Influence of steps on the interaction between adsorbed hydrogen atoms and a nickel surface

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We have studied the effect of an extended array of defects on the two-dimensional phase behavior of adsorbed hydrogen on a Ni surface using helium atom scattering. Specifically, the interaction of hydrogen with the stepped Ni(977) surface was examined and compared with similar interactions with the flat Ni(111) surface. The phase behavior of hydrogen on Ni(977) is qualitatively the same as that of hydrogen on Ni(111); however, the temperature at which the order–disorder transition occurs is elevated. On the stepped surface, the ordered (2×2)-2H phase exists at a temperature 40 K higher than on the flat surface. This reversible phase transition is second order and is best fit with $T_c = 310$ K and $\beta = 0.12$, indicative of two-dimensional Ising behavior. Stabilization of the ordered phase is attributed to pinning from the step edges. The cross section for diffuse elastic He scattering by adsorbed hydrogen and the temperature-dependent domain size of ordered hydrogen along the step edges are also discussed. © *1999 American Institute of Physics.* [S0021-9606(99)01443-9]

INTRODUCTION

The interaction of hydrogen with metal surfaces is of broad interest. On a fundamental level, because hydrogen is the most theoretically tractable adsorbate, the interaction of hydrogen with a flat metal surface serves as a testbed for our understanding of adsorbate-surface interactions. Understanding the processes involved when hydrogen approaches, and subsequently comes in contact with, a metal surface is crucial to a more basic understanding of gas-surface interactions. On a more applied level, uses for hydrogen-metal systems range from heterogeneous catalysis, where hydrogen can be either a reactant or product molecule, to the synthesis of hydrocarbons and ammonia. Additionally, understanding hydrogen's role in materials science and metallurgy is essential to studying practical phenomena such as hydrogen storage, corrosion, and embrittlement.

One of the goals of surface science is to describe and predict macroscopic material properties based on a careful examination of microscopic interactions. To that end, significant effort has been made to study the interaction of hydrogen with flat metal surfaces. Particular emphasis has been placed on the transition metal nickel because of its technological value. While understanding how hydrogen interacts with a perfect crystal is an important first step, much of the physics and chemistry that takes place on real materials is nucleated at defects.[1–6] Examining the role of defects is, therefore, an essential extension to bridge the gap between ideal and real systems.

The literature contains a plethora of studies done on vicinal surfaces. Attention has been given to clean and adsorbate covered surfaces ranging from open, highly corrugated (311) surfaces to lower step density miscut surfaces. Illustrative

examples for which hydrogen's influence has been explored are Ni(311),[7] (410),[8] (511)[9] and (510);[10,11] Rh(311)[12–17] and (332);[18] Pt(557)[19,20] and (997);[21,22] Cu(410);[8,23] W(310);[24] and Pd(510).[10] The literature details step-induced behavior as drastic as an entirely new phase diagram on Rh(311)[17] and as elementary as preferential adsorption at a step edge.[20]

In this study we examine the interaction of hydrogen with Ni(977) using helium atom scattering. Helium atom beams are nonperturbing and nonpenetrating because they are scattered by the interface's electron density approximately 3 Å from the surface. Also, the interaction with the surface is weak; He-surface well depths are ca. 6 meV with probe energies ranging from 15–60 meV.[25] Most other methods interact strongly with the surface, penetrating many layers into the bulk and occasionally even creating surface defects.

The stepped surface studied in these experiments consists of 8 atom wide (111) terraces separated by monatomic (100) steps (Fig. 1). Differences between the behavior of this system and the H/Ni(111) system can therefore be attributed to step effects. We have examined the adsorption behavior in the low coverage limit, the cross section for diffuse scattering of elastic He atoms by adsorbed hydrogen, step-induced variations on the phase diagram, and the temperature-dependent domain size of ordered hydrogen measured parallel to the step edges. Qualitatively, these properties are similar to those for flat Ni(111); however, significant quantitative variations are observed.

The most notable variation involves a change in the stability of the ordered (2×2)-2H superstructure at a coverage of 0.5 monolayers [1 ML≡1 hydrogen per Ni(111) surface unit cell].[26] As the substrate is heated, this phase undergoes an order–disorder transition. While the transition temperature occurs at 270 K for Ni(111), we have found that the order–disorder transition does not occur until a substrate

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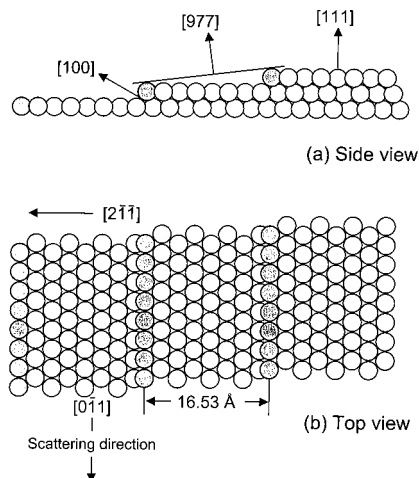[b]Present address: Eltron Research, Inc., 5660 Airport Blvd., Boulder CO 80301.

FIG. 1. A schematic of the Ni(977) surface as viewed for the side (a) and from above (b). The surface consists of (111) terraces which are eight atoms wide and separated by single atom high steps. The scattering plane and several high symmetry directions are indicated.
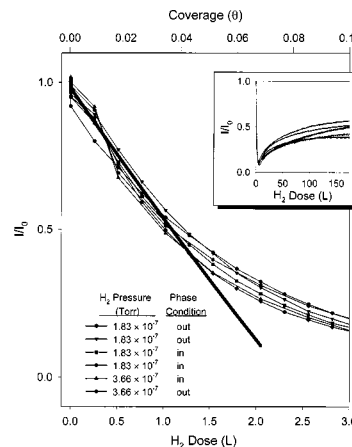

FIG. 2. Helium specular reflectivity as a function of hydrogen exposure. The surface temperature is 150 K, and the beam energy is 24.1 meV. The dose condition and phase of the beam (with respect to adjacent terraces) are indicated for each data set. In-phase scattering corresponds to $\theta_i = 24.55°$ while for out-of-phase scattering $\theta_i = 37.26°$. The straight bold line indicates the slope of the initial signal suppression used to calculate a scattering cross section for the helium beam and the hydrogen overlayer. Higher doses result in a partial recovery of the specular signal (inset).

temperature of 310 K on Ni(977), indicating that steps stabilize this ordered structure.

EXPERIMENT

These experiments were carried out in a high momentum- and energy-resolution helium atom scattering apparatus. This instrument has been described in detail elsewhere,[27,28] and will only be summarized here. It consists of a supersonic helium beam source, an UHV scattering chamber equipped with appropriate surface characterization tools, and a rotating, long flight path (crystal to ionizer distance of 1.005 m) quadrupole mass spectrometer based detector. The angular collimation yielded a resolution of 0.22°. The Ni(977) crystal used in these studies was cleaned by repeated cycles of sputtering with 1 keV Ne$^+$ ions followed by annealing above 1000 K until C and S levels were below our Auger detection limit. A sharp LEED pattern with splitting of the (111) spots (characteristic of the stepped surface) confirmed surface crystallinity. For these experiments, the scattering plane was oriented parallel to the step edges (see Fig. 1). Note that because the sample is a stepped crystal, the scattering kinematics can be chosen such that the incident wave vector is either in-phase (Bragg scattering) or out-of-phase (anti-Bragg scattering) with respect to the terraces.[5]

INITIAL HYDROGEN UPTAKE

Helium scattering is a powerful technique for probing the initial uptake of hydrogen because it is very sensitive to the presence and concentration of adsorbates on metal surfaces.[29] Poelsema *et al.* have shown that by monitoring adsorption isotherms, it is possible to measure the cross section for diffuse scattering.[30] First, a calibration for the coverage must be established. For many hydrogen on metal systems, including H/Ni(111), a linear relationship between exposure and the quantity $\theta/(1-\theta)$, where θ is hydrogen coverage, has been found to be valid[31,32] because hydrogen adsorbs with second order kinetics. The relation

$$\frac{\theta}{1-\theta} = 0.036 \times \text{Exposure}(L) \qquad (1)$$

is obtained for our system; this is based on the observation that maximum order of the (2×2) hydrogen superstructure, which corresponds to a coverage of 0.5 ML,[26] occurs at a dose of 27.4 L. Calibration based on these data yields a sticking coefficient of 0.04, comparable to the value of 0.05 reported for hydrogen adsorbing to clean Ni(111).[33]

The specular intensity of our He atom beam, normalized to the signal level scattered from the clean surface, is plotted as function of hydrogen exposure in Fig. 2. These data were taken with a dosing pressure $P_{H_2} = 1.83 \times 10^{-7}$ torr, $T_{xtal} = 150$ K, $T_{beam} = 112$ K (or 19.1 meV), and with incident angles of $\theta_i = 37.26°$ and $\theta_i = 24.55°$ corresponding to out-of-phase and in-phase Bragg kinematics, respectively. The data are reproducible and agree with data (not shown) taken at a variety of different substrate temperatures, dosing pressures, and kinematic conditions. Initial suppression of the specular signal is caused by the large elastic cross section for H/He diffuse scattering. There is moderate recovery of the specular signal as the coverage increases (Fig. 2 inset), which occurs due to the formation of the ordered (2×2)-2H overlayer structure. A similar recovery of signal has been seen in other systems including H/Pt(111)[34] and H/Rh(111).[35]

The observed suppression of the specularly reflected helium signal is related to the cross section for diffuse scattering, σ. From classical arguments, there is a linear relation for elastic scattering of waves from a surface with random impurities:[30]

$$\frac{I}{I_0} = 1 - \sigma \times \frac{\theta}{A}. \qquad (2)$$

Here, I is the specular signal, I_0 is the signal with no hydrogen present, A is the surface unit cell area (5.365 Å^2), and θ
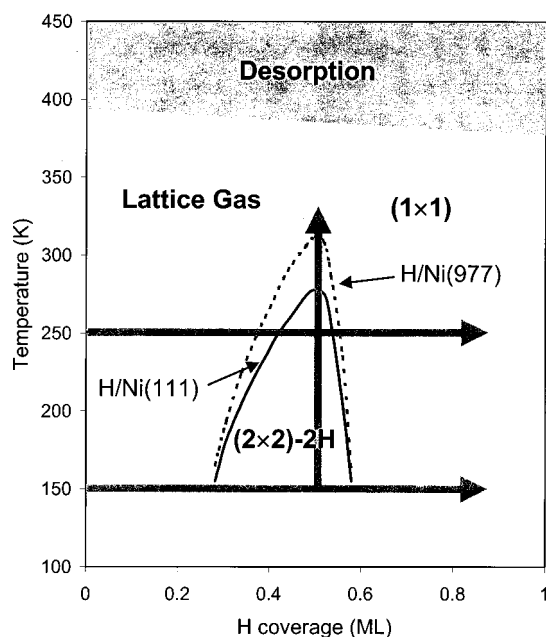
FIG. 3. Coverage-temperature phase diagram. The solid line is for H/Ni(111) as reported by Christmann *et al.* (Ref. 26). The three arrows represent the cuts through phase space studied in this experiment and reveal a qualitative similarity in shape for H/Ni(977) depicted as a dashed curve.

is the coverage in ML. By using the dose-coverage relationship calibrated in Eq. (1), we fit our data to Eq. (2) (the dark solid line shown in Fig. 2) and obtain a cross section for diffuse scattering of $\sigma = 2.38$ Å$^2 \pm 0.03$ Å^2. While this value is noticeably smaller than the gas phase value of ~ 50 Å^2,[36] it is still large enough to induce significant diffuse scattering at low coverage and Bragg scattering at ordered, higher coverage. Poelsema *et al.*[30] measured a similar value of 5.32 Å^2 for helium scattered from H/Pt(997). While not directly comparable to H/Ni(977), the qualitative similarity indicates analogous perturbation of the surface electronic corrugation.

PHASE DIAGRAM

Phase diagrams are central to experiments involving adsorbates, and although the hydrogen on Ni(111) phase diagram is well understood (Fig. 3), it cannot be assumed that the phase behavior will be identical on Ni(977). For example, the H/Rh(311) phase diagram contains a wealth of phases that do not exist on the respective flat surface.[17]

In order to verify the qualitative phase similarity between H/Ni(111) and H/Ni(977) and to elucidate the effect of steps on the nature of this transition, three cuts through the coverage-temperature parameter space were studied (shown as arrows in Fig. 3), two are a function of dose and the third is a function of sample temperature. The H/Ni(111) system consists of three distinct phases.[26] At the lowest coverages, hydrogen behaves as a lattice gas, i.e., the hydrogen atoms are distributed randomly on the surface. As coverage is increased a (2×2) symmetry emerges. In this ordered phase, hydrogen atoms occupy both fcc and hcp sites in a graphitic structure with two hydrogen atoms per surface unit cell at 0.5
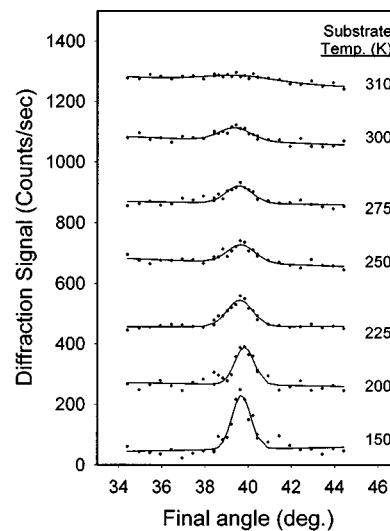
(a)
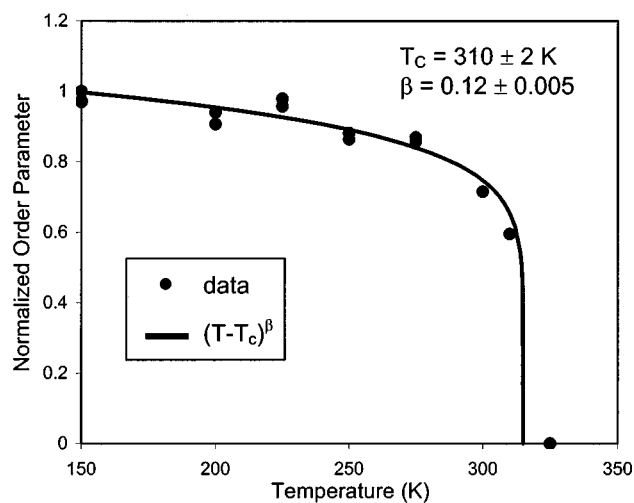
(b)

FIG. 4. (a) Representative data set showing the dependence on crystal temperature of the half-order diffraction peak area (H$_2$ dose=27.4 L). The initial scattering conditions were $\theta_i = 26.34°$ and $E_i = 65.7$ meV. (b) Order parameter, normalized for Debye–Waller effects, as a function of substrate temperature. The solid dots are the data and the line represents a second-order phase transition fit with $T_c = 310$ K and $\beta = 0.12$.

ML coverage. As adsorbate coverage or surface temperature is increased further, the hydrogen superstructure adopts the symmetry of the substrate.

To monitor the change in order across the phase diagram, we measured the evolution of the half order (2×2)-2H superstructure peak that occurs at 2.52 Å^{-1} in the $[01\bar{1}]$ direction. For all three cuts, an incident angle of $\theta_i = 26.34°$ and an incident energy of $E_i = 65.7$ meV were used. At each scattering condition the specular peak was also measured for normalization purposes including Debye–Waller corrections. The results bear qualitative resemblance to the H/Ni(111) phase diagram (Fig. 3).

The top panel of Fig. 4 shows the helium diffraction spectra of the half order peak as a function of substrate temperature. The lower panel of this figure has the corresponding peak area vs dose corrected for Debye–Waller effects.

As the temperature is increased, the superstructure peak disappears, indicating either a phase transition to a disordered phase or desorption of the hydrogen. If the sample is recooled, the peak returns in full indicating that this is indeed a reversible order–disorder phase transition.

The solid line through the data is a fit assuming a second order phase transition, as occurs on the H/Ni(111) system.[37] From this fit we derive a transition temperature of $T_C = 310 \pm 2$ K and critical exponent of $\beta = 0.12 \pm 0.005$. The critical exponent is comparable to the values of $\beta = 0.11–0.15$ (Ref. 37) found for hydrogen on the Ni(111) surface, however this transition temperature is 40 K higher than that found on the flat surface.[26] This increase in the order–disorder transition is indicative of an energetic shift in the adatom potential wells. Step effects are the most likely source for these energetic changes. We conjecture that the increased coordination available at the step edge pins hydrogen atoms. These pinned atoms, in turn, affect the registry of atoms further from the step. In this way, the effect is propagated out onto the terrace. If pinning occurs at both top and bottom step edges, confinement effects may also play a role.

If one treats the H/Ni(977) system within the two-dimensional Ising model, as suggested by our experimental value of the critical exponent (theoretical $\theta_{2D,Ising} = 0.125$), then a hydrogen–hydrogen interaction energy, ω_2, can be approximated by the analytical expression:[38]

$$\omega_2 = 1.76 \cdot k_B T_C \qquad (3)$$

giving a value of 0.047 eV for $T_C = 310$ K. A more rigorous Renormalization-group theory calculation[39] results in $\omega_2 = 0.076$ eV. Again, the repulsion is probably stronger adjacent to steps due to pinning effects and weaker in the middle of terraces, so these values represent an *effective* adatom–adatom interaction averaged over the entire overlayer. Using the critical temperature of 270 K, as is observed on Ni(111), these values are 0.040 eV and 0.066 eV, respectively. Because the substrate mediated H–H repulsion is strengthened by the steps on the order 7 to 10 meV, additional thermal energy is required to disorder the graphitic (2×2)-2H.

It is common for adsorbates to stick preferentially to steps or defects due to either an increase in coordination or an altered electronic structure. For instance, it has been observed that Xe attaches to isolated step edges of Pt(111),[40,41] preliminary reports show that oxygen nucleates at the step edges of Ni (Ref. 42) and it has been well documented that hydrogen prefers step sites.[10,22,23,43–47] On Ni(977), it has been found that the phonon modes localized at the steps[48] disappear in the presence of hydrogen.[49] This indicates either a modification of the bonding at the step, a screening of the step phonons by the adsorbed hydrogen, or an increase in kink mobility leading to disordered steps. From thermal desorption spectroscopy (TDS), we also have an indication that hydrogen preferentially bonds to the steps on Ni(977). Upon desorbing hydrogen from our surface, we observe two broad but distinct desorption peaks. The physical geometry of our experimental apparatus precludes any quantitative analysis of the TDS data, but the existence of two peaks means multiple desorption sites, most likely representing step and terrace population.

Having evidence that hydrogen prefers to stick to Ni steps, the question of step effects on the stabilization of the ordered (2×2)-2H remains. In the literature, there is corroboration that the steps are responsible for the increase in the order–disorder transition temperature. Pfnür *et al.* showed that increasing the number of defects affects the order–disorder transition temperature.[37] During studies of the H/Ni(111) system, they discovered that defects such as oxygen or deuterium atoms increased the transition temperature by as much as 10 K. Additionally, van de Walle *et al.*[50] imaged the H/Ni(111) system with an STM and observed small domains of the (2×2)-2H structure at step edges persisting at room temperature. They attributed the existence of the ordered phase at 300 K to a high partial pressure of hydrogen. However, given our observations, it is likely that they were able to image the superstructure at this temperature because of the altered phase behavior near the step edge. The results of these studies, coupled with our observations, indicate that the steps play a significant role in stabilizing the (2×2)-2H overlayer.

DOMAIN SIZE

In an attempt to further elucidate the role of steps in stabilizing the (2×2)-2H structure, we analyzed the ordered domain size as a function of substrate temperature. To first approximation, the helium beam is scattered coherently within domains of length l_c. Coherence length, i.e., island size, of the (2×2)-2H structure, can be extracted from the diffraction peak widths. Following Lapujoulade *et al.*,[51] after deconvoluting the instrument broadening, the observed half-order peak widths, $\Delta\theta_f$, provide a measure of the domain size:

$$\Delta\theta_f = \frac{5.564}{l_c |\vec{k}| \cos\theta_i}, \qquad (4)$$

where $|\vec{k}|$ is the magnitude of the incident wavevector. From this analysis comes the trend of a smooth decrease in island size with surface temperature (Fig. 5). As the overlayer order collapses near the critical temperature, the domain size is comparable to the mean terrace width (16.5 Å). This size similarity may be coincidental, or it might suggest that the terrace size is a key parameter in determining the transition temperature. STM experiments with this system are under development to further study this effect.

SUMMARY

We have probed the nature of the interaction between hydrogen and a stepped Ni(977) surface in order to isolate the effect of a known type of defect. Our results demonstrate that the qualitative behavior is the same as with a flat Ni(111) surface: the cross section for diffuse scattering of elastic He is roughly the same as seen on other systems; the phase diagram has the same regimes with an ordered (2×2)-2H occurring at intermediate coverages and temperatures; and the domain size of the ordered patches decreases smoothly with substrate temperature. Quantitatively, however, the order–disorder transition occurs 40 K higher than
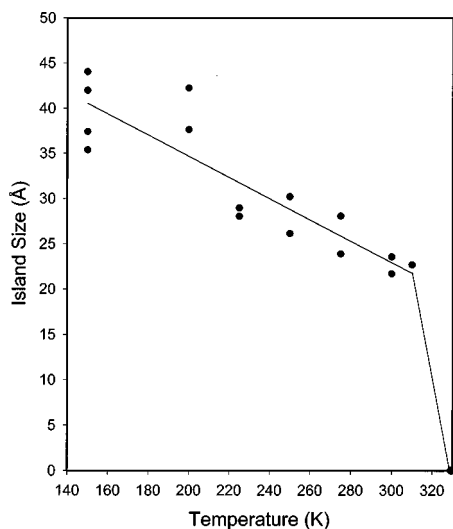
FIG. 5. A plot of the ordered (2×2)-2H island size at $\theta=0.5$ ML (H_2 dose=27.4 L) as a function of substrate temperature. Island size was determined from the fractional order peak widths shown in Fig. 4. The straight lines through the points serve to guide the eye.

on the flat Ni surface, representing an *effective* 7–10 meV increase in the substrate mediated hydrogen–hydrogen interaction. We attribute this effect to pinning of the ordered (2×2)-2H structure by step edges.

ACKNOWLEDGMENTS

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