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Hydrogen promotion of surface self-diffusion on Rh(100) and Rh(311)

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Field ion microscope observations show that the rate of surface self-diffusion for individual atoms on the (100) and (311) planes of Rh is significantly increased by exposure of the surface to hydrogen. On Rh(100) admission of hydrogen at partial pressures in the 10^{-9}-Torr range causes the onset temperature for migration of a Rh adatom to decrease from 290 to 240 K. Once the adatom is mobile, its mean-square displacement is constant as a function of time. Similar exposures of hydrogen lower the onset temperature for self-diffusion on Rh(311) from 180 to 120 K. Here the mean-square displacement increases monotonically as a function of time after admission of hydrogen. The continuous increase indicates that the enhancement of the diffusion rate due to hydrogen is coverage dependent. The difference between the results for Rh(100) and Rh(311) is attributed to the higher temperatures required for self-diffusion on Rh(100). At the higher temperatures, a significant amount of hydrogen is thermally desorbed during the diffusion intervals and the coverage remains relatively constant as a function of time. The observed coverage dependence indicates that the mechanism of hydrogen promotion involves more than a simple lowering of the activation barrier of surface diffusion by the attachment of a hydrogen atom to a Rh atom. [S0163-1829(97)04212-4]

I. INTRODUCTION

The ability to control the evolution of surface morphology during crystal or thin-film growth by modifying elementary steps in the growth process has wide potential application in the synthesis of materials. The use of adsorbed atoms or molecules, often referred to as ''surfactants,'' to increase the smoothness of deposited films has attracted considerable interest in recent years.[1–9] Although much of the work in this area has focused on the effects of group-V and -VI surfactants such as As, Sb, and Te,[3–8] difficulty in removing the surfactant atoms has limited the application of these materials in actual growth situations. This has stimulated efforts to use common gaseous adsorbates as surfactants,[2,9] which are easily removed by thermal desorption. Hydrogen, in particular, has been shown to be a good candidate for the modification of epitaxial growth on both metal and semiconductor surfaces.[2,10,11] However, our understanding of the atomic-scale processes that lead to modified growth by adsorbed gases such as hydrogen is still in its infancy.

A common assumption in describing the effect of surfactants is that the chemical adsorbate in some way changes the diffusion rate of atoms involved in the growth process. For example, the formation of a smoother film may be attributed to an increase in the diffusion rate of atoms across terraces or to a reduction in the barrier for diffusion over steps.[7,9] However, there are a number of steps involved in the overall process, any one of which may be subject to modification by adsorbates. To sort out the details of the different effects, it is therefore important to be able to isolate the individual steps of the growth process and determine how the adsorbate affects each one individually. In the case of atom migration across terraces, one specifically needs to know whether a given adsorbate will promote or inhibit the diffusion process.

In this study the field ion microscope (FIM) is used to investigate how hydrogen influences surface self-diffusion on Rh(100) and Rh(311). The ability of the FIM to track the motion of an individual atom as it migrates on a perfectly defined single-crystal plane[12] makes it possible to separate the effect of hydrogen on the diffusion rate of a single adatom from the other steps involved in film growth. In past studies, the FIM has been successfully employed to examine the migration of individual atoms on clean surfaces and determine diffusion parameters for a variety of metal-metal combinations.[13–15] Considerable care is taken in these studies to ensure that no contaminant atoms or molecules (especially hydrogen) are present on the surface during the measurements. In the experiments reported here the procedures are essentially the same, except that hydrogen is intentionally introduced to determine its effect on adatom diffusion.

There are two previous FIM studies that address the question of how hydrogen influences the mobility of metal adatoms on metal surfaces. In a study of self-diffusion on various planes of Ni, Tung and Graham[16] note that the presence of hydrogen dramatically increases the diffusion rate for Ni atoms on the (110), (311), and (331) planes of Ni. They find that when the Ni surfaces are prepared by thermal annealing (without hydrogen), the onset of adatom motion is observed at temperatures around 150 K. When the surface is prepared by hydrogen-promoted field evaporation, however, adatoms are found to move freely at the base temperature of 30 K. Even after removing the hydrogen from the system and repeated annealing and field evaporation of the substrate, residual effects of hydrogen are observed. These residual effects appear to be the most pronounced for self-diffusion on the Ni(110) plane.

The effect of hydrogen on self-diffusion on W(321) is markedly different from that discussed above for diffusion on Ni surfaces. FIM studies by Casanova and Tsong[17] indicate that the presence of hydrogen on the W(321) surface actually reduces the diffusion rate of a W adatom. In this case, the effect is relatively small: the activation energy of surface diffusion increases by only 0.05 eV over the barrier on the clean surface. The hydrogen partial pressure used in

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these studies was $\sim 10^{-5}$ Torr and the temperature during the diffusion intervals was ~300 K. The authors indicate that under these conditions there should be a saturation coverage of hydrogen on the surface during the diffusion intervals.

Theoretical studies also indicate that the influence of hydrogen on metal-atom diffusion is system specific. First-principles calculations by Stumpf[18] show that a hydrogen atom adsorbed on top of a Be atom reduces the self-diffusion barrier on Be(0001) by a factor of 3. A strong H-Be bond weakens the bond of the adatom to its surface neighbors, i.e., a ''skyhook'' effect. In contrast, classical-potential total-energy calculations by Haug *et al.*[19] predict that a hydrogen atom acts as weak trapping center for Ni atoms on Ni(100), effectively slowing down the rate of self-diffusion. The trapping is attributed to the fact that the hydrogen atoms prefer to occupy quasisubsurface-interstitial sites. This result also appears to be at odds with the experimental result for Ni surfaces mentioned above, although the (100) surface was not addressed specifically in the experimental study.[16]

To develop a clearer picture of the role of hydrogen in promoting or inhibiting surface diffusion, it is obvious that more systems need to be examined. Self-diffusion on Rh was chosen for this study for several reasons. Past FIM studies by Ayrault and Ehrlich[20] provide an extensive database relating to self-diffusion on clean Rh surfaces. They find that diffusion on Rh(100) takes place near room temperature, whereas diffusion on Rh(311) sets in at much lower temperatures (~200 K). Hence investigations on these two surfaces permit one to examine the influence of hydrogen in different temperature regimes. It has also been shown that self-diffusion on Rh(100) proceeds by ordinary hopping-type displacements,[21] as opposed to the exchange-type displacements observed for self-diffusion on the (100) surfaces of Pt (Ref. 22) and Ir.[23] An additional motivation for this study was to determine whether or not the presence of hydrogen changes the diffusion mode from hopping to exchange. The ability to control the mechanism by which atoms migrate across surfaces would be very useful in efforts to modify the growth of crystals and thin films.

II. EXPERIMENTAL DETAILS

The experimental procedures used in FIM investigations of single-atom surface diffusion are described in detail in several recent review articles.[13–15] A brief overview of these procedures is given here to aid in the discussion of the observations. In a ''standard'' FIM surface diffusion study a field emitter surface is cleaned by a combination of annealing, ion sputtering, and field evaporation. An image of the surface is obtained by applying a high electric field to the sample in the presence of an inert gas (e.g., He or Ne). Images are recorded with the sample at 77 K. Individual atoms are deposited on the crystal plane of interest by heating a wire coil to a temperature near the melting point of the metal. Atoms deposited on low index crystal planes appear as high-contrast image spots on a uniformly dark background. Motion of the deposited atom is induced by warming the surface to a preset value for a fixed interval of time in the absence of an applied electric field. The imaging gas remains in the system during the heating interval. Images are recorded immediately following each heating period. Displacements of the atoms are determined from the recorded images using site-visitation maps to calibrate the distance scale. The diffusion coefficient D at a given temperature is obtained from the measured mean-square displacement $\langle r^2 \rangle$ and the time interval according to $D = \langle r^2 \rangle / 2n\tau$, where n is the dimensionality of the random walk.

In the present experiments, a single Rh adatom is deposited on the crystal plane of interest with pure neon at a pressure of 2×10^{-4} Torr in the system. 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 neon, 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 to added hydrogen. Subsequent measurements are made with the mixture of neon and hydrogen as the imaging gas. The partial pressure of hydrogen is typically in the low 10^{-9}-Torr range. At lower partial pressures, hydrogen has a negligible effect on the diffusing adatoms. At hydrogen partial pressures above $\sim 10^{-8}$ Torr, Rh adatoms field desorb from the surface during field ion imaging.[24] This point is discussed further below.

During the course of the experiments the surface is subjected alternatively to elevated temperatures (at zero electric field) and elevated electric fields (at 77 K). The results (discussed below) indicate that some hydrogen is removed from the surface during the diffusion intervals at elevated temperatures by thermal desorption, but hydrogen is not removed by the electric field (typically ~3.0 V/Å) during field ion imaging. This latter observation is consistent with previous studies of thermal field desorption of chemisorbed hydrogen from Rh surfaces.[25] The primary effect of the electric field is on the adsorption of hydrogen. The electric field used for imaging can polarize hydrogen atoms in the gas phase and attract them to the surface thereby enhancing the arrival rate.[24] This effect, combined with the possibility of field-induced migration of hydrogen from the tip shank to the surface, makes it impossible to determine the actual hydrogen coverage in the present experimental setup. However, it is possible to investigate qualitatively the effects of increasing hydrogen coverage by examining the mobility of the adatom as a function of time, keeping the hydrogen partial pressure constant.

A series of field ion micrographs illustrating the general procedure used in this investigation is shown in Fig. 1. Figure 1(a) shows a single Rh adatom on Rh(100) imaged in pure Ne at 77 K. Figure 1(b) shows the same adatom after a 30-sec heating interval at a temperature of 275 K in pure Ne. Measurements of the adatom's coordinates indicate that the location of the adatom is the same in Figs. 1(a) and 1(b). In ten subsequent diffusion intervals at 275 K with only Ne in the system, the position of the atom did not change. Figure 1(c) shows the same adatom after a heating interval during which 2×10^{-9} Torr of hydrogen was added to the imaging gas. Two effects of the hydrogen are observed. First, the presence of hydrogen in the imaging gas changes the characteristics of the image spot associated with the Rh adatom. In Fig. 1(c) the image spot appears larger and with less contrast than the spot in Figs. 1(a) and 1(b). This can be attributed to field-adsorbed hydrogen atoms as discussed below.[24] More importantly, the addition of hydrogen causes the ada-

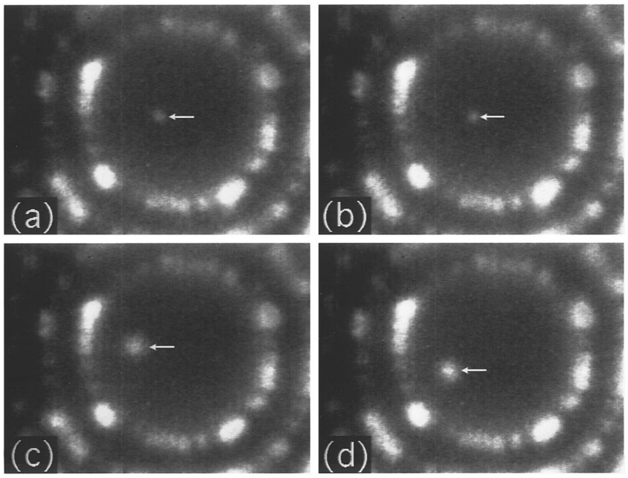

FIG. 1. Field ion microscope images showing the diffusion of an individual Rh adatom on Rh(100). Between each photograph the sample was warmed from its base temperature of 77 K to 275 K. The introduction of hydrogen between (b) and (c) induces adatom mobility as discussed in the text.

tom to make a noticeable displacement. As discussed later, this is the result of chemisorbed hydrogen on the surface. Figure 1(d) shows the adatom after an additional heating interval of 275 K. Again the position of the adatom has changed significantly. From over 100 observations following heating intervals at 275 K with hydrogen present, the mean-squares displacement of the atom is found to be 7.3 ± 1.7 Å^2. This corresponds to approximately one nearest-neighbor displacement per diffusion interval. Thus the addition of hydrogen causes the initially immobile atom to migrate at an easily detectable rate.

From the orientation of the map of sites that the atom visits as it moves across the surface, it is determined that the mechanism of diffusion is ordinary bridge hopping, not the exchange mechanism found for self-diffusion on (100) surfaces of Pt and Ir.[22,23] Since self-diffusion on Rh(100) in the absence of hydrogen also takes place by ordinary hopping, this result indicates that the presence of hydrogen does not change the diffusion mechanism.

III. RESULTS

A. Self-diffusion on Rh(100)

Figure 2 shows a plot of the measured mean-square displacement for a Rh adatom on Rh(100) as a function of time after admission of approximately 3×10^{-9} Torr hydrogen to the vacuum chamber. The diffusion intervals are 30 sec in length at a temperature of 275 K. The bin size for each data point is 20 diffusion intervals (i.e., 20 displacements were squared and averaged for each point plotted). At a temperature of 275 K and with the hydrogen present, the mean-square displacement is in the range 5–10 Å^2, corresponding to approximately one nearest-neighbor hop per diffusion interval. From Fig. 2 it is apparent that the mean-square displacement is essentially constant as a function of time. As discussed later, this result is markedly different from that found for self-diffusion on Rh(311).

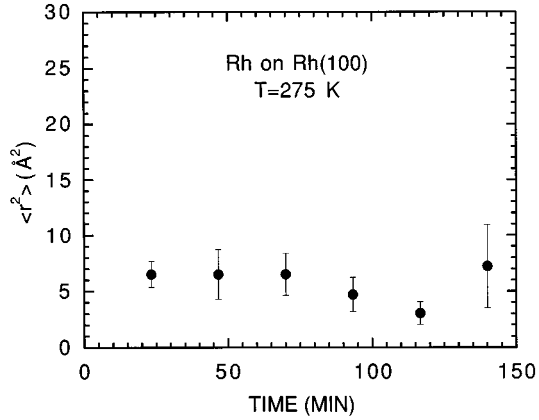

FIG. 2. Mean-square displacement $\langle r^2\rangle$ of a Rh adatom on Rh(100) in the presence of hydrogen remains essentially constant as a function of time.

Figure 3 shows how the mean-square displacement for self-diffusion on Rh(100) changes when the partial pressure of hydrogen is increased. The temperature during the diffusion intervals in this experiment is 280 K. At time $t=0$ hydrogen at a partial pressure of 1×10^{-9} Torr is admitted. Over a period of 90 min, the mean-square displacement increases from a negligible value to ~2 Å^2. When additional hydrogen is added (approximately 1×10^{-9} Torr), the mean-square displacement increases to ~4 Å^2. With the addition of even more hydrogen (approximately 2×10^{-9} Torr) the mean-square displacement jumps to 13 Å^2. Thus an increase in hydrogen partial pressure increases the mobility of the adatom. The results shown in Fig. 4 suggest that the magnitude of each increase tends to diminish over a period of time, but the statistics are insufficient to establish the trend conclusively.

Figure 4 shows the temperature dependence of the mean-square displacement for self-diffusion on Rh(100) plotted in Arrhenius form for both clean and hydrogen-exposed surfaces. Qualitatively, one notes that the mobility of the adatom increases monotonically as the temperature is increased for both cases, but the rate of increase is much less for the hydrogen-exposed surface. Figure 4 also indicates that a linear relationship is followed in the Arrhenius plots for both

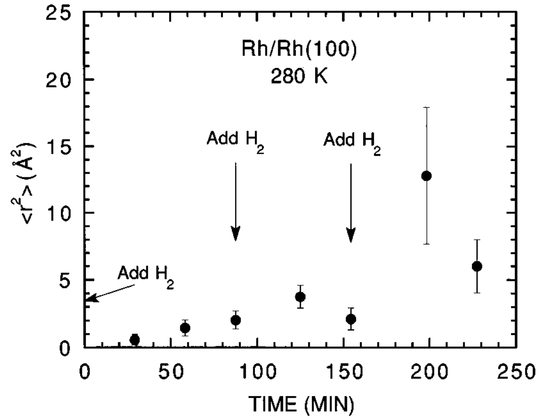

FIG. 3. Mean-square displacement $\langle r^2\rangle$ of a Rh adatom on Rh(100) increases upon addition of hydrogen to the background gas.

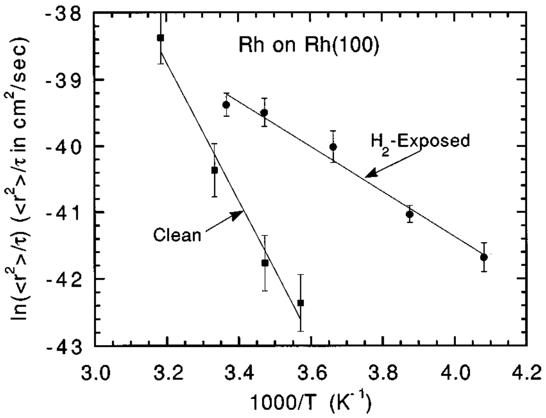

FIG. 4. Temperature dependence of the mean-square displacement $\langle r^2 \rangle$ for self-diffusion on Rh(100) plotted in Arrhenius form for clean and hydrogen-exposed surfaces. The presence of hydrogen leads to a large (apparent) reduction in the activation energy and Arrhenius prefactor.

situations. The activation energy and Arrhenius prefactor determined for self-diffusion on the clean surface (0.89 eV and 4×10^{-3} cm^2/sec) agree with previous measurements by Ayrault and Ehrlich (0.88 eV and 1×10^{-3} cm^2/sec). For the hydrogen-exposed surface the activation energy and prefactor are both exceptionally low (0.29 eV and 1×10^{-12} cm^2/sec). It should be noted, however, that the results of such an analysis are misleading because, as discussed below, the coverage of hydrogen is dependent on the surface temperature during the heating interval. At higher temperatures, the coverage of hydrogen is lower. Since the mobility of the adatom is dependent on hydrogen coverage, the linear relationship observed in the Arrhenius plot for the hydrogen exposed surface is most likely fortuitous and the extracted diffusion parameters cannot be interpreted in the conventional way.

B. Self-diffusion on Rh(311)

The time dependence of the mean-square displacement for self-diffusion on Rh(311) in the presence of hydrogen is markedly different from that for self-diffusion on Rh(100). Figure 5 shows the results for two separate experiments with different initial hydrogen exposures. The plots show the measured mean-square displacement during 10-sec diffusion intervals at 140 K. Prior to admission of hydrogen, the adatom is immobile. After hydrogen is added to the background gas, the adatom remains immobile for 10–15 diffusion intervals. The mean-square displacement then increases monotonically as a function of time. The curves drawn through the data points are fits to a power-law dependence. The exponents obtained from these fits are approximately 2, indicating a square dependence of the mean-square displacement with time (i.e., a linear dependence of the root-mean-square displacement with time).

Qualitatively, these results provide compelling evidence that hydrogen promotion of surface diffusion is indeed coverage dependent. Quantitatively, however, one cannot determine the actual coverage dependence of the mean-square displacement from the measurements. Although the thermal desorption studies mentioned below indicate that the coverage should increase linearly as a function of time, one must also consider the field enhancement of the supply from the gas phase during field-ion imaging as well as an additional supply due to hydrogen diffusion along the tip shank.[24] Direct knowledge of the time dependence of these effects is not available, making a direct conversion of the measured time dependence into a coverage dependence beyond the scope of this study.

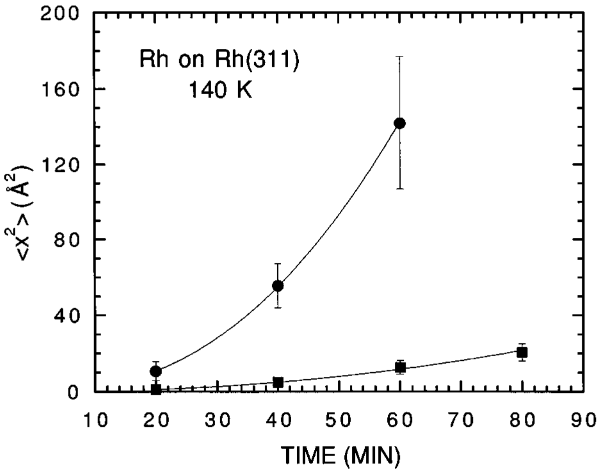

FIG. 5. Mean-square displacement $\langle x^2 \rangle$ of a Rh adatom on Rh(311) in the presence of hydrogen increases rapidly as a function of time. The two curves are for two different hydrogen exposures at 140 K. Both curves fit a power-law dependence with an exponent of ~2, indicating a square dependence of the mean-square displacement with time.

The temperature dependence of adatom mobility for self-diffusion on Rh(311) in the presence of hydrogen was also investigated. As in the case of self-diffusion on Rh(100), the mean-square displacement increases with increasing temperature. However, because the mean-square displacement also increases as a function of time as discussed above, it is not possible to determine quantitatively the change in mean-square displacement as a function of temperature at a constant hydrogen coverage.

IV. DISCUSSION

A general discussion of hydrogen promotion of self-diffusion on Rh(100) and Rh(311) is facilitated by a brief review of past temperature-programmed desorption (TPD) investigations of hydrogen on these crystal surfaces. On Rh(100) Kim, Peebles, and White[26] find that deuterium adsorbs dissociatively with an initial sticking coefficient of 0.53±0.05. At low coverages corresponding to 0.05 L ($1\ \mathrm{L}=10^{-6}$ Torr sec), the maximum of the TPD peak (taken at a heating rate of 25 K/sec) occurs at 361 K. As the exposure increases, the peak maximum temperature decreases, indicating second-order desorption kinetics. For exposures between 0.5 and 1 L, a shoulder appears at about 260 K. At exposures of 0.8–1.0 L, a low-temperature desorption peak also appears and the high-temperature peak broadens on its low-temperature side. Measurements of the areas under the TPD curves indicate that the coverage of deuterium versus exposure is linear up to about 0.5 L of deuterium. The thermal desorption kinetics for hydrogen on Rh(100) are presumed to be identical to those for deuterium.

On Rh(311) TPD measurements by Nichtl-Pecher *et al.*[27] indicate that five distinct binding states are populated upon hydrogen exposures at 90 K. These states originate from dissociatively adsorbed hydrogen as proven by isotope exchange experiments. The value of the initial sticking coefficient is ~0.25. The highest-temperature (lowest-coverage) peak is at about 350 K. A large low-temperature peak (~175 K) begins to grow in at exposures above 0.6 L. Two additional peaks appear at intermediate exposures. Above exposures of 1 L, an even lower-temperature (~125 K) peak appears.

These TPD studies make it clear that hydrogen adsorbs dissociatvely on both the (100) and (311) surfaces of Rh with a relatively high sticking coefficient. It is therefore reasonable to assume that the observed promotion of self-diffusion on both surfaces is due to adsorbed atomic hydrogen. This being the case, it is somewhat surprising to find that the time dependence of the measured mean-square displacement is qualitatively different for the two different substrates. On Rh(100) the mean-square displacement of a Rh adatom increases upon exposure of the surface to hydrogen, but then remains constant as a function of time after exposure (Fig. 2). At first glance, this suggests that the hydrogen promotion effect is independent of coverage because the coverage is expected to increase as a function of time with a constant pressure in the background. On Rh(311), however, the mean-square displacement increases dramatically as a function of time (Fig. 5). This indicates a strong dependence of the diffusion rate on hydrogen coverage.

The difference in the time dependence for the two crystal planes can be explained by the difference in the temperature required to initiate self-diffusion on the two surfaces. On the clean Rh(100) surface the onset of self-diffusion occurs at temperatures near 300 K. Exposure of the surface to hydrogen lowers the onset temperature to ~260 K. In this temperature range, the thermal desorption studies mentioned above indicate that a substantial fraction of adsorbed hydrogen will thermally desorb from the surface during the heating intervals. Hydrogen is readsorbed during the time between the heating intervals (i.e., during field ion imaging). A steady-state hydrogen coverage is established and the diffusion rate remains constant as a function of time.

This argument explains why the self-diffusion rate on Rh(100) increases when additional hydrogen is added to the system (as shown in Fig. 3). The higher partial pressure causes an increase in hydrogen coverage. The subsequent decreases suggested by the data shown in Fig. 3 can be explained by thermal desorption of hydrogen over the successive heating intervals, i.e., it takes a number of desorption cycles before a steady state is reestablished. As indicated earlier, this explanation is also consistent with the observed temperature dependence of the mean-square displacement on Rh(100) and the exceptionally low (apparent) diffusion parameters (Fig. 4). Thermal desorption of hydrogen during the heating intervals causes the steady-state coverage of hydrogen to be higher at successively lower temperatures. As the temperature is lowered in the experiments, the rate of diffusion is enhanced due to the higher hydrogen coverage. In an Arrhenius plot, this has the effect of reducing both the slope and the prefactor leading to unrealistic values of the diffusion parameters.

On Rh(311) the situation is quite different. Here the temperature range of the experiments is 120–160 K. According to the thermal desorption studies,[27] little hydrogen will be thermally desorbed at these temperatures during the diffusion intervals. This allows the hydrogen coverage to build up over a period of time and, as the coverage builds up, the diffusion rate increases. One therefore observes a marked increase in the measured mean-square displacement as a function of time.

It is interesting that the mobility of an adatom exposed to hydrogen in the low 10^{-9}-Torr range increases as a function of time for over 1 h, but the adatom does not field desorb. Yet, if the partial pressure of hydrogen is raised to $\sim 10^{-8}$ Torr the adatom immediately desorbs. Apparently, the desorption of the adatom is promoted by field-adsorbed hydrogen (weakly bound hydrogen held on the surface by polarization forces due to the applied electric field[24]) from the gas phase, whereas the mobility of the adatom is promoted by chemisorbed hydrogen on the surface. When the surface is heated, field-adsorbed hydrogen is removed, but chemisorbed hydrogen remains. This field adsorbed hydrogen also explains the change in image spot size as mentioned above.

It is important to emphasize that the diffusion rate is coverage dependent for self-diffusion on both Rh(100) and Rh(311), but the coverage dependence manifests itself as a time dependence in the measured mean-square displacement only in the case of Rh(311). On Rh(100) the coverage dependence is inferred from the increase in the diffusion rate upon the addition hydrogen to the background and on the temperature dependence of the mean-square displacement as discussed above. From a mechanistic standpoint, the observation of a coverage-dependent effect in the promotion of diffusion by hydrogen rules out a simple skyhook effect[18] (i.e., a weakening of the metal-metal bonds by a strong H-metal bond). In this case, one would expect a single-step increase in the diffusion rate corresponding to when a hydrogen atom attaches itself to the Rh adatom. The monotonic increase in the diffusion rate with hydrogen coverage indicates that if a skyhook effect exists at all, it is a transient effect, i.e., once a displacement occurs, the hydrogen is no longer bound to the diffusing atom.

The results of this study are also inconsistent with the conclusions of theoretical studies for the effect of hydrogen on the diffusion rate of Ni atoms on Ni(100).[19] The calculations predict that the presence of hydrogen should decrease the rate of self-diffusion on Ni(100), whereas the result reported here for Rh(100) indicates that the presence of hydrogen increases the rate. This suggests either that the effect of hydrogen is totally different for self-diffusion on Rh(100) and Ni(100) or, perhaps, the calculations, which involve only one hydrogen atom per metal adatom, are not an adequate representation of the experimental situation.

Having ruled out a simple skyhook effect as the mechanism of promotion, it is natural to speculate on alternative possibilities. It could be that the diffusion barrier is lowered by an interaction similar to a skyhook effect, but in the process of making a displacement, the hydrogen atom detaches itself from the adatom. Another possibility is that the promotion effect is not due to a direct interaction of the hydrogen

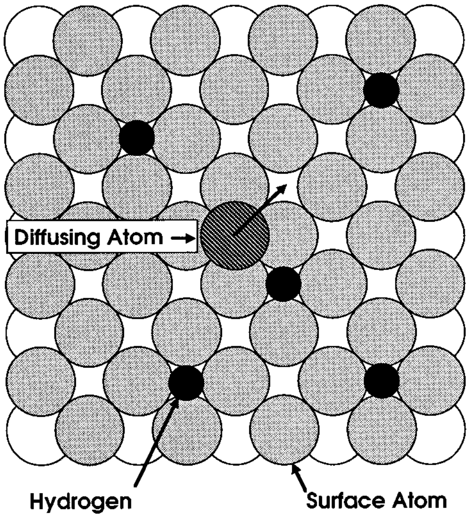

FIG. 6. Schematic drawing of a Rh atom on Rh(100), indicating a possible mechanism for the promotion of diffusion by the presence of hydrogen.

with the diffusing atom, but due to the interaction of the hydrogen with the surface atoms in the vicinity of the adatom. A plausible scenario for the case of self-diffusion on fcc(100) surfaces is shown in Fig. 6. When a hydrogen atom occupies a fourfold hollow site next to the adatom, the interaction of the hydrogen with the substrate atoms may reduce the diffusion barrier for the adatom by either weakening its binding to the substrate at the equilibrium position or lowering the energy of the saddle point at one of the bridge sites. Previous studies of hydrogen diffusion on other metal surfaces indicate that at temperatures high enough to induce motion of a Rh adatom, hydrogen atoms will be highly mobile.[28] Once the hydrogen atom promotes a displacement, it moves quickly away from the vicinity of the adatom. In order for the adatom to displace again, another hydrogen atom must come along. As the coverage increases, the probability of a hydrogen atom finding itself next to the adatom becomes higher, leading to a coverage-dependent promotion effect. The coverage dependence would be enhanced if hydrogen atoms were required at two of the neighboring sites instead of just one.

Obviously, the above mechanisms cannot be verified by the present experiments. To gain further insight into the promotion mechanism, a method is needed to determine the actual coverage of hydrogen during the experiment. This may be possible by the measurement of field emission work-function changes carried out during the course of the field ion microscope studies. For a given dipole moment and a given tip radius, the change in work function due to the adsorption is directly related to the coverage of the adsorbed species.[29] Unfortunately, such measurements are not feasible in our current experimental setup. Further insight into the promotion mechanism could also be obtained from detailed calculations of the energetics associated with a hydrogen atom in the vicinity of a metal adatom.

V. CONCLUSION

The results of this investigation lead to three important conclusions: (i) the adsorption of hydrogen on both the (100) and (311) planes of Rh significantly enhances the rate of surface self diffusion, (ii) the promotion effect is dependent on the coverage of hydrogen, and (iii) the presence of hydrogen does not change the diffusion mechanism from hopping to exchange. With regard to the use of hydrogen as a surfactant as discussed in the Introduction, the second conclusion is significant in that it suggests the possibility of a controllable adjustment in the diffusion rate of atoms across terraces, of one of the elementary steps in the growth process. Although the inability to characterize the actual coverage of hydrogen in the experiments makes it difficult to interpret the results in a quantitative fashion, the observed time and temperature dependences allow us to eliminate a simple skyhook effect as a mechanism of promotion and make some speculations as to what the mechanism might be. In experiments planned for the near future, the effect of hydrogen on diffusion for a system that the exchange mechanism is energetically favorable [e.g., self-diffusion on Pt(100)] will be examined to determine if hydrogen changes the preferred mechanism in the reverse direction, i.e., from exchange to hopping.

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