Hydrogen Inhibition of Exchange Diffusion on Pt(100)

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(Received 9 June 1997)

Field ion microscope observations show that the diffusion rate of Pt atoms on Pt(100) is significantly reduced when the surface is exposed to hydrogen. A hydrogen partial pressure of 1×10^{-10} Torr causes the exchange diffusion rate to decrease by ~3 orders of magnitude over 2–3 hours. Higher pressures suppress exchange displacements to the point where hopping displacements become energetically accessible. The ability to influence both the displacement rate and the transport mechanism indicates that hydrogen may be used to control thin-film growth at the atomic level. [S0031-9007(97)04634-6]

The migration of individual atoms across single-crystal terraces and their incorporation into the top layer of surface atoms play important roles in the growth of crystalline solids and epitaxial films. The development of methods to manipulate these fundamental processes at the atomic level offers the exciting possibility to tailor crystal and thin-film growth for specific materials applications. Indeed, past studies have shown that adsorbed atoms or molecules, often referred to as "surfactants," can be used either to change the surface morphology of growing films [1] or to suppress intermixing at the substrate-film interface [2]. Although it is often assumed that the observed changes in these studies are due to the effect of the foreign species on surface diffusion, there are a number of elementary steps involved in the overall growth process, any or all of which may be subject to modification by adsorbates. To sort out the details of the different effects, one must isolate the individual steps of the growth process and determine how a given adsorbate affects each one individually. Whether considering atom migration across terraces or atom incorporation into the surface layer, one specifically needs to know if a given adsorbate will promote or inhibit the process.

Single-atom diffusion on the (100) crystal planes of fcc metals is an excellent model system for investigation of adsorbate-mediated surface diffusion and atom incorporation processes. It has been shown that surface diffusion on these surfaces proceeds by one of two mechanisms: ordinary hopping or exchange [3]. Hopping results from the adatom being displaced over the minimum in the potential barrier between two adjacent binding sites, whereas exchange displacements involve a process in which the adatom plunges down into the surface layer and pushes a surface atom up into a diagonally opposite fourfold hollow. By studying surface diffusion on fcc (100) surfaces, one can derive information on how adsorbates affect both the rate of surface diffusion as well as the energy barrier for incorporation of adatoms into the surface layer.

Hydrogen is a common adsorbate used in a variety of surface science studies and appears to be a good candidate for the modification of epitaxial growth on both

metal [1(a)] and semiconductor surfaces [4]. In this study the field ion microscope (FIM) is used to investigate how hydrogen influences the diffusion of single Pt atoms on Pt(100). Past studies show that self-diffusion on Pt(100) proceeds exclusively by the exchange mechanism at temperatures from 160–230 K [3]. The purpose of this investigation is to determine if hydrogen enhances or inhibits diffusion by exchange displacements and whether or not it can change the preferred mechanism from exchange to hopping.

The experimental procedures used in FIM investigations of single-atom surface diffusion are described in detail in several recent review articles [5] and are not repeated here. In the present experiments, a single Pt adatom is generated by field evaporation of the topmost (100) plane. The field evaporation process is quickly terminated when a single atom remains on the surface. A sequence of diffusion intervals is carried out to establish the mean-square displacement of the adatom in the *absence* of hydrogen. Without removing the imaging gas (neon at 2×10^{-4} Torr), hydrogen is leaked into the system to a preset partial pressure. The leak valve is calibrated in control experiments (without Ne) to determine the partial pressure of added hydrogen. Subsequent measurements are made with the mixture of neon and hydrogen as the imaging gas. The partial pressure of hydrogen in this study is in the low 10^{-10} to 10^{-9} Torr range. At lower partial pressures, hydrogen has a negligible effect on the diffusing adatoms. At hydrogen partial pressures above ~10^{-8} Torr, Pt adatoms field desorb from the surface during field-ion imaging [6]. The background pressure of the system without hydrogen or neon is 2×10^{-11} Torr.

A series of field-ion micrographs indicating the effect of hydrogen on self-diffusion on Pt(100) is shown in Fig. 1. Figure 1(a) shows a single Pt adatom on Pt(100) imaged in pure Ne at 77 K. Figures 1(b)–1(d) show the same adatom after 30-sec heating intervals at 200 K in pure Ne. Displacements of the adatom across the surface are obvious. The mean-square displacement at this temperature is several hundred Å^2. Figures 1(e)–1(f) show the
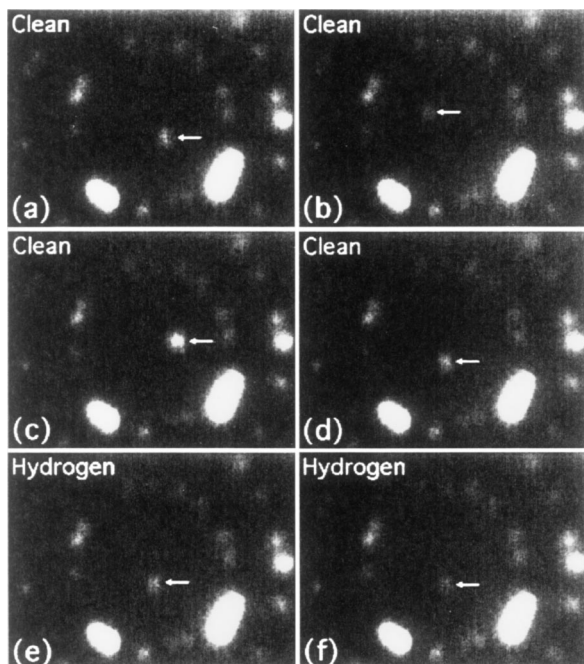
FIG. 1. Field-ion microscope images showing the diffusion of an individual Pt adatom on Pt(100). Between each photograph the sample was warmed from its base temperature of 77 to 200 K. The introduction of H_2 between (d) and (e) stops the migration of the adatom.

same adatom after admission of hydrogen at a partial pressure of 1×10^{-9} Torr. Measurements of the adatom's coordinates indicate that the adatom is now stationary during the heating intervals. In subsequent diffusion intervals no further motion of the adatom is detected. Thus, exposure of the surface to hydrogen at a partial pressure of 1×10^{-9} Torr completely stops self-diffusion on Pt(100) at 200 K.

Although it is not possible to determine the hydrogen coverage with the present experimental setup, we can examine trends associated with the coverage by measuring the adatom's mean-square displacement as a function of time after admission of a fixed hydrogen partial pressure and as a function of the hydrogen partial pressure itself. Figure 2 shows plots of the measured mean-square displacement as a function of time after admission of 1×10^{-10} and 2×10^{-10} Torr hydrogen. The diffusion intervals are 30 sec in length at a temperature of 195 K. The bin size for each data point is 25 diffusion intervals. It is obvious that the mean-square displacement decreases monotonically as a function of time after adding hydrogen to the system. This monotonic decrease indicates that the inhibition of self-diffusion is dependent on the hydrogen coverage. As the amount of hydrogen builds up on the surface, the diffusion rate decreases. It is also obvious from Fig. 2 that doubling the hydrogen partial pressure causes the mean-square displacement to decrease much more rapidly as a function of time. This observation is further evidence that the inhibition due to hydrogen is coverage dependent.
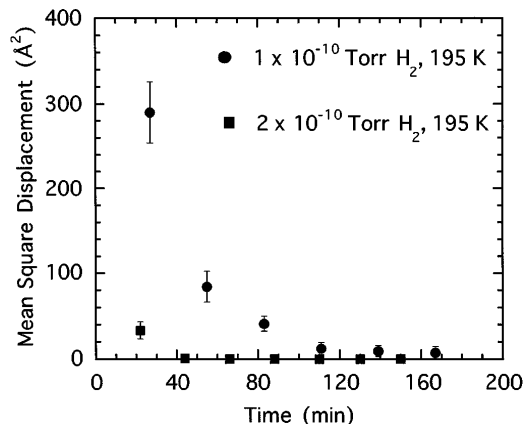
FIG. 2. The mean-square displacement of a Pt adatom diffusing on Pt(100) at 195 K in the presence of H_2 decreases continuously as a function of time. The decrease is much faster in 2×10^{-10} Torr H_2 (squares) than 1×10^{-10} Torr H_2 (circles).

Figure 3 shows a similar plot for the case in which the hydrogen partial pressure is 3×10^{-10} Torr. Here, the mean-square displacement immediately falls to zero, i.e., the diffusion completely stops upon exposure to hydrogen. This plot also shows the result of increasing the temperature to 230 K following 90 min of heating cycles at 195 K in 3×10^{-10} Torr H_2. The adatom, which is completely immobile for 90 min at 195 K, makes significant displacements at 230 K. The measured mean square displacement upon increasing the temperature is ~ 100 Å^2. Note that after increasing the temperature, the mean-square displacement does not stay constant as a function of time, but gradually decreases over the next 2 h. This implies that even though the atom is immobile during the first 90 min at 195 K, the surface is not totally saturated with hydrogen. In a background of 3×10^{-10} Torr H_2, the surface coverage increases continuously over a period of several hours.
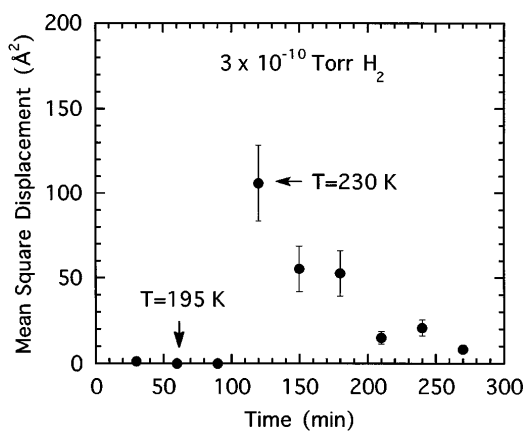

FIG. 3. In 3×10^{-10} Torr H_2 the mean-square displacement at 195 K falls to zero immediately. Increasing the temperature to 230 K after 90 min of H_2 exposure causes the adatom to move. The mean-square displacement the higher temperature also falls off as a function of time.

Having established a pronounced effect of hydrogen on the diffusion rate, we next address its effect on the diffusion mechanism. As shown in previous studies, one can distinguish between exchange displacements and hopping displacements on fcc (100) surfaces by examination of the map of sites the adatom visits as it migrates across the surface [3]. Figure 4(a) shows the map for a Pt adatom diffusing on Pt(100) at 175 K in the absence of hydrogen. As found in previous studies [3], the square pattern has sides parallel to $\langle 001 \rangle$ [i.e., the map is $c(2 \times 2)$] implying diffusion by exchange. Figures 4(b)–4(d) show site visitation maps for higher partial pressures of hydrogen and higher temperatures. At temperatures of 195 and 230 K the maps remain $c(2 \times 2)$ indicating that the diffusion mechanism at these temperatures is still exclusively exchange [Figs. 4(b) and 4(c)]. The hydrogen background pressure in these experiments was 1×10^{-10} Torr and 3×10^{-10} Torr, respectively. Under these conditions, the hydrogen strongly affects the diffusion rate, but not the mechanism. At 250 K and approximately 1×10^{-9} Torr H_2, the map becomes (1×1) [Fig. 4(d)]. This is direct experimental evidence that hopping displacements become accessible for self-diffusion on Pt(100) at temperatures between 230–250 K. At these temperatures, it is difficult to collect statistical samples equivalent to those obtained at lower temperatures because the adatom typically migrates off the plane edge within a few diffusion cycles.

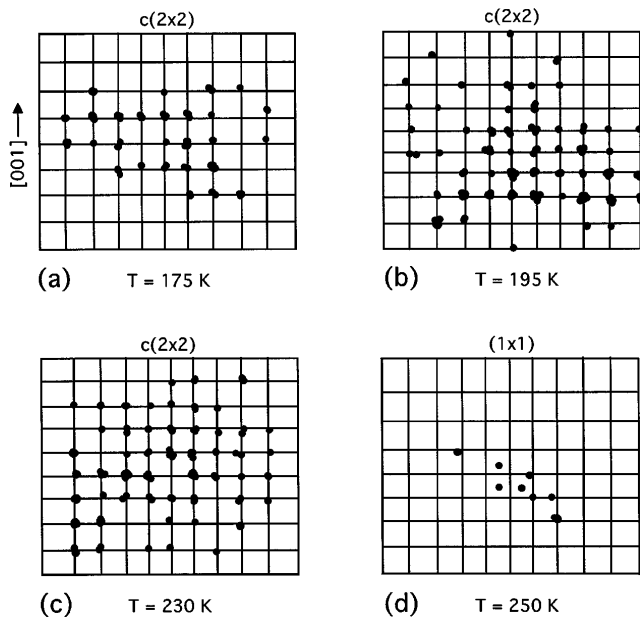It should be noted that diffusion at 250 K in the absence of hydrogen cannot be examined in the FIM because exchange diffusion at 250 K is so fast that the adatom migrates off the crystal plane in a single diffusion interval. Thus, the effect of hydrogen is to inhibit exchange displacements to the point where hopping displacements can be observed. From the onset temperature for hopping displacements and the assumption of the conventionally accepted prefactor, the activation energy for hopping displacements is estimated to be 0.63–0.66 eV. This activation energy is nearly 0.2 eV higher than the measured activation energy for exchange displacements on Pt(100) and is consistent with estimates based on a previous study in which exchange displacements were inhibited by a high electric field [7].

The results reported here lead to three important conclusions concerning hydrogen's effect on Pt(100) self-diffusion: (1) small amounts of adsorbed hydrogen decrease the rate of exchange displacements on Pt(100); (2) the effect of hydrogen is coverage dependent; and (3) exchange displacements can be suppressed to the point where the rates of hopping and exchange displacements become comparable. The first observation is significant in that the effect of hydrogen on Pt(100) self-diffusion is opposite to that found for self-diffusion on Rh(100) and Rh(311) [8]. In these systems, for which the displacement mechanism is ordinary hopping, increasing coverages of hydrogen actually *increase* the diffusion rate. Although more systems need to be studied to establish a true correlation, the results point to the intriguing possibility that chemisorbed hydrogen, in general, promotes hopping displacements but inhibits exchange displacements. If true, this would establish hydrogen as an extremely useful and versatile tool for manipulating thin film growth at the atomic level.

Equally important with respect to manipulating nucleation and growth processes is the observation that the effect of hydrogen is coverage dependent over a large range of diffusion rates. The ability to adjust the diffusion rate of single atoms on terraces in a continuous manner provides an exceptional degree of control in guiding atomic-scale processes to achieve a desirable growth morphology. This is especially true in light of the previous observation that the promotion of hopping displacements by hydrogen is also coverage dependent [8]. The third observation concerning the effect of hydrogen on the displacement mechanism has interesting consequences in relation to the growth of thin surface films and multilayered structures. Typically, one wishes to grow structures with atomically sharp interfaces. However, if exchange displacements have a lower activation barrier than hopping displacements, there will always be intermixing at the interface at temperatures required for growth. These results thus identify hydrogen as a promising candidate for suppression of interfacial intermixing in the growth of multilayered thin films.

Although this investigation has established that hydrogen has a strong influence on both the diffusion rate and the transport mechanism for Pt atoms on Pt(100), the experiments in themselves do not identify the underlying cause

FIG. 4. Site visitation maps for Pt on Pt(100) for different temperatures and H_2 partial pressures. (a)–(c) Maps with $c(2 \times 2)$ periodicity indicate that the mechanism of displacement is exclusively exchanged for temperatures of (a) 175 K; (b) 195 K; and (c) 230 K. (d) A (1×1) map for diffusion at 250 K indicates that hopping displacements take place. The H_2 partial pressures are (a) 0; (b) 1×10^{-10} Torr; (c) 3×10^{-10} Torr; and (d) 1×10^{-9} Torr.

of the effect. The Pt(100) surface examined in this study is an unreconstructed (1×1) surface prepared by field evaporation at low temperatures. This is not the stable structure produced by standard sputtering and annealing techniques. As a result, there have been no temperature programmed desorption or vibrational spectroscopic studies of hydrogen on the unreconstructed Pt(100) surface to characterize the nature of hydrogen adsorption. However, based on studies of hydrogen adsorption on other surfaces of Pt [9], as well as on the (100) surfaces of other fcc metals [10], it is reasonable to assume that hydrogen adsorbs dissociatively on Pt(100) with a relatively high sticking coefficient. This implies that the observed inhibition of self-diffusion is due to chemisorbed atomic hydrogen.

How might chemisorbed hydrogen inhibit exchange displacements? In general, exchange displacements are energetically favorable when the energy gain due to the adatom's higher coordination at the saddle point of the transition compensates for the energy cost in creating a surface vacancy to achieve this configuration. Inhibition can be achieved either by increasing the height of the barrier at the saddle configuration or by increasing the vacancy formation energy. It has been suggested that on clean fcc (100) surfaces, lateral relaxations of neighboring surface atoms due to the presence of the adatom reduce the vacancy creation energy and promote exchange displacements [11]. In fact, inhibition of exchange displacements due to an externally applied electric field was explained in terms of a model in which a field-induced charge transfer lifted the atom off the surface and reduced the surface atom relaxations [7]. It is conceivable that a hydrogen atom, chemisorbed on top of a Pt adatom, could have the same effect. Charge transfer from the adatom to the hydrogen could reduce the surface relaxations and inhibit exchange displacements. However, the observed coverage dependence would suggest that the chemisorption would necessarily be transitory in this type of process; i.e., the hydrogen leaves the adatom after every diffusion event.

More likely is the scenario in which mobile hydrogen atoms visit sites next to the Pt adatom and increase the diffusion barrier by increasing the energy required to bring a surface atom up from the substrate. At low coverages the probability of a hydrogen being in a neighboring site is low. As the coverage increases, so does the probability of a hydrogen occupying a neighboring site. The prevention of an exchange displacement by a hydrogen atom in a neighboring site is consistent with the observed coverage dependence. On a macroscopic scale one could view this phenomenon as an increase in surface stress brought about by the adsorption of hydrogen. Recent calculations show a convincing correlation between surface stress and the

propensity for exchange displacements on fcc (100) surfaces [12]. Clearly, more modeling of this sort is needed to explain the mechanism of hydrogen inhibition observed in this investigation.

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