Direct Observations of Adatom–Surface-Atom Replacement: Pt on Ni(110)

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Field-ion-microscope observations provide direct evidence that Pt adatoms replace Ni(110) surface atoms at temperatures above 105 K. The directions of the individual displacements in this replacement process are consistent with a model involving concerted motion of the adatom and substrate atom. The activation barrier for the exchange is estimated to be 0.28 eV.

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A knowledge of the interaction between an isolated adatom and a clean surface is fundamental to the understanding of various crystal and epitaxial growth processes. It is generally assumed that a metal atom on a metal surface is immobile at very low temperatures and, above a given temperature, begins to migrate across the surface by a series of jumps between adjacent binding sites. It is the interaction of such diffusing adatoms which provides the basis for the nucleation of subsequent atomic layers and ultimately leads to the growth of the crystal or epitaxial film.

Contrary to this intuitive picture of surface diffusion, it is now established that adatom motion may take place by a mechanism in which the individual displacements are not atomic jumps [1-7]. For certain adatom/substrate systems, field-ion-microscope (FIM) observations show that migration proceeds by an exchange process in which an adatom replaces a substrate surface atom leaving the displaced surface atom to continue the migration. The first evidence for this type of diffusion resulted from FIM observations of self-diffusion on Pt(110) reported by Bassett and Webber [1]. The relative ease at which atoms were seen to move across the $[1\bar{1}0]$ atomic rows (actually comparable to motion within the $[1\bar{1}0]$ channels) suggested that an exchange process between the adatom and a channel-wall atom might be involved in the migration. Confirmation of this type of exchange process was provided in an atom-probe field-ion-microscope investigation by Wrigley and Ehrlich [2]. Time-of-flight mass analysis of adatoms before and after their displacements proved unambiguously that W adatoms exchange with substrate atoms on the Ir(110) plane. This result has led to the reasonable assumption that cross-channel displacements observed in self-diffusion on the (110) surfaces of Pt, Ir, and Ni also involve exchange between the adatom and channel-wall atom [1-3]. More recently, compelling evidence, both theoretical [4,5] and experimental [6,7], has been reported which indicates that self-diffusion on certain fcc (100) surfaces also takes place by an exchange-type process. On these surfaces the displacements involve a concerted motion of the adatom and neighboring substrate atoms which provides an increased coordination through the transition state.

In this Letter an experimental investigation is reported which addresses the detailed mechanism by which adatom–surface-atom exchange takes place on fcc (100) surfaces. The system of Pt on Ni is ideal for this study because Pt and Ni are easily distinguished in the field-ion microscope by the large difference in their evaporation fields. The exchange process is therefore confirmed without the use of an atom probe. Moreover, the exchange process for Pt on Ni(110) is found to take place at a temperature below the onset of migration of either the adatom or the displaced substrate atom (105 K). The absence of migration makes it possible to measure the direction of an individual exchange displacement event. As shown below, the displacement directions are consistent with a model involving a concerted motion of the adatom and substrate atom, similar to replacement events on fcc (100) surfaces [4-7].

The experimental procedures used to generate individual adatoms on perfectly smooth single-crystal planes and to examine their migration behavior in a field-ion microscope are well documented [8]. Here, I report only those experimental details relevant to this particular investigation. The Ni tip was prepared from Marz-grade Ni wire electropolished in a solution of 40% HCl. The tip surface was cleaned by a combination of vacuum annealing at 600 K, sputtering with Ne ions, and field evaporation. Images were obtained at 77 K in 2×10^{-4} Torr Ne, cleaned by diffusion through a Vycor bulb. The background pressure in the system after extensive vacuum processing was 3×10^{-11} Torr. An internal channel plate was used for image intensification and images were recorded with either a video camera recorder or a 35-mm still camera. Pt adatoms were deposited from a heated Pt wire coil placed a few cm from the sample tip. The tip temperature was controlled and monitored by the standard resistance-heating-resistivity method common to FIM surface diffusion studies [8].

Ion sputtering was found to be an essential step in the cleaning process to produce images with good contrast in the region of the (110) plane. As reported previously by Tung and Graham [3], conventional annealing and field evaporation of Ni surfaces produces images with dark areas extending through the (110) plane [i.e., some of the edge atoms of the (110) plane and underlying layers are not imaged]. In addition, field evaporation does not remove certain contamination atoms (e.g., sulfur [9]) from Ni surfaces. The ion sputtering procedure, described in detail for Ni in a previous publication [10], was found to produce images free of the dark areas and free of contamination atoms resistant to field desorption.

Prior to the investigation of Pt on Ni(110), experiments were carried out to determine the evaporation field and migration onset temperature for Ni adatoms on Ni(110). To determine the evaporation field, several Ni atoms were deposited at 77 K and the applied voltage at which each adatom desorbed was measured. Adatoms at the edge of the plane (where the field is higher at a given voltage) desorbed at a voltage approximately 10% lower than atoms at the center of the plane. At 77 K, Ni adatoms were found to field evaporate at (75–85)% of the Ni-substrate evaporation voltage [i.e., the applied voltage for which the (110) plane field evaporated at 0.2 layer/sec]. Given the accepted value of 35 V/nm for the evaporation field of the Ni substrate [8], the evaporation field for Ni adatoms on Ni(110) is thus 26–30 V/nm.

The onset temperature for Ni migration on Ni(110) was found by raising the temperature (in the absence of the applied field) until motion of the adatom was subsequently detected. Migration was first observed at 140 K in a 30-sec time interval. This result is in agreement with more detailed studies of self-diffusion on Ni(110) reported by Tung and Graham [3].

The observation that the evaporation voltage of Ni on Ni(110) occurs at (75–85)% of the substrate evaporation voltage made it easy to distinguish Pt from Ni atoms on this plane. Pt adatoms were found to resist field desorption up to the evaporation field of the Ni substrate. Upon increasing the applied voltage, the Ni(110) plane would shrink in size until the edge of the evaporating plane encountered the Pt adatom. Only at this point would the Pt adatom field desorb. Thus, Pt adatoms have a higher desorption field than even the Ni substrate atoms. It is interesting to note that, in most cases, Pt adatoms could also be distinguished by their spot size, which was considerably larger than Ni image spots.

Direct confirmation that the cross-channel displacement of Pt adatoms on a Ni(110) substrate involves an adatom–substrate-atom replacement process is provided by the field-ion micrographs shown in Fig. 1. The high-contrast spot near the center of the photograph shown in Fig. 1(a) is a Pt adatom on a Ni(110) substrate. This adatom is identified by its resistance to field desorption and large spot size. The arrow on the photograph indicates the direction of the $[1\bar{1}0]$ atomic rows and surface channels. A micrograph of the same surface after warming the sample to 112 K for 1 min (with the applied voltage off) is shown in Fig. 1(b). The poorer contrast is the result of a longer exposure time at a lower imaging voltage. Note that there is an image spot (adatom) in the same general location as the Pt adatom from the previous photograph, except the spot is much smaller in size. Upon increasing the voltage, the image spot shown in Fig. 1(b) disappeared at 78% of the substrate evaporation field (i.e., at 27 V/nm). Figure 1(c) shows the substrate with the adatom removed.

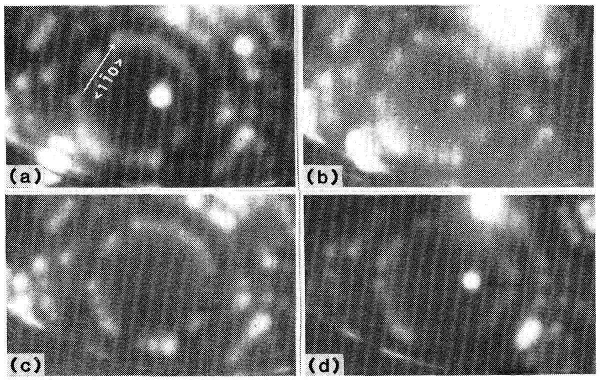

FIG. 1. A series of Ne field-ion micrographs confirming that Pt adatoms exchange with Ni substrate atoms on Ni(110). (a) A single Pt adatom on Ni(110). The arrow indicates the direction of the surface channels. (b) The same surface after heating to 112 K for 1 min. The adatom is now Ni, identified by its lower desorption field. (c) The Ni(110) plane after desorption of the Ni adatom. (d) The same surface after removal of one Ni(110) layer. The Pt adatom within the substrate plane is revealed.

As mentioned above, a Pt adatom does not desorb below the evaporation field of the substrate. Based on its lower desorption field, which is within the measured range for Ni, and the smaller image spot size, the adatom in Fig. 1(b) is identified as Ni. Given that this Ni adatom is produced by a replacement process, there should be a Pt adatom within the topmost Ni(110) layer near its original position. An image of the same Ni(110) surface after field evaporation of one atomic layer is shown in Fig. 1(d). The adatom revealed by removal of the topmost layer of Ni atoms is indeed Pt, as evidenced by its larger spot size and resistance to field evaporation. The sequence of events illustrated in Fig. 1 was repeated several times. Each time the Pt adatom exchanged with a Ni substrate atom, and each time, field evaporation revealed a Pt adatom within the topmost layer of Ni adatoms.

A reasonable estimate for the activation energy of the replacement process can be obtained from the onset temperature at which displacements are observed. With the assumptions of (1) a single displacement at the measured onset temperature of 105 K in a 45-sec time interval and (2) the accepted Arrhenius prefactor of 1×10^{-3} cm^2/sec (Ref. [8]), the activation energy for Pt displacements on Ni(110) is determined to be 0.28 eV.

Exchange-mediated displacement events have been confirmed previously for W adatoms on an Ir(110) surface with an atom-probe field-ion microscope [2] (a mass spectrometer which can identify atoms in a field-ion-microscope image). An important difference between this study involving Pt on Ni and the previous study involving W on Ir is that the exchange between Pt and Ni takes place at a very low temperature (as low as 105 K), which is below the onset of Ni adatom motion. As a result, the Ni adatom does not diffuse away from the site of the replacement process and the direction of the motion for an individual event can be measured. The direction is important in determining the atomic process involved in the exchange.

The schematic drawing shown in Fig. 2 illustrates how measurements of the displacement direction can provide information on the exchange mechanism. The upper diagram shows a top view of the Ni(110) plane, which consists of rows of close-packed atoms in the $[1\bar{1}0]$ direction separated by a surface channel. A side view of the same surface is shown in the lower diagram. A Pt adatom is indicated schematically by a larger, striped circle. Although the adsorption site for a Pt adatom on Ni(110) has not been determined, symmetry suggests the site indicated in the figure. It is reasonable to assume that the exchange occurs between the adatom and a neighboring channel-wall atom (i.e., the atom labeled "1" in Fig. 2 or one of the three other equivalent channel-wall atoms). In their original report of cross-channel diffusion on Pt(110), Bassett and Webber [1] proposed a two-step process in which a vacancy was formed in the channel wall (atom 1) followed by motion of the adatom to fill the vacancy. In this two-step process, the proposed final site of the displaced channel wall was either of the two equivalent sites "*a*" or "*b*" indicated in the upper diagram of Fig. 2. According to this model, there should be an equal number of displacements along the $[1\bar{1}2]$ and [001] directions.

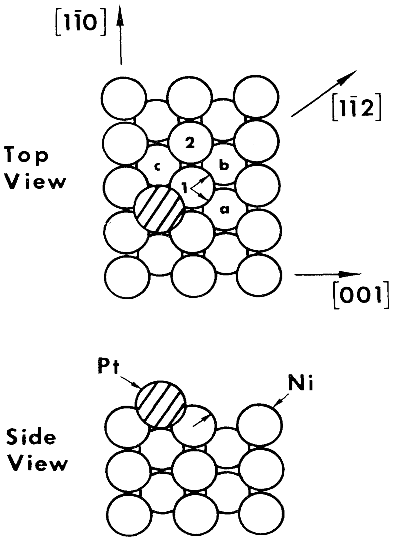

FIG. 2. A schematic representation of the Ni(110) plane showing the different exchange-displacement directions for a Pt adatom as discussed in the text.

To determine the displacement direction experimentally, the sequence of events illustrated by the field-ion micrographs of Fig. 1 was repeated 16 times. A video camera recorder was used to record the location of the Pt adatom and Ni adatom before and after exchange, respectively. The coordinates were determined with a video pointer and the direction of the displacement relative to the $[1\bar{1}0]$ surface channels was determined. In ten of the sixteen trials the channel-wall atom moved in a $[1\bar{1}2]$ direction to site *b*. Surprisingly, the channel-wall atom was never observed to move in a [001] direction to site *a*. In the other six trials the displaced atom was found back in the original channel in the site indicated by "*c*." The fact that displacements in the [001] direction were not observed rules out the two-step vacancy process described above.

The observation of $[1\bar{1}2]$ as the dominant displacement direction provides direct evidence that the exchange process involves a concerted motion between the adatom and the displaced channel-wall atom. Calculations by Feibelman [4] have shown that on fcc (001) surfaces the ability to maintain high coordination throughout the displacement event significantly lowers the activation barrier for replacement processes and leads to exchange-mediated diffusion. Measurements of the displacement directions for self-diffusion on Pt(100) and Ir(100) surfaces confirm this mechanism [6,7]. Feibelman [11] has also suggested that a similar process involving concerted motion of the adatom and channel-wall atom occurs during cross-channel jumps on fcc (110) surfaces. In contrast to the two-step vacancy process, here the adatom and the displaced channel-wall atom move in unison during the transition. For this process, site *b* is favored for the final position of the displaced atom, because the displaced channel-wall atom maintains its coordination with atom "2" in Fig. 2 throughout the transition, whereas motion towards site *a* results in a loss of coordination with this atom. Thus, the observed lack of any displacements in the [001] direction (to site *a*) provides strong evidence for an exchange mechanism that involves concerted displacements similar to those occurring on fcc (001) surfaces. Very recent FIM experiments along with Monte Carlo simulations by Chen and Tsong [12] indicate that cross-channel jumps of Ir on Ir(110) also occur preferentially along the $[1\bar{1}2]$ direction.

The observation of the displaced channel-wall atom at site *c* of Fig. 2 is puzzling since Ni adatoms do not diffuse on Ni(110) surfaces at such low temperatures. Apparently, the presence of the larger Pt atom within the Ni substrate (after exchange to site *b*) induces a return cross-channel displacement, which does not occur for Ni on Ni(110). A possible return path involves a Ni-Ni exchange with channel-wall atom 2 followed by a hop within the channel to site *c*. Both of these displacements are induced by the presence of the Pt adatom in the Ni substrate. However, this rather complicated process, which is still consistent with the proposed concerted-displacement mechanism, has not been confirmed and will be the subject of further investigation.

According to the mechanism proposed above, the Pt atom in the Ni substrate after exchange should be at position 1 between the original site of the Pt adatom and the site labeled *b*. Since field evaporation of the topmost Ni(110) layer uncovers the Pt atom, one would expect to be able to observe this position in the field-ion-microscope image. Unfortunately, field evaporation of the Ni layer surrounding the Pt atom typically produces some movement of the Pt adatom even at 77 K. As the Ni(110) plane edge sweeps past during field evaporation, the Pt adatom frequently moves to a new location one or two sites away and is not found at the expected position.

Preliminary field-ion-microscope results indicate that exchange also occurs for Pt adatoms on Ni(100) surfaces [13], but only at much higher temperatures (~250 K). In contrast, the dominant diffusion mode for Pt on Ni(311) is in-channel hopping [13]. The fact that exchange does not occur on the (311) plane, which has a wider channel separation than the (110) plane, suggests that adatom-induced relaxations of the substrate surface atoms [expected to be less on the (311) surface] may be a factor in the exchange process. A detailed comparison of Pt diffusion on various Ni surfaces and further investigation of relaxation effects will be published in a more extensive article [13].

In summary, the field-ion-microscope observations have provided conclusive evidence that Pt adatoms exchange with Ni(110) substrate surface atoms at temperatures as low as 105 K. This result provides further evidence that cross-channel displacement processes on fcc (110) surfaces in general are due to adatom–substrate-atom exchange and not due to hopping over the channel walls. In addition, the direction of the individual displacements involved in the replacement has been measured and is consistent with a concerted-displacement mechanism similar to that proposed for exchange processes on fcc (100) surfaces. Clearly, the observation of exchange at such low temperatures in a heterogeneous system has important practical implications concerning the growth of epitaxial layers, particularly when atomically sharp interfaces are required.

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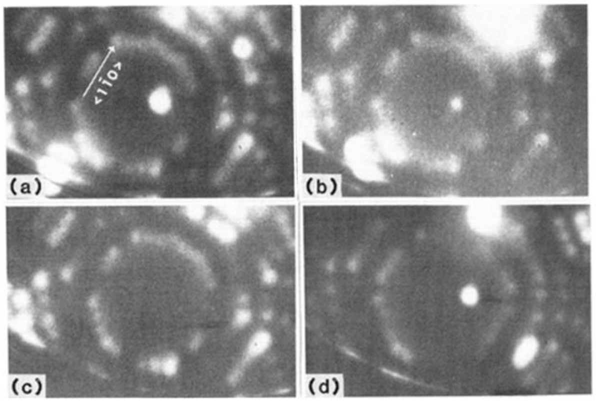

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