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Enhanced Self-Diffusion on Cu(111) by Trace Amounts of S: Chemical-Reaction-Limited Kinetics

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We find that less than 0.01 monolayer of S can enhance surface self-diffusion on Cu(111) by several orders of magnitude. The measured dependence of two-dimensional island decay rates on S coverage (θ_S) is consistent with the proposal that Cu_3S_3 clusters are responsible for the enhancement. Unexpectedly, the decay and ripening are diffusion limited with very low and very high θ_S but not for intermediate θ_S. To explain this result we propose that surface mass transport in the intermediate region is limited by the rate of reaction to form Cu_3S_3 clusters on the terraces.

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Surface self-diffusion is important in materials processing such as sintering and thin-film growth. Most surfaces of practical interest are not perfectly clean. Motivated by the need to understand and to control self-diffusion on such surfaces, the effect of adsorbates on surface diffusion has been extensively studied [1–7]. For instance, an early investigation showed that mass flow, absent on clean Au(111) surfaces, is activated in air or by adsorbate deposition in vacuum [1]. Oxygen is reported to activate low-temperature island coarsening and film smoothing on the Ag(100) surface and to change the coarsening mechanism from island diffusion to Ostwald ripening, i.e., material transfer from smaller to larger islands due to the Gibbs-Thomson effect [2,8]. Similarly, hydrogen has been shown to enhance self-diffusion on various metal surfaces [4–6]. All these studies provide evidence that adsorbates can significantly enhance surface mass transport.

In general, little is known about the underlying atomic mechanisms by which adsorbates enhance mass flow. Among the cases studied, a Pt-H complex was shown to have a much larger diffusivity than Pt atoms on the Pt(110) surface [4]. The change in surface dynamics on the oxygen-exposed Ag(100) surface was attributed to a Ag_nO species [2]. It is proposed that O atoms bond strongly with Ag atoms to form an Ag_nO species with much lower detachment and surface diffusion barriers, thus favoring Ostwald ripening over island diffusion [2]. Similar "skyhook" mechanisms, in which a strong bond between adsorbate and substrate adatom weakens the bond of the adatom to its surface neighbors, have also been suggested in other systems [3,6]. Feibelman's proposal that Cu_3S_3 clusters promote transport on Cu(111) is somewhat different [7]. Instead of lowering the detachment or diffusion barrier, the effect of S is to reduce the formation energy of movable Cu-containing species without increasing their diffusion barrier too much. This postulate is particularly interesting because S is a common contaminant in metals. Unfortunately, as other adspecies on (111) metal surfaces, the Cu_3S_3 species is difficult to observe directly. The matter is further complicated by evidence that the species may condense to an ordered structure at low temperature as its mobility decreases [9]. In this report, we study the effect of S on Cu(111) surface mass transport using low-energy electron microscopy (LEEM) and scanning tunneling microscopy (STM). After providing evidence in support of Feibelman's postulate, we show that *where* clusters form, an issue that has not been raised in previous studies, has an important effect on the resulting mass transport kinetics.

We monitored the decay rate of Cu island stacks and 2D Cu island arrays on Cu(111) as a function of S coverage (θ_S) and temperature (T). The Cu(111) crystal was treated with ~5% hydrogen in an argon atmosphere at 950 °C for ~24 h to deplete the bulk S content. The surface was then cleaned with cycles of Ne and Ar sputtering and annealing in vacuum. The decay rate of Cu islands on the clean surface was measured as a function of T, yielding an activation energy of 0.8 eV, consistent with reported values [10,11]. Sulfur was dosed onto the Cu surface, at a typical rate of four millimonolayers (mML) per minute, from an *in situ* solid-state electrochemical cell [12]. Sulfur coverage was determined, assuming a constant sticking coefficient, from the time-integrated S signal measured by a mass spectrometer, which was calibrated against the saturated S coverage on the Cu(111) surface [13]. The effect of S on Cu island decay was observed with LEEM and STM, and the ripening of Cu island arrays, which were nucleated by depositing Cu at ~80 °C, was observed with LEEM.

Figure 1 illustrates how a trace amount of S strikingly alters surface mass transport on Cu(111). Figure 1(a) is a time sequence of a monatomic-high Cu island. Before S exposure (<0 min), there is no measurable shrinkage of the island. After exposure to 14 mML S, however, it vanishes within 8.5 min. On the clean surface, the vanishing time for a much smaller island (area = 0.2 μm^2) at the same temperature was 94 min, more than 100 times longer than the decay time (<0.5 min) of a 0.2 μm^2

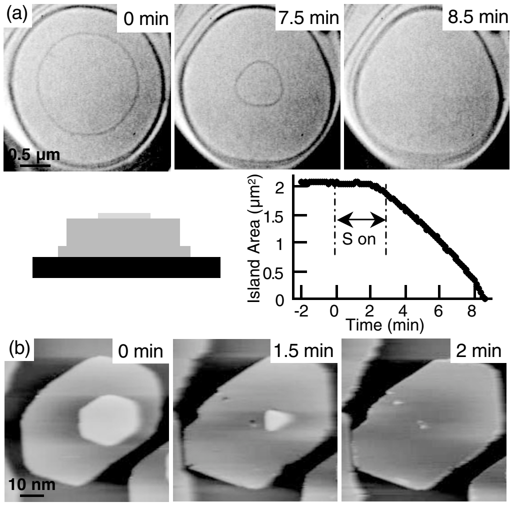

FIG. 1. Trace S drastically speeds up self-diffusion on Cu(111). (a) LEEM images showing the decay of a Cu island (dark innermost circle) at 215 °C after exposure to 14 mML S. The cartoon illustrates the configuration of the decaying Cu island (light gray), which is monolayer high sitting on top of a thick Cu stack (dark gray). (b) STM results showing similar speedup in the decay of a Cu island at −60 °C after exposure to ~5 mML S. Both LEEM and STM observe a change in the Cu island shape from hexagonal to triangular during the decay (more prominent in the STM images because of the lower temperature) due to the preferential decoration of S at the {100} microfacet step edges [9].

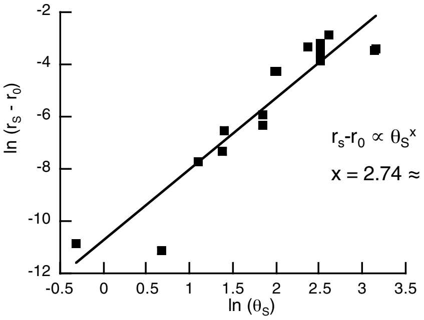

FIG. 2. S-mediated decay rate as a function of S coverage θ_S at 215 °C. Averaged decay rates r_S of Cu islands with area 0.2 μm^2 for different θ_S are compared to the clean Cu island decay rate $r_0 = 1/94$ min.

island with 14 mML S. Accelerated island decay is also observed at low temperature with STM [Fig. 1(b)]; mass from the top island is quickly transferred to the bigger island beneath and elsewhere. The decay rate of a similarly sized 7000-atom island on the clean Cu surface was negligible (extrapolating from Ref. [14] to −60 °C, one would predict the decay time to be on the order of 100's of years), but with less than 10 mML of S the island vanished within 2 min. S has sped up the surface mass transport dramatically.

In Feibelman's picture, there is a dilute gas of Cu_3S_3 clusters in equilibrium with the Cu and S adatoms on the terraces between steps. The equilibrium density of the clusters is proportional to the cube of θ_S [7]. By computing the formation energy of the clusters, Feibelman showed that at high θ_S the cluster density can be orders of magnitude greater than the thermal Cu adatom concentration, leading to enhanced Cu self-diffusion even though the barrier for cluster diffusion is larger than the Cu adatom barrier. To determine the model's validity, we measured the decay rate of Cu islands as a function of θ_S at fixed T. We observed the decay of Cu islands on island stacks similar to the configuration shown in Fig. 1(a). The decay rate (r_S) was taken to be the inverse of the vanishing time of an island with an area of 0.2 μm^2. The island decay rate for different θ_S at 215 °C was compared to the decay rate for a same size island on the clean Cu surface. The results are plotted in Fig. 2. The linear dependence of the log-log plot, with a slope close to 3, suggests that the speedup of the decay rate is proportional to θ_S^3. This relation suggests that the mass-carrying species contain three S atoms, consistent with the proposal that the enhanced transport is due to the formation of Cu_3S_3 clusters [7].

Unexpectedly, however, the decay kinetics of Cu islands changed as a function of θ_S (see examples in Fig. 3). The island decay rate on clean Cu is limited by the rate of Cu adatom diffusion on the terrace [10]. The time evolution of the area of a clean Cu island in Fig. 3(a)

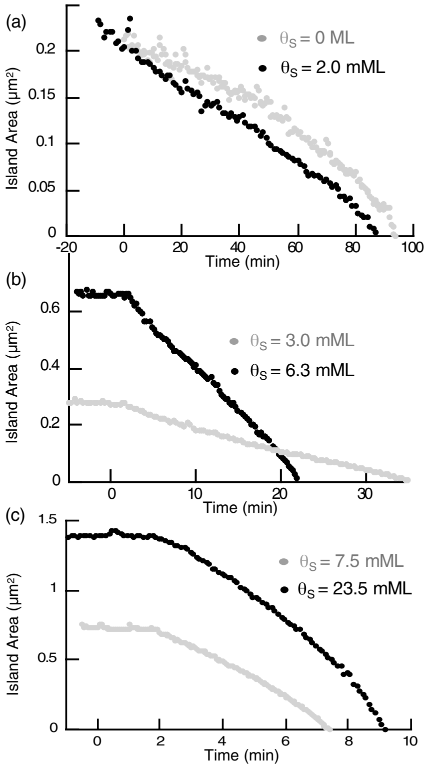

FIG. 3. The three regimes of island area evolution as a function of time t during Cu island decay at 215 °C. Surface is exposed to S at $t = 0$ min. (a) Clean Cu limit. (b) Intermediate θ_S with linear t dependence. (c) High θ_S.

has the dependence of approximately $-t^{2/3}$ expected for diffusion-limited decay [15]. This diffusion-limited kinetics also holds with very small θ_S [2.0 mML in Fig. 3(a)]. With more S [Fig. 3(b)], island area decays differently: linearly with time. However, the decay kinetics reverts to diffusion limited as θ_S increases further [Fig. 3(c)]. The three regimes of decay kinetics with S observed were $\sim -t^{2/3}$, $\propto t$, and back to $\sim -t^{2/3}$, for $\theta_S \lesssim 2.0$ mML, $2.0 \text{ mML} \lesssim \theta_S \lesssim 6.5$ mML and $\theta_S \gtrsim 6.5$ mML, respectively.

We also found that the *coarsening* kinetics of 2D Cu island arrays changed similarly with θ_S and T. 2D coarsening on clean Cu proceeds by Ostwald ripening, with big islands growing at the expense of neighboring smaller ones [14]. Figure 4(a) shows an example. With an exposure of S at a moderate temperature, mass diffusion is sped up but Ostwald ripening is no longer observed [Fig. 4(b)]. Instead, all islands shrink and mass is transported to distant step edges of little curvature; no local ripening occurs. As θ_S or T increases, mass transport is sped up even more and, interestingly, Ostwald ripening is observed again [Fig. 4(c)]. Just as in the island-stack decay kinetics, three regimes were observed in island-array kinetics—ripening for clean Cu and low θ_S or T, no ripening at intermediate θ_S or T, and ripening at higher θ_S or T.

The linear island decay rate in Fig. 3(b) and the lack of diffusion currents between nearby islands of different size are usually associated with kinetics, that is, attachment-detachment-limited at step edges [15,16]. The energetic barrier responsible for such kinetics could arise if it is difficult for clusters to decompose at the step edge. While it seems plausible that such a barrier would exist (especially since the step edges are decorated with S atoms likely with units of Cu_4S [9]), step-attachment-limited kinetics does not naturally explain the crossover to diffusion-limited kinetics at high θ_S; there is no obvious reason why increased amounts of S on the terraces should make it easier for clusters to decompose at the step edges. We next propose a model, however, that also yields the linear decay at moderate θ_S or T and predicts the crossover in a simple way

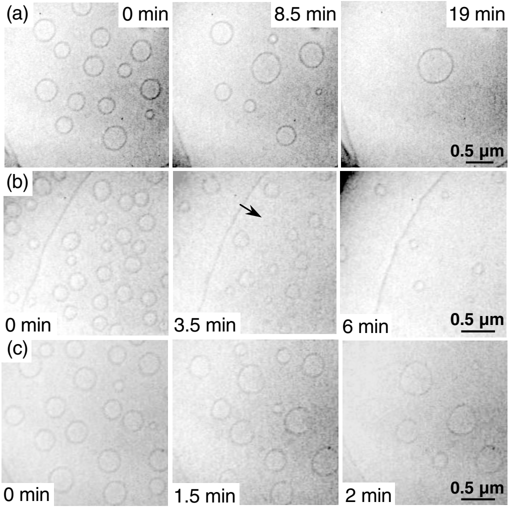

FIG. 4. Three coarsening regimes observed by LEEM. (a) Clean Cu at 270 °C. Ostwald ripening is observed with one big Cu island left after 19 min. (b) No Ostwald ripening with 11.8 mML S at 160 °C. Mass from islands is added to the step, which advances to the right on the lower terrace (arrow). (c) With 12.3 mML S at 215 °C, Ostwald ripening occurs again but at accelerated rate.

While it will be easy for a Cu adatom to find an attachment site, the Cu_3S_3 does not as simply attach to Cu step edges. Our model assumes that cluster attachment at the step edge rarely occurs because of a high barrier. Instead, clusters decompose (and are created) only on the terraces, and the released Cu adatoms attach to the step edge with no barrier, as on the clean surface. We assume for simplicity that the cluster decomposition and formation rates, β and α, are proportional to the cluster and Cu adatom densities, respectively. (The detailed dependence of reaction rate on the concentration does not qualitatively affect the argument below.) Both of these rates will increase with the amount of S and with temperature. The rates α and β couple the steady-state diffusion equations for the Cu adatom concentration c_1 and the cluster concentration c_2 on the terraces: $D_1\nabla^2 c_1 - \alpha c_1 + \beta c_2 = 0$ and $D_2\nabla^2 c_2 - \beta c_2 + \alpha c_1 = 0$, where the D's are the diffusion coefficients. The rates α and β are not independent: the requirement of equilibrium in the absence of diffusion gradients gives the relation $\alpha/\beta = c_2^{\text{eq}}/c_1^{\text{eq}}$. The assumption that Cu_3S_3 does not decompose or form at steps gives the boundary condition $\nabla c_2 = 0$ at the step edges. The assumption that Cu adatoms have no barrier for attachment at the step edge gives the boundary condition that c_1 near the step edge has the value determined by the Cu chemical potential of the step edge.

To show the physical consequences of this model, we analyze a simple geometry, a straight step edge at high chemical potential separated by a distance L from a nearby step edge with a lower chemical potential. Solving the coupled diffusion equations for this geometry, we find that the flux j_1 of the Cu adatoms c_1 between the step edges is

$$j_1 = [c_1^{\text{eq}} D_1 (c_1^{\text{eq}} D_1 + c_2^{\text{eq}} D_2)\sigma]/[c_1^{\text{eq}} D_1 L + 2c_2^{\text{eq}} D_2 L_D \tanh(L/2L_D)], \qquad (1)$$

where $L_D = \{\sqrt{(\alpha/D_1)}[1 + (c_1^{\text{eq}} D_1/c_2^{\text{eq}} D_2)]\}^{-1}$ and σ is proportional to the differences of the Cu concentrations at the two step edges: $\sigma = [c_1(0) - c_1(L)]/c_1^{\text{eq}}$. Since $\sqrt{D_1/\alpha}$ is roughly how far a Cu adatom diffuses before it becomes incorporated into a cluster, L_D is a measure of the diffusion length of Cu adatoms.

If the reaction rate of creating/destroying clusters on the terrace is very small (θ_S or T very low), the density of Cu clusters will also be small and Cu monomers will be the dominant active species on the surface

($c_1^{\mathrm{eq}}D_1 \gg c_2^{\mathrm{eq}}D_2$). Then, Eq. (1) shows that the flux is $j_1 = c_1^{\mathrm{eq}}D_1\sigma/L$. As expected, the Cu flux is limited by the Cu adatom gradient between steps (i.e., $j_1 \propto 1/L$): the farther apart the steps, the smaller the flux.

For higher θ_S the clusters become capable of enhancing self-diffusion when $c_1^{\mathrm{eq}}D_1 \ll c_2^{\mathrm{eq}}D_2$. In this case, Eq. (1) reduces to

$$j_1 = c_1^{\mathrm{eq}}D_1c_2^{\mathrm{eq}}D_2\sigma/[c_1^{\mathrm{eq}}D_1L + 2c_2^{\mathrm{eq}}D_2L_D\tanh(L/2L_D)].$$

As θ_S increases in this regime, L_D will decrease. In the regime when L_D is still large compared to L, Eq. (1) still gives the clean Cu limit: $j_1 = c_1^{\mathrm{eq}}D_1\sigma/L$, even though in principle mass transport by Cu clusters would be more efficient. This occurs because the Cu adatoms can quickly diffuse between steps before they can react to form clusters. In this regime, increasing S has no influence on self-diffusion [consistent with Fig. 3(a)].

This situation changes only when L_D becomes smaller than L. If $c_1D_1/c_2D_2 \ll L_D/L$, Eq. (1) gives $j_1 = c_1^{\mathrm{eq}}D_1\sigma/2L_D$. When $2L_D/L < 1$, Cu surface transport is accelerated compared with the clean surface. Significantly, the flux no longer depends on the distances between steps. The rate-limiting process now is the reaction between S and the Cu adatoms detaching from the step edge to form clusters—diffusion of the clusters is fast compared with this process. As the reaction rate increases with increasing θ_S or T, L_D decreases and the flux between steps increases. Because the flux does not depend on the environment of the steps at distances greater than L_D away from the step edge, the total adatom flux from the step edge is simply proportional to the length of the step. This is similar to the case of attachment-limited kinetics [15], and when applied to equilibrium shaped islands gives an area decay rate independent of time. Also, no local ripening occurs in this regime because the distance to neighboring step edges does not limit mass flow. These results would account for our experimental observations with the intermediate θ_S or T regime reported in Figs. 3(b) and 4(b).

When the reaction rate increases even further such that $L_D/L \ll c_1D_1/c_2D_2$, $j_1 = c_2^{\mathrm{eq}}D_2\sigma/L$. The flux between step edges again decreases with increasing step separation. This solution is very similar to the diffusion-limited Cu-monomer-dominated case but with $c_2^{\mathrm{eq}}D_2\sigma$ replacing $c_1^{\mathrm{eq}}D_1\sigma$. The reaction rate to form clusters is now so fast that the concentration of clusters near the step edge is in equilibrium with the step edge. The agents of mass transport are now the much more abundant Cu_3S_3 clusters instead of the Cu monomers. The model's crossover to diffusion-limited behavior agrees well with our experimental observations for high θ_S [Figs. 3(c) and 4(c)].

We have thus arrived at three different regimes of surface diffusion: first the clean Cu limit, when Cu monomers dominate the surface transport; then the intermediate regime at low θ_S or T, when the clusters are becoming important but surface mass transport is limited by the terrace-reaction rate; and finally for high enough θ_S or T, when the Cu_3S_3 clusters dominate the surface transport with kinetics similar to the Cu-monomer transport. These three regimes precisely reproduce our experimental results.

In summary, we have quantitatively investigated the effect that trace amounts of S have on the self-diffusion of the Cu(111) surface. We find that less than 0.01 ML S can speed up the Cu self-diffusion by several orders of magnitude. Our investigation of the decay-rate speedups as a function of θ_S supports Feibelman's proposal that Cu_3S_3 clusters are responsible for the accelerated transport [7]. We also find different regimes of island decay and ripening kinetics depending on θ_S as well as T, which we explain by a terrace-reaction model. This terrace-reaction-limited kinetics is fundamentally different from the mechanisms previously discussed in the literature [8,10,15,16]. The fact that terrace-reaction rates determine overall surface mass transport rates is likely to be common because the complex entities that can efficiently carry mass between step edges [2,3,6] are not necessarily what attach easily at step edges (i.e., single atoms on metal surfaces). Our work shows that, in this case, it is important to consider where the reaction between these two species takes place.

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