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Surfactant-Modified Diffusion on Transition-Metal Surfaces

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Abstract

Wanting to convert surface impurities from a nuisance to a systematically applicable nano-fabrication tool, we have sought to understand how such impurities affect self-diffusion on transition-metal surfaces. Our field-ion microscope experiments reveal that in the presence of surface hydrogen, self-diffusion on Rh(100) is promoted, while on Pt(100), not only is it inhibited, but its mechanism changes. First-principles calculations aimed at learning how oxygen fosters perfect layerwise growth on a growing Pt(111) crystal contradict the idea in the literature that it does so by directly promoting transport over Pt island boundaries. The discovery that its real effect is to burn off adventitious adsorbed carbon monoxide demonstrates the predictive value of state-of-the-art calculation methods.

Surfactant-Modified Diffusion on Transition-Metal Surfaces

Introduction

Because defects can dominate diffusive and chemical processes on surfaces, and particularly because they are attractive to low valence species, surface impurities, whether adventitious or deposited purposely, can have an important, even a *dominant* effect on surface morphology and its time-evolution. With this in mind, we have explored how surface species as common as H and O modify basic surface diffusion processes on transition metal surfaces. The hope was, and is that the results of such studies will yield paradigms of "surfactant" behavior.

Our theoretical effort¹ was motivated by the dramatic results of Esch, et al.'s Scanning Tunneling Microscopy (STM) study² of Pt epitaxy on Pt(111). It showed that between 300 and 400 K, Pt-deposition on a clean surface produces 3-dimensional, pyramidal islands. But if the surface is O-precovered, then growth is virtually ideal layer-by-layer. According to Esch, et al., it is by assisting downward transport of Pt adatoms at island boundaries that O inhibits island-nucleation on pre-existing islands, and thus eliminates pyramid formation. We undertook to confirm this notion theoretically, and to understand its mechanism, starting with a study of interlayer transport on O-free, stepped Pt(111).

Our Field Ion Microscope study of H-modified self-diffusion on the (100) faces of Pt³ and Rh,⁴ and of Rh(311),⁴ was aimed at learning whether hydrogen acts as a "skyhook," binding to an adsorbed atom and facilitating its diffusion.⁵ Equally important, we wished to determine whether adsorbed H has an effect on self-diffusion mechanism. This question is of considerable interest because on clean Pt(100), an "exchange diffusion" process dominates at low temperatures,⁶ whereby an adsorbed atom moves by substituting for a surface atom instead of simply hopping from site to site. In inhomogeneous systems, exchange is a low-temperature mechanism for surface alloying. It is thus important to know if this process can be controlled, i.e., turned on or off, by the addition of impurities.

Accomplishments

1) Theory of inter-layer self-diffusion on stepped Pt(111)

To confirm Esch, et al.'s idea of how preadsorbed O modifies epitaxy on Pt(111),² we began by investigating Pt interlayer transport on O-free, stepped Pt(111). We performed *ab-initio* barrier calculations for downward diffusion of Pt adatoms at steps on Pt(111), with surprising results.¹

The most important is that E_A , the barrier to self-diffusion down a (100)-microfacet or *A-type* step is only \sim 20 meV bigger than E_T , the self-diffusion barrier on Pt(111). Thus, $E^S(A) \equiv E_A - E_T$, the so-called Schwoebel barrier⁷ that impedes transport down *A-type* steps, is small *even in the absence of O*. This result conflicts with Ref. 1's finding that pyramid edges on clean Pt(111) at 400 K are mainly *A*-steps, and with the contention that O-assisted interlayer transport is what promotes layer-by-layer epitaxy. Since pyramids grow when islands *stack* instead of dissipating onto lower terraces, they should be bounded by edges that present large, not minute Schwoebel barriers. Moreover, as long as *A*-steps form a substantial part of each island's boundary in epitaxy, as in Ref. 2, transport of Pt adatoms off islands will be facile without the assistance of adsorbed-O.

A second surprising theoretical result is that E_B , the downward self-diffusion barrier across "B-type" or (111)-microfacet steps, is not \sim 0.02 but 0.35 eV bigger than E_T . *Thus the B-step Schwoebel barrier, $E^S(B) \equiv E_B - E_T$, is more than an order of magnitude larger than $E^S(A)$.* This contrast on Pt(111), though finally not so mysterious, is quite unexpected. The only previous *ab initio* study of self-diffusion on a stepped, close-packed metal surface, Al(111), yielded a much weaker anisotropy.⁸

Having computed and interpreted barriers to downward diffusion of Pt adatoms at steps on Pt(111), compared to experiment and to other theoretical work. Concerning theoretical attempts to account for the epitaxial-growth morphology of Pt(111) based on semi-empirical^{9a} or on data-fit^{9b} energetics, comparison with our *ab-initio* energy barriers shows that this is an unlikely route to lasting, transferable interpretation. Despite some coincidences in barrier and

site-occupation energies, the semi-empirical results bear no systematic resemblance to those of the *ab initio* calculations.¹

The surprisingly small Schwoebel barrier for A-steps is the most important kinetic parameter to emerge from the *ab initio* results. Its smallness is hard to reconcile with the suggestion² that O acts as a surfactant by assisting interlayer transport. Initially this was a matter of considerable concern. But this problem was soon resolved with the discovery that CO contamination at very low levels, *enough, however, to saturate all steps on the growing surface*, was what caused the disagreement.¹⁰ When the growth experiment was repeated at much lower levels of CO, the island morphology changed into agreement with our predictions!

Our results show that in contrast to widely applied “semi-empirical” simulations, current first-principles structural calculations are predictive for rather complex, “real-world” surfaces, to the extent that they can be trusted to critique the validity of experimental results. The discovery that the real effect of the O is to remove small coverages of CO emphasizes the importance of our initial problem: Trace amounts of relatively weakly bound background gases can play an important, and in principle controllable role in determining the morphology of growing crystalline films.¹⁰

2) How adsorbed H affects self-diffusion on Rh and Pt- *Manipulating Surface Diffusion Rates and Transport Mechanisms*

Our direct observations of diffusing atoms in the field ion microscope show that chemisorbed hydrogen strongly influences the rate of atom migration on the Rh(100), Rh(311) and Pt(100) crystal planes. The influence of hydrogen is striking -- pressures in the 10^{-10} Torr range can change the diffusion rate by several orders of magnitude. We also found that the effect of hydrogen is coverage dependent in all cases indicating that hydrogen can be used as a variable-speed control for single-atom diffusion on surfaces. Even more intriguing is the discovery that hydrogen speeds up the diffusion process on Rh(100) and Rh(311) where the mechanism is ordinary hopping, but slows it down on Pt(100) where the mechanism is concerted exchange. In the latter case, exchange displacements can be suppressed to the point where hopping displacements become energetically accessible. Thus, hydrogen can be used to tailor the mechanism as well as the rate of diffusion on certain surfaces. From the observed coverage

dependence and opposite behavior for exchange and hopping displacements, we suggest that the effect of hydrogen is not a “skyhook”-type interact with the diffusing atom, but rather a phenomenon in which the hydrogen influences interactions with neighboring substrate atoms. This explanation is consistent with previous measurements of the effect of applied electric fields on surface diffusion.¹¹ From a practical standpoint, this research has shown that hydrogen is a promising surfactant to control thin film growth and prevent intermixing at atomically sharp interfaces.

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