Kinetic Monte Carlo study of the effect of hydrogen on the two-dimensional epitaxial growth of Ni(100)

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The effects of hydrogen on Ni(100) submonolayer homoepitaxy have been investigated by kinetic Monte Carlo (KMC) simulations of the Ni growth process with and without the presence of a small hydrogen impurity. The two-dimensional KMC simulations are based upon rate constants for a set of uncorrelated Ni site-to-site hopping mobilities with and without the presence of hydrogen atoms which are found to act as a catalyst. The rate constant activation energies are determined by classical-potential total-energy calculations with semiclassical zero-point energy corrections for the hydrogen atom. This set of KMC simulations extends preliminary work on the activation energies which were reported along with their connection to available experiments in Ref. 1. We find that fast diffusion of H atoms occurs on the flat Ni(100) surface and the presence of these highly mobile H atoms is found to have significant effects on the mobility of lone Ni adatoms, and therefore also on the Ni islands which form during the epitaxial growth. The H atoms increase the mobility of lone Ni adatoms across the flat Ni(100) terrace by stabilizing the transition state for site-to-site hopping of the Ni adatom. While the effects of the H atom on the Ni mobility are primarily catalytic, the kinetically determined Ni island morphologies differ substantially as a function of H atom concentration over time periods which are long on the deposition time scale, and therefore the morphology differences can become frozen in place. Even quite low H atom coverage, by acting to increase lone Ni atom mobility, tends to decrease Ni island density which results in a corresponding increase in the average Ni island size. This suggests that the H atoms are acting as an antisorfacant in the Ni(100) homoepitaxy at low H coverage.

I. INTRODUCTION

The experimental interest in growing thin, smooth metallic films has led to a theoretical effort in understanding the microscopic growth and mobility mechanisms. The growth of such metallic islands can be described in terms of the competition of the rates for various processes involved: the deposition rate, the mobility rate of a lone adatom across a surface, the condensation of a lone atom with other adatoms to form islands, the evaporation of such islands as lone adatoms break off, and the peripheral diffusion of atoms along the edge of an island.

A question of additional importance in the growth process is what role impurities play in the competition of rates described above. Some experimental reports have noted that impurities can help to induce the layer-by-layer growth of a metal: the work of Esch et al. suggested that the cause was the oxygen impurity enhancing the mobility of the Pt metal at steps, while the work of Vrijmoeth et al. suggested that the cause was Sb impurity pinning the Ag metal adatoms in place.

In this paper we report computational experiments which examine the effect of adsorbed hydrogen atoms, as a low concentration impurity, on the epitaxial growth of Ni(100) in the low surface coverage regime leading to 2D islands. We desire to understand from a microscopic level how the impurity alters the Ni adatom and Ni island mobility and therefore the morphology of the growth pattern which is observed. We address these issues by carrying out kinetic Monte Carlo (KMC) simulations of the epitaxial growth of the Ni(100) surface in the presence and absence of H adatoms, by using all nearest-neighbor uncorrelated hopping events for the Ni adatoms together with their H-atom catalyzed counterparts. The rate constants involved in the KMC simulation are determined from classical-potential total-energy calculations with semiclassical hydrogen zero point energy (ZPE) corrections.

We find very low hopping barriers for H atoms in this study, and therefore fast diffusion of H atoms occurs on the flat Ni(100) surface. Fast H diffusion also occurs in the presence of Ni adatoms, islands, and steps which are created during the epitaxial growth. The presence of these highly mobile H atoms is found to have significant effects on the mobility of lone Ni adatoms, and also on the Ni islands which can form during the epitaxial growth. The H atoms increase the mobility of lone Ni adatoms across the flat Ni(100) terrace by stabilizing the transition state for site-to-
site hopping of the Ni adatom. The H atoms also diminish the stability of Ni islands at corner and kink Ni sites by again stabilizing the transition state for evaporation of Ni from these corner and kink sites, but the H atoms also accelerate the formation of islands by catalyzing the condensation steps; and these accelerated evaporation and condensation effects tend to cancel one another out. The remaining key effect is the lone Ni atom accelerated mobility upon the flat terrace. While the H atom effect on this lone Ni mobility is primarily catalytic, the kinetically determined Ni island morphologies differ notably as a function of H-atom concentration over time periods which are long on the deposition time scale and therefore the morphologies can become frozen in place. Even at low H-atom surface concentration, the increase in lone Ni atom mobility tends to dominate the growth process and results in a decrease in Ni-island density and a corresponding increase in the average Ni-island size.

In addition to the above, we more briefly note the effects on the final Ni-island morphology of varying Ni atom deposition rates, varying Ni coverage, and the effect of H-atom deposition following Ni deposition rather than prior to the Ni deposition.

II. THEORY

Since the hopping of an adsorbed Ni from one binding site to another nearest neighbor site on the Ni(100) surface is a rare event (the hopping time is on the order of $10^{-3}$ s versus the vibrational period of the Ni in the binding site of the order of $10^{-13}$ s) a direct simulation of growth process is not computationally feasible. The theoretical description of the growth process therefore divides into a twofold description: (i) calculating thermal activation energies for many individual hopping events which then allow for the use of transition state theory (TST) to give thermal rate constants for the hopping events; and then (ii) using a kinetic Monte Carlo (KMC) simulation of the deposition and growth process based upon the thermal rate constants for the individual hopping events.

A. Activation barrier energies

The activation energies we use are calculated using a slab of Ni consisting of 77 dynamically active Ni atoms arranged in three layers and surrounded by a “basin” consisting of two layers of Ni atoms rigidly held in equilibrium (100) positions. The combined number of active and rigid Ni atoms making up this slab is 322. The Ni and H island adatoms are placed in the central area of the surface slab. All of the active slab atoms along with the Ni and H surface adatoms are free to move. Sample calculations were performed with a larger slab to ensure that the energy barriers for site-to-site mobility are numerically converged to about 0.005 eV. The interaction energy used for modeling the system is the embedded-atom method (EAM) potential energy proposed by Daw and Baskes as modified by Wonchoba, Hu, and Truhlar (we used the model which they designate as EAM5). This potential is realistic in the sense that it has been parameterized to fit the Ni-Ni equilibrium distance, the H-Ni equilibrium distance, the surface binding energy, and hydrogen vibrational frequency, with the added result that it also gives reasonable barrier heights for the H and Ni diffusion.

To determine the energy barrier height for the various hopping events we first determine initial and final relaxed configurations for all of the dynamically active molecules by starting from the rigid lattice atom positions, by use of damped molecular dynamics until zero-temperature equilibrium positions are found. The minimum-energy profile along the reaction path connecting the initial and final configuration is then mapped out by a restricted total-energy relaxation scheme in which one degree of freedom (typically one coordinate of one atom) is fixed at a set of intervals connecting the initial and final configurations, while all other degrees of freedom are fully relaxed. When a local minimum along the path is indicated the algorithm reverses direction with a smaller step size, etc. until a preselected accuracy in the energy barrier is attained; the algorithm then moves back toward the final configuration to complete the rest of the reaction path (in case of multiple barriers). Zero-point-energy (ZPE) effects are included for the H atom by calculating the classical vibrational frequencies at each step along the reaction path. If the hydrogen motion is unbound in any direction and an imaginary frequency results (as at a saddle point) the unbound coordinate is disregarded in the ZPE calculation. For several different H and Ni configurations, we compared the classically estimated H-atom ZPE to a fully quantum-mechanical ZPE, computed by a fast-Fourier transform technique discussed by Hang and Metiu. We found that the classical ZPE is consistently about 20% lower than the quantum ZPE, both at the transition state and in the reaction and product wells. Therefore, errors in the classical ZPE will tend to cancel out for the energy barriers which are used here.

The H atom prefers the surface fourfold hollow site using the EAM5 potential, and will hop from site to site by overcoming a 0.17 eV potential barrier. In addition, the H atom can also sit in a subsurface interstitial site, but must overcome a potential barrier of 0.67 eV to do so, and in the KMC results reported here we have ignored subsurface H atoms. Although it is well known experimentally that H can occupy bulk interstitial sites in many metal systems, experiments at low surface coverage of H have also shown that only a small amount of H is needed to substantially modify the growth dynamics of metal surfaces, which suggests that at low coverage the H is remaining at the surface.

The Ni adatoms on Ni(100) also prefer the fourfold hollow site, and a lone Ni adatom will hop from site to site by overcoming a 0.61 eV potential barrier using the EAM5 potential. When Ni islands form, there are various classes of hopping diffusion events which can occur, a few of which are summarized in Table I, along with the energy barriers and time constants, defined by Eq. (2) below, for the hopping process. Included also in Table I are the energy barriers and time constants for the analogous Ni hopping events when assisted by the presence of hydrogen. Note that Table I is only a sampling of the barriers used in the KMC studies in which we include all uncorrelated single hopping Ni events along with their hydrogen catalyzed counterparts, denoted graphically in Fig. 1 and the Fig. 1 caption. As noted in Ref. 1, not all Ni hops are uncorrelated. A Ni-Ni dimer can shift
as a unit, for example, with a barrier height of 1.03 eV (which may occur as an incoherent hop as the ‘‘rear’’ member of the dimer makes a hop toward its partner and pushes the partner one binding site ahead rather than being a coherent two-atom hop). Since this type of correlated multiple hop vastly complicates the number of possible moves that may occur on the growing surface, and in the belief that they are reasonable rare events given the relative barrier height compared to some of those listed in Table I, we have included only the uncorrelated Ni hopping events in the KMC studies reported below.

Correlated hopping is necessary for studying the influence of the hydrogen as an impurity. The H atoms act principally as a catalyst, stabilizing the transition state for site-to-site Ni hopping by formation of a Ni-H bond, while leaving the reactant configuration and product configuration energy wells at essentially the same level. Therefore, the change in morphology of the Ni growth layer is a kinetically controlled effect due to the presence of the H atoms. This is sensible in terms of the experimental result \(^1\) that only a small amount of H is needed to clearly distinguish the effect of H on the growth of the Cu\(^{100}\) surface, which we expect to be qualitatively similar to the Ni\(^{100}\) surface.

The physical origin of the effect of H on the Ni was discussed briefly in Ref. 1. The key finding is that while Ni and H at equilibrium in nearest neighbor sites have only a small stabilization energy \(^0\)0.02 eV, the H atom is very responsive to the Ni as a barrier crossing by the Ni atom is attempted in the H-atom direction, and the resulting Ni-H ‘‘bonding’’ acts to stabilize the transition state and lower the activation energy by about 0.14 eV \(^0\)1.17 eV (see Fig. 2 and Table I, rows 2 and 3). The H atom is pushed one binding site further ahead by the hopping Ni atom. For the short time period of

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**TABLE I.** A sampling of activation barrier energies, \(E\) in eV, and time constants, \(\tau\) in seconds from Eq. (2), for selected hopping events specified using the notation given in Fig. 1. In the Fig. 1 notation, a value of ‘‘0’’ indicates that the site is empty, a value of ‘‘1’’ indicates the site is occupied by a Ni atom, a value of ‘‘H’’ indicates that the site is occupied by a hydrogen atom. The values for \(\tau\) are denoted such that \(5.1 \times 10^{-10}\).

<table>
<thead>
<tr>
<th>Event</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>(E) (eV)</th>
<th>(\tau) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isolated H hop</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.17</td>
<td>5.1(-10)</td>
</tr>
<tr>
<td>Isolated Ni hop</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.61</td>
<td>3.8(-1)</td>
</tr>
<tr>
<td>Isolated NiH dimer shift</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>H</td>
<td>0.47</td>
<td>5.7(-4)</td>
</tr>
<tr>
<td>Ni-Ni bond formation</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.57</td>
<td>5.9(-2)</td>
</tr>
<tr>
<td>H-assisted Ni-Ni bond formation</td>
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<td>0</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>H</td>
<td>0.44</td>
<td>1.4(-4)</td>
</tr>
<tr>
<td>Ni-Ni bond breaking</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.98</td>
<td>1.1(+7)</td>
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<tr>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>H</td>
<td>0.88</td>
<td>1.1(+5)</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0.90</td>
<td>2.7(+5)</td>
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<tr>
<td>H-assisted Ni island corner breakup</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>H</td>
<td>0.83</td>
<td>1.0(+4)</td>
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<tr>
<td>Ni hop along island edge</td>
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<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.30</td>
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<td>1</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>H</td>
<td>0.27</td>
<td>5.3(-8)</td>
</tr>
</tbody>
</table>

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**FIG. 1.** Ni atom binding site labels on the Ni\(^{100}\) terrace used to determine the set of single site Ni hopping rate constants used in the KMC simulation. In all cases, a Ni adatom at initial binding site ‘‘i’’ hops to binding site ‘‘f’’ which may be occupied by a H-atom but not by another Ni atom. Each neighboring site labeled 1–6 may or may not be occupied by other Ni atoms. Activation energy barriers for each of these events is evaluated. Some of the activation energy barriers are listed in Table I.

**FIG. 2.** Activation energy (in eV) of Ni hopping one binding site vs Ni atom reaction path coordinate (in angstroms). The top curve is for a lone Ni atom, and the lower curve is for Ni hopping to a site previously occupied by a H atom. In the latter case, the H atom is displaced one binding site further ahead of the Ni (this simulation was stopped with the H atom in a slightly activated final state which results in the asymmetry of the lower curve).
the transition, we can usefully think of the Ni-H unit as a dimer which has hopped one binding site along the surface. Due to the high mobility of the H atom, however, the next time this Ni member of the dimer hops it will likely do so with a different H-atom partner. The presence of H atoms can also catalyze the formation and evaporation of Ni islands by a similar transition state stabilization mechanism, with barriers reduced on the order of 0.10 to 0.13 eV for the simplest condensation and evaporation processes noted in Table I (rows 4, 5, 6, and 7). The net result in the KMC studies of the H atom’s accelerating Ni island condensation is largely counteracted by the acceleration of Ni island evaporation; therefore, the lone Ni atom’s accelerated mobility in the presence of H atoms dominates the final surface morphology.

### B. Kinetic Monte Carlo

The kinetic Monte Carlo method is a stochastic solution of the master equation governing the deposition and growth processes occurring in this system. It is based upon the assumption that the hopping events are random (the separation between vibrational and translational time periods noted above suggests that the hopping events are random in the present case). With the calculated activation energies, $E_{\text{act}}$, for a given hopping event, the rate constant for the event is assumed to follow from transition state theory (TST) as

$$k = \frac{k_B T}{h} \left( \frac{Q^s}{Q} \right) \exp\left(-\frac{E_{\text{act}}}{k_B T}\right)$$

where $k_B$ is Boltzmann’s constant, $T$ is the temperature, $h$ is Planck’s constant, and $Q/Q^s$ is the vibrational partition function of the reactant (transition state) configuration. The vibrational partition function ratio $(Q^s/Q)$ for the Ni hopping events is on the order of unity and we set it equal to unity in the KMC simulation discussed here, since quantitative errors in $E_{\text{act}}$ due to flaws in the potential energy function we are using will tend to swamp the $Q^s/Q$ term in any case.

To more easily compare the relative hopping rates used in our KMC study, we have also included in the far right-hand column of Table I the time constants $\tau$ for each hopping process noted there, defined as

$$\tau = 1/k,$$

where ‘$k$’ is the rate constant from Eq. (1) above evaluated at $T = 250$ K, a typical experimental temperature.\(^1\) For comparison purposes, a typical experimental deposition time scale, which we use in the results presented below, is a time of 500 s to deposit one monolayer of Ni.\(^1\) From the values of $\tau$ given in Table I, we can see that very wide ranging time scales are involved in the hydrogen catalyzed Ni growth process.

The KMC procedure we now discuss is set up to handle the different time scales in an approximate manner.

We follow a KMC procedure similar to that outlined by Lu and Metiu.\(^2\) The Ni atoms are deposited on the surface with a deposition rate, as noted above, taken from the experimental work on Cu deposition in Ref. 1, and then are moved from site to site with probabilities for a move proportional to the appropriate rate constant via.

$$P_i = k_i/k_{\text{ref}},$$

where $k_i$ is the rate constant for event ‘$i$’ which refers to a given Ni hopping event and $k_{\text{ref}}$ is taken to be the rate constant corresponding to the fastest relevant process among those which we wish to distinguish. Since $k_{\text{ref}}$ sets the digital clock unit for the system, all processes happening faster than the reference rate are not distinguished. (For example, if this reference process sets the digital second hand on my clock, then I can distinguish events which happen on the 1 s vs 10 s time scales, but I cannot distinguish if an event is happening on the 1 s vs 0.1 s time scale as they will happen in the same ‘tic’ of the clock.) For the studies reported here, $k_{\text{ref}}$ is set by an activation energy of 0.41 eV, corresponding to a time constant $\tau = 3.5 \times 10^{-3}$ s, which, from Table I, is clearly not the fastest process in the system. This choice does, however, effectively distinguish the lone atom hopping rates, and most of the evaporation/condensation rates which are of greatest importance in determining Ni island size, but the choice does not distinguish many of the peripheral diffusion rates (see for example Table I, rows 10 and 11). This choice for $k_{\text{ref}}$ resulted from a computational efficiency compromise. In our case, there is a wide variation in the activation energies for various configurations of the system and for computational efficiency we must make some compromises. For example, the H-atom hopping activation barrier of 0.17 eV results in a lone H-atom hopping rate constant $7.4 \times 10^{-8}$ times larger than the lone Ni atom hopping rate constant at $T = 250$ K. The H atoms are therefore essentially in a different random thermal distribution each time that a Ni atom is attempting a move. We therefore re-randomize the H-atom positions according to a thermal distribution at each time cycle of our clock. Some of the Ni hopping events are also occurring with rate processes faster than our chosen reference, but in this case re-randomization is not a possibility since the particular configuration of the Ni island is crucial to the rate constant. In this case, we allow such a move to occur at each attempted move with probability of unity, following Eq. (3) above, which is equivalent to slowing down the event to match our reference rate. This could lead to some long-term effects on the growth pattern (to modify Thoreau: one cannot cheat time without injuring eternity). We have, however, tested several cases in which slightly smaller and larger reference rates were used and found no statistically significant differences in the observable for the set of rate processes used in our KMC; so we believe that we are distinguishing the rates of the most relevant events in the growth process. All of the work reported here uses the reference rate constant noted above.

Our KMC simulations, reported below, make use of the complete set of uncorrelated single hopping events as denoted in Fig. 1, which gives rise to 128 rate constants (some of which are equivalent by symmetry). Forward and reverse rate constants for hopping events are both determined and therefore detailed balance is built into the KMC study.

### III. KMC RESULTS

Most of the results reported here involve simulating the deposition of a low monolayer coverage (0.2 ML unless otherwise noted) of Ni onto a Ni(100) surface which has been
FIG. 3. Average Ni-atom island size vs time (in seconds) for various H-atom coverages. The H-atom coverage is zero, 0.01, 0.05, and 0.10 ML for the lowest to highest curves, respectively. The Ni atom coverage is zero at time zero and rises to 0.2 ML at the 100 s mark at a steady deposition rate. The H atoms, when present, are deposited prior to the Ni deposition.

An interesting thing happens with the presence of hydrogen. The upper three curves in Fig. 3 correspond to 0.01, 0.05, and 0.1 ML of H precoverage, respectively, from the second lowest to the uppermost curve. A small amount of hydrogen is able to catalyze the formation of larger islands at short times after the Ni deposition begins, principally by speeding the diffusion of lone Ni atoms across the surface via the Ni-H dimer model noted above. By the end of the Ni deposition time (100 s in Fig. 3) and for equivalent times thereafter, the Ni island size is larger when a small dose of hydrogen is present than in the absence of hydrogen. The hydrogen, recall, is very mobile on the Ni(100) surface and even a small amount of hydrogen is able to catalyze many isolated Ni hopping events. This effect of hydrogen on the growth rate of the Ni islands turns on gradually for H-atom dosages of zero, 0.01, 0.05, and 0.1 ML of hydrogen and the growth pattern emerges. Periodic boundary conditions are used so that if any adatom leaves the surface on one side of the 2D surface slab it will instantaneously reappear on the other side. The simulations use a two-dimensional surface size of 30×30 to 50×50 lattice binding sites, depending upon the hydrogen coverage in the particular calculation performed. In several simulations we have tested various 2D slab sizes to verify that edge effects are not significant (details noted below for one case). The temperature is set at 250 K.

The key observable followed in the simulation is the island size vs time (where our time scale is set by the deposition rate) and lone Ni atoms are counted as an island of size one. We carry out multiple simulations (typically 20–50) of the experiment using different random number seeds to govern the absorption and diffusion events and then average the resulting island size vs time over the simulations. This diminishes the effect of any rare configuration from skewing the results, and also allows us to establish statistical confidence limits on the average island size values which are reported below.

A. Effect of hydrogen on Ni-island morphology

In this study, summarized in Fig. 3, 0.20 ML of Ni is deposited onto a Ni(100) surface which is predoped with dosages of zero, 0.01, 0.05, and 0.1 ML of hydrogen and the growth pattern is examined. For zero dosage of hydrogen, a 30×30 surface lattice size is used, for 0.01 ML of hydrogen, a 40×40 lattice is used, and for 0.05 and 0.1 ML of hydrogen, a 50×50 lattice is used. The deposition rate is set at 0.002 ML/s i.e., the deposition time is 500 s per monolayer of Ni which means that in Fig. 3 the Ni atoms are deposited over the first 100 s. Without the presence of hydrogen on the surface (the lowest curve in Fig. 3), the Ni island size rises rapidly during the deposition time to a value of about 28 Ni adatoms/island, and then drifts slowly upward during the remainder of the simulation to a value of about 40 adatoms/island as lone atoms and smaller islands dissipate and the evaporated Ni’s tend to condense onto larger islands. The inflection in the curve at about 100 s occurs since no new Ni adatoms are being deposited after 100 s.

An important aspect of the catalyst activity for the lone Ni hopping noted in Fig. 2 above, is further apparent in the Fig. 4 where the average number of lone Ni atoms per 900 site (30×30) surface area vs time (in seconds) for various H-atom coverages is shown. The H-atom coverages are zero, 0.01, 0.05, and 0.10 ML for the highest to lowest curves, respectively (the opposite order of Fig. 3). The total Ni atom coverage is zero at time zero and rises to 0.2 ML (180 atoms on the 900-site surface) at the 100 s mark at a steady deposition rate. The H atoms, when present, are deposited prior to the Ni deposition.

The importance of H as a catalyst for the lone Ni hopping noted in Fig. 2 above, is further apparent in the Fig. 4 where the average number of lone Ni atoms on the surface is plotted as a function of time for the various H-atom coverage cases just discussed with respect to Fig. 3. In all cases, the average number of Ni atoms are reported per 900 binding sites (i.e., adjusted uniformly to a 30×30 surface as the standard unit area, even though the nonzero hydrogen coverage
The lower solid curve uses a 40×30 observable for the 0.05 ML H coverage. The top curve in Fig. 4 presents the effects of grid size on our average Ni island size versus time. The 50×50 lattice averaged over 40 configurations. We see from this study that a 30×30 lattice allows for edge effect contamination for times greater than about 100 s, while the 40×40 lattice which gives a curve in good agreement with the 50×50 lattice appears to have eliminated this edge effect contamination for this H-atom and Ni adatom coverage. Note that the lower dashed line in Fig. 5 (the 50×50 case) is the same curve as the 0.05 ML, H coverage curve shown in Fig. 3. Note also that the Monte Carlo standard deviations in Fig. 5 are lower for the 50×50 case due to the higher number of configurations. The Monte Carlo standard deviations associated with the curves in Fig. 3 (in the 100–150 s time region) are on the order of ±5 for the undoped surface, ±8 for the 0.01 ML, and 0.05 ML H coverages, and ±16 for the 0.10 ML H coverage.

B. Sensitivity studies

The antisurfactantlike effect of H, noted in Sec IIIA above, in which the average Ni island size is increased due to the H-atom coverage, was further examined by a set of sensitivity studies of the rate constants controlling various Ni hopping events. We examined the 0.2 ML Ni coverage case by arbitrarily increasing and/or decreasing the rate constants for various hopping processes noted in Table I, but in all cases maintaining detailed balance, to study the sensitivity of the simulation results with respect to the various rate constants. As originally predicted in Ref. 1, we found that the H-assisted hopping of lone Ni atoms across the surface is a predominant factor in showing increased Ni island size. If only the hydrogen assistance of lone Ni hopping is suppressed, the island size evolution for hydrogen precoverage at the 0.05 ML level, becomes effectively indistinguishable from the island size evolution when no hydrogen is present (as shown in Fig. 3, lower curve). Conversely, if all other hydrogen assistance is suppressed except that of accelerating the lone Ni-atom mobility, the island evolution is approximately the same as that given in Fig. 3 for the 0.05 ML H precoverage case. The hydrogen assistance with respect to the condensation/evaporation of the islands is essentially unimportant in the Ni-island evolution at the hydrogen coverage studied. This is consistent with the picture presented in Fig. 4 as well, in which the number of the lone atoms on the surface is clearly linked to the concentration of hydrogen.

The result of this sensitivity study also predicts that if H atoms are deposited after the Ni islands have already formed, no notable effect on the 2D Ni island morphology will be seen. We tested this by depositing 0.2 ML Ni over the first 100 s, and then maintaining the Ni coverage while depositing H atoms at the same rate as Ni deposition) at the 600 s mark, with no observable effect on the Ni island size over the next 600 s time span in agreement with the prediction. (In preliminary studies of Ni island growth including 3-D Ni islands, we find that H can catalyze Ni island flattening, by catalyzing a Ni atom stepping down a plateau particularly along a straight edge.)

C. Effects of Ni-atom deposition rate and Ni coverage

In another set of studies, we have examined small variations of the Ni-atom deposition rate which have, as perhaps expected, only a small effect on the Ni-island size except at short times during which fewer or greater numbers of Ni atoms are present on the surface depending on the deposition rate. In simulations in which the deposition time (for a 1 ML Ni coverage) is varied to 250 s and 1000 s while the total final Ni coverage is fixed at 0.2 ML and the H-atom precoverage is 0.05 ML, we found that the results noted in Fig. 3 (for the 500 s deposition time) are mainly just rescaled, as if one were stretching or condensing the time scales.

Another study examined three Ni deposition coverages (0.1, 0.2, and 0.3 ML) for no H-atom precoverage vs a H-atom precoverage of 0.05 ML. A 30×30 grid was used in this case for the 0.2 and 0.1 Ni ML cases and a 40×40 grid was used for the 0.3 ML case. The results, again, are very similar to those of Fig. 3 so the details are not given here. But in all three cases of Ni coverage, the presence of 0.05 ML hydrogen precoverage resulted in a steady state average island size about 70% larger than for the same three cases of Ni coverage in the absence of hydrogen. This is consistent with the catalytic picture noted above in which only a small amount of hydrogen, due to its rapid mobility, is enough to catalyze a great many Ni hopping events.

IV. SUMMARY

We have calculated activation energies for a set (see Fig. 1) of uncorrelated Ni hopping events representing the Ni
Adatom diffusion upon a Ni(100) substrate, by using classical reaction path dynamics and a realistic potential energy surface. The effect of a nearest neighbor H atom upon the activation energies of the same Ni hopping events has also been calculated in the same manner, but with hydrogen zero point energy included by a semiclassical approximation.

This set of activation energies gives us rate constants for the various hopping events which we have folded into a KMC simulation of the 2D Ni(100) epitaxial growth process. We find that the H atoms modify the Ni island size as a function of time (see Fig. 3), principally by lowering the energy barrier for the lone Ni atom mobility on the open Ni terrace (see Fig. 2). By beginning with a microscopic level activation energy analysis, we find that the H-atom impurity alters the Ni adatom mobility and the macroscopic Ni island morphology is altered during the growth process.

Since there are very low hopping barriers for H atoms on this surface, fast diffusion of H atoms occurs and even a small amount of hydrogen (on the order of 0.01 ML) is found to have observable effects on Ni island size. The effect of H on Ni island size differs over time periods which are long on the deposition time scale and therefore the morphology differences can become frozen in place. The resulting decrease in Ni island density and a corresponding increase in the average Ni island size due to the H impurity shows that, in the 2D simulation, the H is acting as an antisurfactant, gathering the Ni atoms together more effectively than they would tend to gather on their own.

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31C. F. Walters, Z. Y. Zhang, D. M. Zehner, and W. E. Plummer (unpublished); (private communication).