Cu}) \approx 57$ meV again agrees.

These results constrain ideas of how S promotes Cu transport at 300 K. For example, since little can be gained by lowering a barrier close to $2k_BT$ (= 51.7 meV), *S must act by increasing the concentration of diffusing adspecies.* However, S does not act by reducing the *barrier* to dissociating Cu atoms from island edges onto terraces. On geometric grounds, this barrier must be close to $E_{\mathrm{form}}(\text{ad-Cu}) + E_{\mathrm{diff}}(\text{ad-Cu}) = 0.85$ eV (expt. = 0.78 ± 0.04 eV [6]), i.e., again only ~57 meV larger than the minimum needed to produce an ad-Cu on a terrace.

S impurities must therefore promote island ripening by forming tightly bound, and thus plentiful and mobile, Cu_nS_m adspecies [7]. This raises a general question: *What complex with a divalent impurity can enhance metal adatom transport?* for S/Cu(111), I show that ad-Cu_3S_3 is a good candidate.

Results reported here were obtained with the VASP [8–10] total-energy code, its ultrasoft pseudopotentials (USP's) [11], and the Perdew-Wang '91 GGA [5]. I compute adsorption energies using six- to eight-layer slabs to represent Cu(111), fixing the lower three slab-layer atoms at bulk relative positions and relaxing the rest till forces are <0.03 eV/Å. I set the slab lattice parameter to 3.64 Å, the bulk GGA value for a 60 wave-vector sample of the irreducible $\frac{1}{48}$th of the Brillouin zone (BZ) (expt. = 3.61 Å). To accelerate electronic relaxation, I use Methfessel and Paxton's Fermi-level smearing method (width = 0.3 eV) [12].

USP's yield converged total energies with modest basis size. Here, with a 17.2 Ry plane-wave cutoff, total energies should be accurate to ~10–20 meV. I confirm this expectation by repeating key calculations with the cutoff

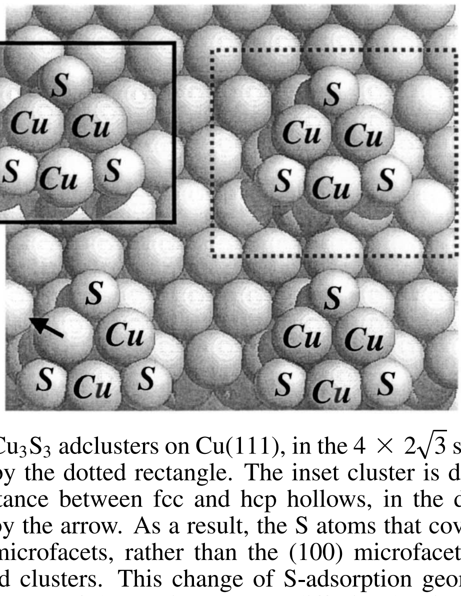

FIG. 1. Cu_3S_3 adclusters on Cu(111), in the $4 \times 2\sqrt{3}$ supercell indicated by the dotted rectangle. The inset cluster is displaced by the distance between fcc and hcp hollows, in the direction indicated by the arrow. As a result, the S atoms that cover it are on (111) microfacets, rather than the (100) microfacets of the undisplaced clusters. This change of S-adsorption geometry is the main source of the 0.35 eV Cu_3S_3 diffusion barrier.

increased 25% to 21.5 Ry. At the same time, I also increase the width of the vacuum region from 3 to 5 times the bulk (111)-layer spacing, allowing cancellation of unphysical dipole fields introduced because only upper slab surfaces are relaxed [13].

The abundance of ad-Cu$_n$S$_m$ is determined by its chemical potential. It equals the chemical potential of ad-Cu$_n$ less that gained by m ad-S's attaching to form a decorated cluster. I compute this gain by reference to the isolated ad-S chemical potential $\mu(\text{ad-S}) = E_B(\text{ad-S})\text{-}k_BT\ln\theta_S$. Here $E_B(\text{ad-S})$ is the ad-S binding energy and $k_BT\ln\theta_S$ accounts for the entropy loss per S, at ad-S concentration θ_S.

To obtain the formation-energy component of $\mu(\text{ad-Cu}_n)$, I consider Cu(111) slabs, L layers thick, with N atoms per supercell in each layer. Imagine removing a layer from n such slabs and distributing their Cu atoms as clusters of n ad-Cu's, one to a supercell, on N slabs, each $L - 1$ layers thick. The original slabs thus lose one "bulk" layer each, for sufficiently large L, and each of the N, $(L - 1)$-layer slabs gains an n cluster per cell. For large L and N, this costs $N \times E_{\text{form}}(n \text{ cluster})$. Thus,

$$\begin{aligned} E_{\text{form}}(n\text{ cluster}) = {} & E_{\text{ad}}(N, L-1) - E_{\text{cln}}(N, L-1) \\ & - n[E_{\text{slab}}(N, L) \\ & - E_{\text{slab}}(N, L-1)]/N\,, \end{aligned} \tag{1}$$

where $E_{\text{ad}}(N, L-1)$ and $E_{\text{cln}}(N, L-1)$ are the energies/supercell of an $(L-1)$-layer slab with one ad-Cu on it, per supercell, or clean. In Eq. (1), the last term is the energy needed to remove bulk Cu atoms, while $E_{\text{ad}}(N, L-1) - E_{\text{cln}}(N, L-1)$ is what they gain by adsorbing as n clusters on slabs. With all contributions to Eq. (1) computed using the same supercell and BZ sample, error cancellation should be good [14].

Cu adatoms.—Values of $E_{\text{form}}(\text{ad-Cu})$ and $E_{\text{diff}}(\text{ad-Cu})$ (see Table I) are derived from total energies of 12 atoms/layer, $3 \times 2\sqrt{3}$ supercells—large enough that interadatom interactions should be small. Based on convergence studies of Cu step and kink formation [15], I sample the surface BZ with a 6×6 grid of k vectors, equally spaced in the x and y directions.

To place bounds on quantum-size effects (QSE), I evaluate $E_{\text{form}}(\text{ad-Cu})$ and $E_{\text{diff}}(\text{ad-Cu})$ for six-, seven-, and eight-layer films. To avoid confusing basis-convergence error with QSE, I use the high plane-wave cutoff of 21.5 Ry. The results show QSE of ~10 meV and also that formation and diffusion energetics are well converged on a six-layer (111) slab. With the lower plane-wave cutoff 17.2 Ry, $E_{\text{diff}}(\text{ad-Cu})$ is 53, 36, and 52 meV for six-, seven-, and eight-layer slabs, respectively. The apparent QSE is a nonconvergence artifact.

Cu adatoms prefer fcc to hcp threefold sites on the six-layer slab, but only by 7 meV (cf. Table I). Correspondingly, the ad-Cu diffusion barrier lies almost equidistant from the threefold hollows at a twofold bridge. To an excellent approximation, $E_{\text{diff}}(\text{ad-Cu})$ is thus the difference in energies for an ad-Cu in an fcc hollow and at the symmetric bridge. The computed sum $E_{\text{form}}(\text{ad-Cu}) + E_{\text{diff}}(\text{ad-Cu}) = 0.85$ eV compares well with the value 0.78 ± 0.04 eV, obtained from STM observations of Cu island decay rates [6]. Effective medium theory calculations by Stoltze yield 0.71 eV and 53 meV for $E_{\text{form}}(\text{ad-Cu})$ and $E_{\text{diff}}(\text{ad-Cu})$, respectively [16], in relatively good agreement with the best *ab initio* results, 0.79 eV and 57 meV.

TABLE I. Cu adatom formation and diffusion barrier energies on L-layer Cu(111) slabs.

L	Adatom site	E_{form}	E_{diff}
6	fcc	0.80 eV	58 meV
6	hcp	0.81 eV	
7	fcc	0.78 eV	58 meV
8	fcc	0.79 eV	57 meV

Cu-S ad-dimers.—If ad-CuS is the plentiful species that accounts for S-enhanced Cu transport [2], at a minimum ad-Cu and ad-S must attract each other. But they do not. An S adatom *loses* 1.08 eV binding energy in approaching the ad-Cu closely, and forming a Cu-S dimer with the S beside the Cu (cf. Table II) *costs* 1.87 eV.

Presumably because the S cannot conveniently form two bonds, repulsion of the same magnitude also inhibits formation of an ad-CuS with the Cu end down. But even

TABLE II. Clean- and S-decorated cluster formation energies E_{form} on a six-layer, Cu(111) slab. N_S and N_{Cu} are the numbers of S and Cu adatoms in each cluster. For Cu dimers and trimers I indicate the face that the S atoms decorate. The "*B*" cases correspond to Cu's in hcp hollows. In all other cases the Cu's occupy fcc sites. When the dipole correction (see text) is included, the vacuum width used is ~5 bulk Cu(111) layer spacings. Otherwise it is ~3 of them. Supercell and PW cutoff are self-explanatory. Values of E_{form} in boldface are "best" values for the various cluster types. For the Cu monomer plus one S adatom, the three E_{form} values are for S down, Cu down, and S-beside-Cu configurations.

N_S	N_{Cu}	Face	Dipole corr.	Supercell	PW cutoff	E_{form} (eV)
0	1		No	$3 \times 2\sqrt{3}$	17.2	0.80
0	1		Yes	$3 \times 2\sqrt{3}$	21.5	**0.79**
1	1		No	$3 \times 2\sqrt{3}$	17.2	**1.26**, 1.87, 1.87
1	2	*A*	No	$3 \times 2\sqrt{3}$	17.2	1.29
2	2		No	$3 \times 2\sqrt{3}$	17.2	**1.06**
0	3	*A*	No	$4 \times 2\sqrt{3}$	17.2	1.66
3	3	*A*	No	$4 \times 2\sqrt{3}$	17.2	0.27
3	3	*B*	Yes	$4 \times 2\sqrt{3}$	17.2	0.62
0	3	*A*	Yes	$4 \times 2\sqrt{3}$	21.5	1.69
3	3	*A*	Yes	$4 \times 2\sqrt{3}$	21.5	**0.28**
3	3	*B*	Yes	$4 \times 2\sqrt{3}$	21.5	0.62
4	4		Yes	$4 \times 2\sqrt{3}$	21.5	**0.49**
5	4		No	$4 \times 2\sqrt{3}$	17.2	1.09

in the S-end down configuration, where S and Cu valence requirements *can* be satisfied, the dimer formation energy (with the CuS in an fcc hollow) is 1.26 eV, compared to $E_{\text{form}}(\text{ad-Cu}) = 0.79$ eV. Thus, the Cu-S adcluster responsible for enhanced Cu-island decay contains more than one Cu atom.

Clean and S-decorated Cu dimers.—One expects Cu's adsorbed on Cu(111) to attract, and indeed (Table III) Cu-Cu attraction lowers $E_{\text{form}}(\text{ad-Cu}_2)$ by 0.27 eV. But does attaching S atoms to such a dimer reduce its E_{form} by *another* 0.53 eV, to make S-decorated Cu dimers more plentiful than Cu monomers? At least for the most obvious S decorations of Cu ad-dimers, the answer is no (cf. Table II). Placing a single S on the side of the dimer, where it is four-coordinated (the "*A*-type" side), lowers the formation energy by 0.04 eV. Adding another, on the other side of the dimer, lowers it 0.19 eV more, not enough to compensate the cost of the second ad-Cu.

Other geometries, e.g., Cu's decorating an S ad-dimer, or S's and Cu's alternating to form a flat tetramer, seem unfavorable. The former requires S's to be nearest neighbors even while S_2 dissociates on Cu(111). The latter is unlikely because, as noted above, an ad-S repels an adjacent ad-Cu. The search for a low energy Cu-S complex thus moves to still larger clusters.

Clean and S-decorated Cu trimers.—S-decorated trimers (cf. Fig. 1) are big enough that using $3 \times 2\sqrt{3}$ supercells to compute their formation energies is a concern. To quantify the interaction of periodically repeated clusters, I compute $E_{\text{form}}(\text{ad-Cu}_3)$ and $E_{\text{form}}(\text{ad-Cu}_3\text{S}_3)$ in both $3 \times 2\sqrt{3}$ and $4 \times 2\sqrt{3}$ supercells. To minimize BZ sampling error, I obtain $E_{\text{form}}(\text{ad-Cu}_3\text{S}_3)$ in each cell using a value of $E_B(\text{ad-S})$ computed in the *same* cell. The results show a small (0.02 eV) reduction in computed formation energy for the pure trimer in the bigger cell, but a considerable one (0.13 eV) for the ad-Cu_3S_3. Accordingly, the conclusions I offer here regarding ad-Cu_3S_3 formation are all based on calculations in the $4 \times 2\sqrt{3}$ cell.

Per adatom, forming Cu adtrimers should cost less than dimers, because each ad-Cu has *two* ad-Cu neighbors, not just one. Counting bonds, with a Cu-Cu bond strength of 0.27 eV (see above), one expects $E_{\text{form}}(\text{ad-Cu}_3) \approx 1.59$ eV, i.e., about triple the monomer formation energy, 2.4 eV, minus 3×0.27 eV.

Direct calculations confirm this logic. The energy needed to form a trimer, with the three Cu adatoms in neighboring fcc hollows bounded by (100)- or A-type microfacets, is ~1.7 eV. If the trimer is rotated 60°, so that its sides are (111)- or "B-type" microfacets, its E_{form} is 0.02 meV less (cf. Table III).

TABLE III. Pure Cu cluster formation energies on six-layer Cu(111).

Cluster	Supercell	$E_{\text{form}}(\text{ad-Cu}_n)$
Monomer	$3 \times 2\sqrt{3}$	0.80 eV
Dimer	$3 \times 2\sqrt{3}$	1.33 eV
A trimer	$3 \times 2\sqrt{3}$	1.68 eV
A trimer	$4 \times 2\sqrt{3}$	1.66 eV
B trimer	$3 \times 2\sqrt{3}$	1.66 eV

Though bond counting predicts $E_{\text{form}}(\text{ad-Cu}_3)$ rather well, a similar approach *greatly* underestimates how much S decoration reduces it. Rather than by 0.1 to 0.2 eV per added S atom, as S + Cu dimer results would suggest, decorating a Cu trimer with three S atoms reduces the formation energy of the complex by 0.47 eV/S atom, for a trimer bounded by A-type microfacets. *Forming S-decorated Cu trimers thus costs only 0.28 eV, much less than Cu monomers.*

In Fig. 2, for insight, I compare *d*-band local densities of states (*d*-LDOS's) of a Cu atom in an ad-Cu_3S_3, a nearby, uncovered surface-layer Cu, and a third-layer (bulk) Cu atom. Note that the *d*-LDOS of the trimer Cu lies well below the uncovered surface Cu atom's (so that its centroid ≈ that of the bulk Cu *d*-LDOS). This implies that *d*-electron energies on the trimer are lowered as charge polarizes from trimer Cu's to S's. *d*-LDOS widths on the trimer- and uncovered-surface Cu are about the same. Thus, the effective coordination of trimer Cu's is "healed" to the level of a surface plane Cu's.

Diffusion of S-decorated Cu trimers.—Given that creating a Cu_3S_3 adcomplex costs just 0.28 eV, and the related fact that S decoration lifts the Cu adatoms ~0.14 Å higher above the nearest surface Cu's, the cluster diffusion barrier should be low. A plausible diffusion path involves moving each Cu from its initial hollow, say an fcc site [17] (along the arrow in Fig. 1) over a neighboring bridge to an

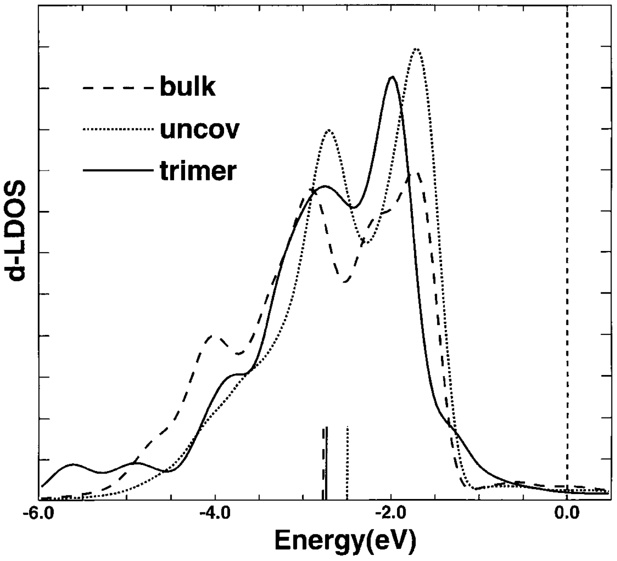

FIG. 2. Gaussian-smeared *d*-band LDOS's for one of the Cu's of a S-decorated trimer, for an uncovered surface Cu in a $4 \times 2\sqrt{3}$ cell containing an ad-Cu_3S_3, as in Fig. 1, and for a third layer, effectively bulk Cu of the same slab. The Fermi energy is at 0.0 eV. Centroids of the *d*-LDOS's are indicated by vertical lines at the bottom of the plot.

adjacent hcp hollow, the three S atoms following more or less rigidly. A lower bound for the barrier along this path is the energy difference between the initial and final configurations of the decorated trimer or (see Fig. 1) between S-decorated trimers with A- vs B-type sides.

This bound is significant, because S atoms have an affinity for Cu's arranged in a square [18]. In the present case, the affinity amounts to an energetic preference of $\sim$0.33 eV for an A-sided trimer. It remains to be learned if the B trimer represents a transition geometry or a metastable state, and if the latter, whether the minimum barrier is much bigger than 0.33 eV.

Applying Jónsson's nudged elastic band method [19] with two replicas of the S-decorated trimer along the path between A trimer in fcc and B trimer in hcp hollows, I find a transition state close to the B-trimer geometry and a barrier of 0.35 eV. Thus $E_{\mathrm{form}}(\mathrm{Cu_3S_3}) + E_{\mathrm{diff}}(\mathrm{Cu_3S_3}) \approx 0.63$ eV, *which is 0.22 eV lower than the similar sum for a Cu adatom.*

Assuming "diffusion-limited" Cu-island ripening [20], the decay *rate* scales with the concentration of Cu-carrying adspecies times their diffusion constant. This product is proportional to $D_0(\text{ad-Cu})\exp\{-[E_{\mathrm{form}}(\text{ad-Cu}) + E_{\mathrm{diff}}(\text{ad-Cu})]/k_BT\}$, for Cu-adatom transport, and to $D_0(\mathrm{Cu_3S_3})\theta_{\mathrm{S}}^3 \exp\{-[E_{\mathrm{form}}(\mathrm{Cu_3S_3}) + E_{\mathrm{diff}}(\mathrm{Cu_3S_3})]/k_BT\}$, for $\mathrm{Cu_3S_3}$ clusters, where the D_0's are diffusion prefactors. The S-induced speedup is proportional to the latter divided by the former. So the predicted $\mathrm{Cu_3S_3}$-mediated decay rate $\approx 5000\theta_{\mathrm{S}}^3 \times D_0(\mathrm{Cu_3S_3})/D_0(\text{ad-Cu})$ that for clean Cu(111).

This result makes it plausible that $\mathrm{Cu_3S_3}$ clusters account for the speedup seen in Ref. [2]. Whether they *really* do depends on the D_0's and other uncertainties in the calculations, notably, the size of the supercell. That k_BT is near the accuracy of DFT results is, of course, a perennial issue in DFT total-energy studies of 300 K phenomena.

Clean and S-decorated Cu tetramers.—The advantages of additional Cu-Cu bonds and S decoration persist beyond Cu trimers. To form ad-$\mathrm{Cu_4S_4}$, e.g., requires only $\sim$0.49 eV [21]. However, since barriers to concerted diffusion of $\mathrm{Cu}_n\mathrm{S}_n$ clusters likely rise with n, Cu transport via S-decorated tetramers, pentamers, etc. should be less facile than via $\mathrm{Cu_3S_3}$, another subject for further study.

Observation of Cu-S adclusters.—Quench experiments that directly reveal $\mathrm{Cu_3S_3}$ on terraces would obviously be desirable. A suggestive result in this direction is that STM of a low-T "honeycomb phase" of S/Cu(111) exhibits one surface protrusion per deposited S, separated by $\sim$4 Å [22]. I find an S-S separation of 4.4 Å for ad-$\mathrm{Cu_3S_3}$.

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