

## Interaction of hydrogen with the Ag(111) surface

Geunseop Lee\*

*Department of Physics, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6396*

E. W. Plummer

*Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996  
and Solid State Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee 37831-6057*

(Received 9 August 1994; revised manuscript received 22 November 1994)

The interaction of atomic hydrogen with the Ag(111) surface was studied with low-energy electron diffraction (LEED), high-resolution electron-energy-loss spectroscopy (HREELS), thermal desorption spectroscopy, and work function measurement. The adsorption of atomic hydrogen at 100 K induces a reconstruction of the Ag(111) surface, as indicated by an intense  $(2 \times 2)$  (at 0.25–0.5 ML) and a mixture of  $(2 \times 2)$  and  $(3 \times 3)$  (at 0.5–0.6 ML) superstructures in LEED. The H-induced work function change ( $\Delta\Phi_{\max} = +0.32$  eV) is uncharacteristically large for the close-packed surface and indicative of the surface structural change. HREELS data show that H occupies a single site of high symmetry for all coverage. The observation of two vibrational modes (one dipole active at 106 meV and the other not dipole active at 87 meV at  $\sim 0.5$  ML) allows an assignment of bonding at a threefold hollow site. Both modes show measurable shifts in energy with increasing coverage, indicating an appreciable H-H lateral interaction. Atomic hydrogen adsorbed on Ag(111) recombines and desorbs at a temperature  $\sim 180$  K, appreciably lower than those for Cu and transition metals. The properties of H adsorption on Ag will be compared to Cu and to transition metals.

### I. INTRODUCTION

The interaction of hydrogen with metal surfaces has been extensively investigated experimentally and theoretically,<sup>1</sup> because in principle, hydrogen is the simplest, theoretically tractable adsorbate and the phenomena embodied in the interaction of hydrogen with a metal surface encompass most of the basic concepts in surface science. However, the H-induced structural and electronic properties are not simple but show diverse phenomena that depend on the specific metal, crystallographic face, coverage, or substrate temperature, etc. These phenomena include the localized and delocalized motion of H,<sup>2–4</sup> the order and disorder of the H-overlayer phase,<sup>5,6</sup> the H-induced reconstruction or relaxation of the substrate,<sup>7,8</sup> and the absorption into the bulk or subsurface,<sup>9,10</sup> as well as the surface adsorption. The majority of these investigations have concerned the interaction of hydrogen with transition metals, where molecular hydrogen at room temperature dissociatively chemisorbs.

Noble and simple metals present a different perspective, since dissociation of H<sub>2</sub> does not occur at room temperature. As an H<sub>2</sub> molecule approaches a metal surface, its bonding orbital feels a Pauli repulsion from the tails of the *s* electrons in the metal. If there exist empty *d* states (*d* holes) at the Fermi energy, an *s* electron can be promoted to the *d* band reducing the Pauli repulsion, and thereby reducing the energy barrier. As expected, transition metals readily dissociate and adsorb hydrogen, while for noble or simple metals, dissociative adsorption of hydrogen is an activated process.<sup>11</sup>

Noble metals are similar to simple metals with respect to the activated adsorption. On the other hand, once hydrogen is adsorbed on the surface, one might expect that they should be similar in chemisorption properties to transition metals rather than to simple metals, because of the similarity in the electronic structure (e.g., existence of *d* electrons).<sup>12,13</sup>

In this paper, we report the results of an experimental study of the adsorption of hydrogen on the Ag(111) surface using low-energy electron diffraction (LEED), high-resolution electron-energy-loss spectroscopy (HREELS), and work function measurements that will be correlated with the absolute H coverage.<sup>14</sup> We have found the following: (i) The adsorption of atomic hydrogen on the Ag(111) surface at a temperature of 100 K induces a reconstruction of the substrate; a  $(2 \times 2)$  in the range of 0.25–0.5 ML and mixed phases of  $(2 \times 2)$  and  $(3 \times 3)$  above 0.5 ML, where the  $(3 \times 3)$  phase is induced by the LEED electron beam; (ii) H occupies a single binding site of high symmetry for all coverages of H and induces a monotonic increase of the work function. The observation of only two modes in HREEL spectra (specular and nonspecular) suggests that H bonds at a threefold hollow site for all phases; (iii) the 6–8 meV coverage-dependent shifts of the loss energies in HREEL spectra indicate an appreciable H-H lateral interaction on this surface; (iv) the desorption of H<sub>2</sub> from Ag(111) occurs at  $\sim 180$  K, appreciably lower than those for Cu and transition metals.

The organization of this paper is as follows. In Sec. II, the experimental details are described. In Sec. III, the results of LEED, work function measurement, and HREELS studies are presented with their interpretations.

Section IV reviews all experimental observations in our study on H/Ag(111) and discusses the comparison with H on transition metals and copper. The final summary and conclusion are given at the end.

## II. EXPERIMENTAL DETAILS

The experiment was performed in an ultrahigh vacuum environment with a base pressure of  $\sim 1 \times 10^{-10}$  Torr. The Ag(111) crystal was cut to within  $\pm 0.5^\circ$  from a single crystal silver rod and mechanically polished before it was introduced into the experimental chamber. The sample was cleaned by repeated cycles of sputtering with 0.5–1-keV  $\text{Ne}^+$  ions and subsequent annealing to  $\sim 720$  K, resulting in a sharp  $(1 \times 1)$  LEED pattern. No evidence of contamination was detected either in Auger electron spectroscopy or in HREEL spectra.

Dosing of either molecular or atomic hydrogen (or deuterium) was performed with the sample held at  $\sim 100$  K. Atomic hydrogen was produced by passing  $\text{H}_2$  through a molybdenum tube ( $\sim 7$  mm in diameter) with a hot coaxial tungsten filament, located 2 cm from the crystal. The coverage of adsorbed H for each exposure was obtained by calibrating the integrated area under the thermal desorption peak to that of the saturation. The absolute coverage of D adsorbed on the Ag(111) surface has been measured using the nuclear reaction analysis (NRA) technique and reported elsewhere.<sup>14</sup> The comparison of the D coverage determined from the thermal desorption spectra (TDS) signal area as a function of exposure with the absolute coverage from NRA is reproduced in Fig. 1. Saturation coverage occurs at a coverage of  $1.38 \times 10^{15}$  atoms/cm<sup>2</sup>, which corresponds to  $0.6 \pm 0.1$  ML [1 ML means one H (or D) atom per one Ag surface atom]. Throughout this paper, the amount of the adsorbed H will be presented in terms of the absolute coverage in ML. The work function changes ( $\Delta\Phi$ ) following the hydrogen exposure were measured using the monoenergetic beam of electrons through the EELS monochromator and

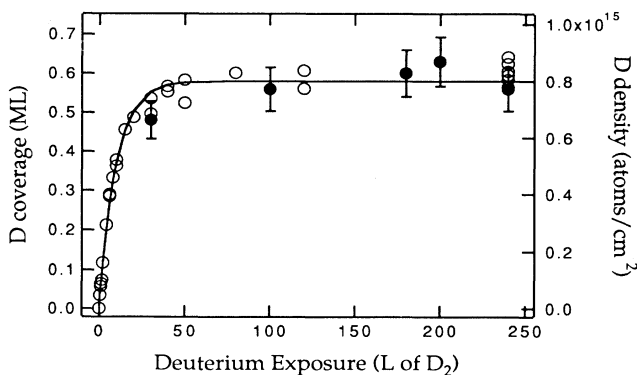


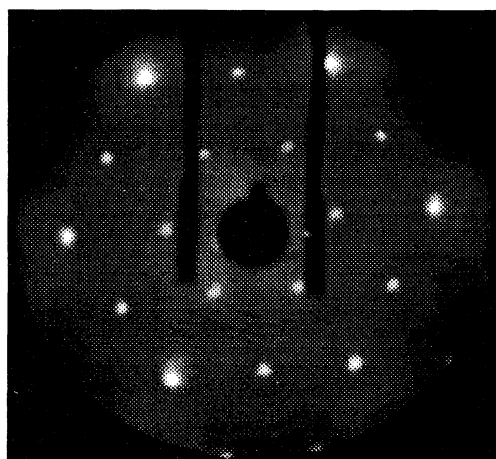
FIG. 1. Atomic deuterium coverage as a function of  $\text{D}_2$  exposure (the line is a guide to eyes). Solid circles ( $\bullet$ ) are from the coverage measurement using NRA (Ref. 14) and open circles ( $\circ$ ) are from the integrated  $\text{D}_2$  TDS signal calibrated to the absolute coverage.

recording the cutoff in the current to the sample as a function of bias voltage. HREEL spectra were taken with various incident electron beam energies ( $E_p = 1.5, 4, 10,$  and  $30$  eV), with both the specular and off-specular geometries where the scattering angle was varied with a fixed incident angle ( $\theta_{\text{in}} = 60^\circ$ ). A typical energy resolution of  $\sim 6$  meV of elastic peak in the specular direction was maintained. Thermal desorption spectra of  $\text{H}_2/\text{D}_2$  were obtained with a quadrupole mass spectrometer using a linear heating rate of 1 K/s and used in the calibration of H coverage. The sample was heated resistively and the temperature was measured using a chromel-alumel thermocouple wire. Intensities of diffraction spots were measured with a computer video system from the reverse viewing LEED system. Intensities of equivalent beam spots were recorded as a function of the incident beam energy with the sample at 100 K.

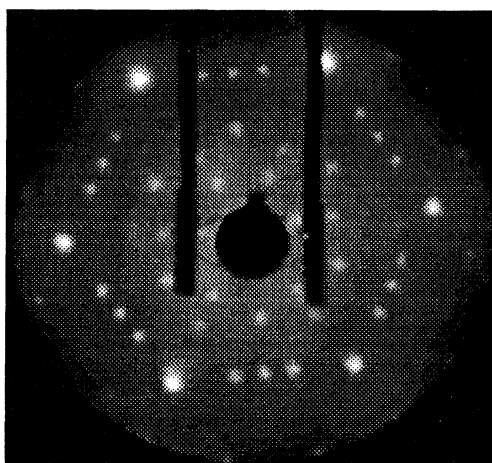
## III. RESULTS AND INTERPRETATION

### A. LEED

Exposing the clean Ag(111) surface ( $T_s \sim 100$  K) to room temperature  $\text{H}_2$  resulted in no observable changes in the surface as determined by LEED, HREELS, TDS, and work function ( $\Delta\Phi$ ) measurement. This indicates the presence of an activation barrier for the chemisorption of  $\text{H}_2$  and is consistent with both the theoretical prediction<sup>15</sup> and previous observations on Ag.<sup>16,17</sup> Atomic hydrogen readily bonded to the Ag(111) surface at a substrate temperature of 100 K, recombined and desorbed as  $\text{H}_2$  from the surface at a temperature  $\sim 180$  K.<sup>14,16</sup> The adsorption of H (or D) on the Ag(111) surface at 100 K was saturated with a coverage  $\Theta_{\text{sat}} = 0.60 \pm 0.1$  ML. Atomic hydrogen induced the superstructures seen by LEED, as shown in Fig. 2. Above  $\sim 0.25$  ML of H (or D), a  $(2 \times 2)$  superstructure began to appear and developed sharp and intense fractional order spots near 0.5 ML [Fig. 2(a)]. At higher exposure, up to saturation, the  $(2 \times 2)$  pattern was initially seen but converted into a mixed  $(2 \times 2) + (3 \times 3)$  phase during the LEED observation [Fig. 2(b)]. During the LEED observation, the intensities of  $(3 \times 3)$  spots increased in time, while those of  $(2 \times 2)$  spots decreased. The conversion of the LEED pattern from a  $(2 \times 2)$  into a mixture of  $(2 \times 2)$  and  $(3 \times 3)$  by the electron beam was confirmed by moving the beam to different parts of the sample. Therefore, it is concluded that the development of additional  $(3 \times 3)$  spots is induced by the LEED electron beam. This conversion was observed only for coverage  $\gtrsim 0.5$  ML. Upon heating, the  $(2 \times 2)$  spots became weak and diffuse, disappearing at  $\sim 140$  K, whereas the  $(3 \times 3)$  spots remained unchanged or increased in intensity up to 140 K, leaving a  $(3 \times 3)$  LEED pattern in the temperature range of 140–150 K before hydrogen desorbed at  $\sim 180$  K [Fig. 2(c)]. When the sample was annealed below the desorption temperature and recooled, the  $(2 \times 2)$  spots were observed to reappear. Therefore, there exists an order-disorder tran-



(a)



(b)



(c)

FIG. 2. LEED patterns of superstructures observed for H/Ag(111) with a beam energy of 57 eV. (a)  $(2 \times 2)$  at 0.5-ML hydrogen at 100 K, (b)  $(2 \times 2) + (3 \times 3)$  at saturation ( $\sim 0.6$  ML) at 100 K, and (c)  $(3 \times 3)$  [with very weak  $(2 \times 2)$ ] after annealing at 140 K, starting from (b).

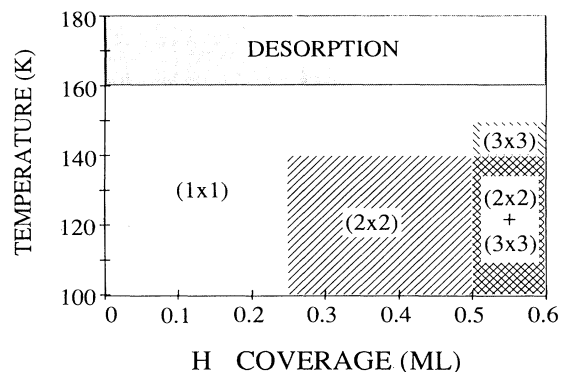


FIG. 3. Phase diagram of superstructures observed in LEED pattern for hydrogen on Ag(111). The  $(3 \times 3)$  phase at above 0.5-ML coverage is induced by  $e$  beam during LEED observation. See the text.

sition of the  $(2 \times 2)$  superstructure in the LEED pattern before hydrogen desorbs from the surface. Figure 3 shows a phase diagram, summarizing the superstructures observed in the LEED pattern at various coverages and temperatures. Remember, the LEED beam induces  $(3 \times 3)$ , so Fig. 3 does not represent accurately the phase diagram in the absence of an electron beam.

Similar superstructures in LEED have been reported for H/Cu(111).<sup>18</sup> The adsorption of H on the Cu(111) surface induces a  $(2 \times 2)$  pattern to form at low coverage and transform into a  $(3 \times 3)$  pattern at saturation. In the absence of the absolute coverage measurement, the H coverages for  $(2 \times 2)$ -H/Cu(111) and  $(3 \times 3)$ -H/Cu(111) were assumed to be 0.5 ML and 0.7 ML, respectively, based on the thermal desorption spectra.<sup>19</sup> It was also reported that the  $(3 \times 3)$  LEED pattern of H/Cu(111) seen at saturation was converted by the  $e$  beam into a mixture of a  $(2 \times 2)$  and a  $(3 \times 3)$  patterns. Although the observed LEED superstructures and  $e$ -beam effects on H/Ag(111) and H/Cu(111) are similar, there is a detailed difference. While the pure  $(3 \times 3)$  phase was observed as a high-coverage phase for H/Cu(111), the  $(3 \times 3)$  LEED spots for H/Ag(111) only appeared from the  $(2 \times 2)$  phase in the presence of an  $e$  beam, making a mixed phase of  $(2 \times 2)$  and  $(3 \times 3)$ . The pure  $(3 \times 3)$  LEED pattern was not observed for H/Ag(111) throughout the entire coverage range unless the  $(2 \times 2) + (3 \times 3)$  pattern was heated to 140 K, above which the beam spots of the  $(2 \times 2)$  pattern became weak and finally disappeared. The conversion of the LEED pattern of H/Cu(111) [ $(3 \times 3) \rightarrow (2 \times 2) + (3 \times 3)$ ] by an  $e$  beam can be easily understood as the effect of electron-stimulated desorption. On the other hand, for the H/Ag(111) system, the appearance of the  $(3 \times 3)$  spots from an original  $(2 \times 2)$  LEED pattern above 0.5 ML seems to be activated by the electron beam. The  $e$  beam induced conversion for H/Ag(111) is also accelerated by a thermal heating. At present, the nature of a  $(3 \times 3)$  phase of H/Ag(111) is not well characterized. A detailed study should be performed to disentangle the  $e$ -beam effect on the H/Ag(111) system. Our data presentation and the related discussion will be restricted to the coverage below 0.5 ML, where no change is induced by the LEED  $e$  beam.

Ag(111) and Cu(111) are not the only fcc(111) surfaces

to show an H-induced  $(2 \times 2)$  superstructure. A  $(2 \times 2)$  LEED pattern was also observed on the Ni(111) surface upon the adsorption of H at low temperature near the coverage of 0.5 ML.<sup>5</sup> When exposed to more hydrogen, the LEED pattern of H/Ni(111) converts continuously into a  $(1 \times 1)$  pattern reaching a saturation at 1 ML. H-induced superstructures at intermediate coverage have also been observed for the H/Pd(111) system,<sup>10</sup> showing  $(\sqrt{3} \times \sqrt{3})\text{-}R30^\circ$  ( $-1\text{H}$  and  $-2\text{H}$ ) patterns at  $1/3$  and  $2/3$  ML, respectively, followed by the transformation into  $(1 \times 1)$  at saturation ( $\Theta_{\text{sat}} = 1$  ML) ( $T \lesssim 80$  K). In general, a  $(1 \times 1)$  structure is observed at the saturation of H on fcc(111) surface. Therefore, the persistence of the superstructure(s) other than the  $(1 \times 1)$  LEED pattern up to the saturation is unique for H/Ag(111) and H/Cu(111), as is a saturation below 1 ML. The comparison with transition metals will be discussed in Sec. IV.

Due to its small atomic number, hydrogen has a small cross section for  $e^-$  scattering. The "extra" contribution in the LEED intensity from an array of hydrogen atoms, is much smaller (typically a few percent) than that from a transition or noble metal substrate. This fact has been used to obtain the agreement between experiments and LEED calculations ignoring the hydrogen atoms for some H-covered surfaces.<sup>20-22</sup> In the case of H/Ni(111), the weak intensity of the fractional order spots in a  $(2 \times 2)$  LEED pattern was originally regarded as being due to the scattering from the  $(2 \times 2)$  H overlayer, without considering substrate reconstruction. However, the observation of the corrugation at the centers of the H-honeycomb arrangement in helium scattering from  $(2 \times 2)\text{-H/Ni(111)}$  indicated the substrate reconstruction.<sup>23</sup> Recently, a detailed LEED  $I$ - $V$  analysis<sup>8</sup> for the half-integer spots of this system, allowing for both the relaxation and buckling in the top substrate layer, has reported that the Ni(111) surface is indeed reconstructed by the adsorption of H. The surface reconstruction is in the form of buckling with the three H-coordinated Ni atoms in the unit mesh lifted ( $0.04 \text{ \AA}$ ) relative to the uncoordinated atoms. Therefore, the large part of the experimentally observed LEED intensity ( $\sim 3\%$ ) of fractional spots of  $(2 \times 2)\text{-H/Ni(111)}$  has been concluded to arise from the reconstructed Ni substrate, not only from the H overlayer.

In the case of  $(2 \times 2)\text{-H/Ag(111)}$ , the relative intensities of the extra diffraction spots are much more intense than that of  $(2 \times 2)\text{-H/Ni(111)}$ . In order to make a quantitative comparison, intensities of both integer and half-integer spots were measured using the video-LEED system. The intensities of fractional order beams<sup>24</sup> ( $\langle I_{\text{half}}/I_{\text{integer}} \rangle_{\text{ave}} \sim 10\%$ ) are much larger than those from the  $(2 \times 2)\text{-H/Ni(111)}$  system ( $< 3\%$ ). The intensity is comparable with fractional beam intensities from H/fcc(110) systems where weak substrate reconstruction has been proposed.<sup>25</sup> Therefore, the Ag(111) surface is reconstructed upon H adsorption. As proposed for the  $(2 \times 2)\text{-H/Ni(111)}$  system, the simplest possible type of reconstruction would be a buckling of the top layer induced by the H adsorption. Additional lateral rearrangement of buckled atoms is also possible.

The fact that H is a weak scatterer makes it more difficult to create a geometrical picture of the surface,

even knowing the LEED pattern and the absolute coverage. It is always possible that the H overlayer is not ordered. Here, we propose a model for the structure assuming that the H atoms are ordered at low temperature and high coverage, forming the long-range order of the H-induced reconstruction. At 0.5 ML, the  $(2 \times 2)$  LEED pattern is fully developed, suggesting two possibilities for the H registry: either one atom per  $(2 \times 1)$  unit cell existing in domains of three orientations rotated by  $60^\circ$  from each other [Figs. 4(a),(b)] or two atoms per  $(2 \times 2)$  unit cell [like an ordered graphitic structure in Fig. 4(c)]. A graphitic structure has been proposed and confirmed as an H registry for  $(2 \times 2)\text{-H/Ni(111)}$  at low temperature.<sup>5</sup> For  $(2 \times 2)\text{-H/Ni(111)}$  with  $\Theta = 0.5$  ML, which shows the same superstructure at the same coverage as H/Ag(111), the registry of the adsorbed H has been investigated by the comparison of the experimental LEED  $I$ - $V$  data of fractional order spot intensity with the calculations for different models of the adsorption structures. The graphitic geometry of hydrogen atoms adsorbed at the threefold hollow site was found to show the best agreement between experiment and theory. With that geometry, a  $(2 \times 2)$  unit cell consists of two hydrogen atoms, one at a fcc site and the other at a hcp site. This adsorption geometry at 0.5 ML has also been confirmed by the transmission channeling experiment where the deuterium was found to adsorb in both types of threefold sites with equal population at equal height above the surface.<sup>26</sup> The formation of a  $(2 \times 2)$  LEED pattern at an H coverage of 0.5 ML on the Ag(111) surface is very similar to that of Ni(111). In addition, the local bonding site is suggested to be the threefold hollow from the analysis of the HREELS data, as will be discussed in the following section. Based on the similarities with  $(2 \times 2)\text{-H/Ni(111)}$

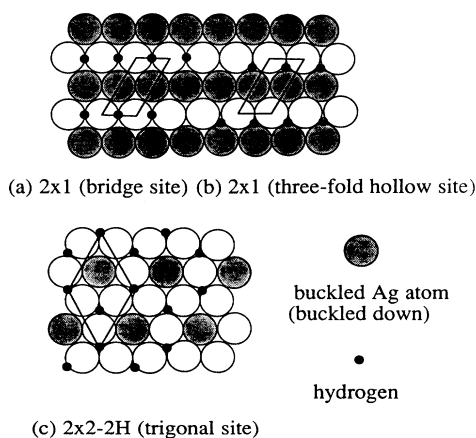


FIG. 4. Structural models suggested to account for the  $(2 \times 2)$  LEED superstructure at 0.5-ML hydrogen in terms of the surface reconstruction. (a) A  $(2 \times 1)$  structure with H at a bridge site, (b) a  $(2 \times 1)$  structure with H at a trigonal site, and (c) a  $(2 \times 2)\text{-}2\text{H}$  structure with H at a trigonal site. Shaded large circles represent Ag atoms that are relatively lower than other Ag atoms (white large circles) on the surface. Hydrogen atoms are represented by small solid circles.

H/Ni(111), we suggest an ordered graphitic structure on the reconstructed surface (buckled surface is most likely) as an adsorption geometry of  $(2 \times 2)$ -H/Ag(111) [Fig. 4(c)].

### B. Work function change

The work function change ( $\Delta\Phi$ ) induced by the adsorption of H on the Ag(111) surface has been measured as a function of coverage and is shown in Fig. 5. The observed work function shows a monotonic increase as the H coverage increases, reaching a maximum value of  $0.32 \pm 0.03$  eV at saturation. The work function change on H/Ag(111) has been reported to decrease upon deuterium adsorption by 0.17 eV at saturation, in the previous study by Zhou *et al.*,<sup>16</sup> in contrast to our finding. The reason for the discrepancy of measured work function change is not clear but it is conjectured that the coadsorption of appreciable amounts of water on the surface may be responsible for the work function decrease in the previous study. It is well established that water adsorption is accompanied by the decrease of work function.<sup>27</sup> In our study, when the sample was overexposed to excessive amounts of H<sub>2</sub> through a doser, work function changes smaller than that of saturation have been observed without changing the H coverage, presumably due to the coadsorption of water.

An increase of the work function upon H adsorption appears to be the rule for H/metal systems with a few exceptions, such as H/Pt(111),<sup>28</sup> H/Fe(110),<sup>29</sup> H/W(110),<sup>30</sup> H/Be(0001),<sup>31</sup> and H/Cu(110) (Ref. 32) where the negative work function change has been reported. The positive work function change induced by the H adsorption may be understood, in a simple way, as being from the formation of a surface dipole in a hydrogen-metal complex. Higher electronegativity of hydrogen compared to metals induces the net flow of elec-

trons from metal to hydrogen. This is the opposite to the case of alkali-metal adsorption on metal surfaces where the decrease of work function is observed. In the zero coverage limit, the effects of other H on each adsorbed H (e.g., depolarization) can be neglected and the initial dipole moment ( $\mu_0$ ) can be deduced from the measured work function change using the simple relation<sup>1</sup>

$$\Delta\Phi = 4\pi\sigma_0\mu_0f, \quad (1)$$

where  $\sigma_0$  is the number of adsorbed H atoms/m<sup>2</sup>,  $f = 1/(4\pi\epsilon_0)$  the conversion factor. The initial dipole moment for H/Ag(111) is determined to be 0.18 D (debye, 1 D =  $3.3 \times 10^{-31}$  C m). This value is exceptionally large compared with the typical values ( $\sim 0.05$  D) obtained for the H/metal systems. H/W(100) is the only example found in the literature where the initial dipole moment ( $\mu_0 = 0.21$  D) is larger than that of H/Ag(111).<sup>33</sup> At high coverage, the work function increase is slower than linear ( $\Delta\Phi \sim \Theta^n$  with  $n < 1$ ). This deviation from linearity is presumably a consequence of the depolarization by a long-range dipole-dipole interaction, or the lateral interaction through the substrate. In some systems, the abrupt change in the slope of the work function change has been observed and attributed to the population of new species, e.g., adsorption at a different site or the change of an ordered phase.<sup>5,31,34</sup> In the case of H/Ag(111), the change in slope is small and varies smoothly up to saturation. Therefore, no abrupt change of adsorption site is expected.

In addition to the large initial dipole moment, the maximum work function change observed for H/Ag(111) is also substantially larger than those of other H-covered close-packed surfaces [fcc(111) and hcp(0001)] of transition metals (typically smaller than 0.2 eV). It is even larger than that observed for the H/Ag(110) system ( $\Delta\Phi_{\max} = +0.22$  eV), whereas the adsorption of H on a more open surface has been observed to induce a larger work function change in most metals. It is tempting to relate the abnormally large work function change and initial dipole moment of the H/Ag(111) system to the surface structural change, i.e., a substrate reconstruction accompanying the adsorption of H. This might be corroborated by the coverage-dependent work function change of the H/Ni(111) system for which a similar H-induced surface reconstruction was reported. The work function change of H/Ni(111) was reported to go through a maximum at a coverage of 0.5 ML, where the  $(2 \times 2)$  surface reconstruction is supposed to be at its maximum. The work function change for the W(100) surface upon H adsorption is also abnormally large ( $\mu_0 = 0.21$  D,  $\Delta\Phi_{\max} = +0.9$  eV) and can possibly be viewed as a consequence of the surface structural change [in this case, the change is from a clean,  $c(2 \times 2)$ -W(100) surface to a  $(1 \times 1)$  bulklike surface by H adsorption<sup>35</sup>]. If a large initial dipole moment and work function change of H/Ag(111) is related to the reconstruction of the surface, the smooth increase of work function may indicate the local nature of the H-induced substrate reconstruction; the substrate is locally reconstructed by the H adsorption at the localized site and becomes ordered above a certain coverage, inducing

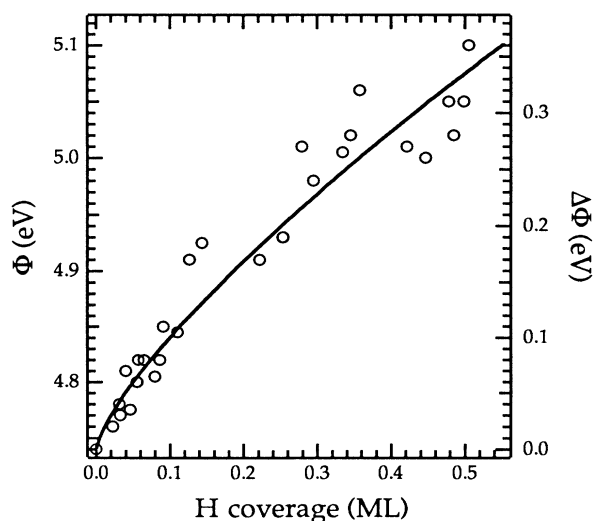


FIG. 5. Work function change induced by adsorption of H on Ag(111) as a function of coverage (the line is a guide for eyes).

the observed LEED superstructures.

In Table I, the initial dipole moments and the maximum work function changes for H-adsorbed surfaces of representative metals are compiled and compared with the work functions of clean surfaces. The sign and the magnitude of  $\Delta\Phi$  seem to be dictated by the work function of a clean surface ( $\Phi_{cl}$ ). It is interesting to notice that the saturated values (i.e., maximum or minimum) of the work function of H-adsorbed surfaces ( $\Phi_H$ ) fall within a narrow range ( $\sim 5.55 \pm 0.2$  eV), regardless of their coverages. Ag surfaces and W(110) seem to be exceptions. The work functions of H adsorbed surfaces ( $\Phi_H$ ) of Ag and of H/W(110) are significantly small compared with those of other metal surfaces. However, since a systematic study of the coverage-dependent work function change for various metals has not been reported, a quantitative prediction of  $\Delta\Phi$  is not possible at present.

### C. Vibrational spectra: HREELS

In Fig. 6, a series of HREEL spectra measured in the specular and off-specular directions are shown as a function of H coverage. In the specular direction, the loss spectrum is dominated by a single peak centered at  $\sim 106$  meV for H with a small shoulder in the low-energy side. On the other hand, when the spectra are taken at  $20^\circ$  off from the specular direction, a second loss peak is seen at

$\sim 87$  meV. These two loss peaks originate from the vibration of the adsorbed H since there is an approximate isotopic shift (to 76 meV and 63 meV, respectively) of these peaks in energy (ratio  $\sim 1/\sqrt{2}$ ) when H is replaced with D. As shown in Fig. 7(b), both the  $\sim 87$ - and 106-meV losses grow in intensity with H coverage but their intensity ratio remains approximately constant, independent of coverage. This indicates that these losses can be assigned to two vibrational modes, corresponding to H occupying a single bonding site on the surface. No significant change has been observed by annealing and re-cooling, except for the slight changes of the peak energies and intensities caused by partial desorption of adsorbed H. Thus, H occupies one bonding site on the Ag(111) surface, for all coverage investigated. This is also consistent with the smooth work function change, as discussed in the previous section.

As the scattering angle is changed, the loss energies of both peaks show very little dispersion [less than 2 meV for  $\Delta q_{\parallel} \sim 0.35 \text{ \AA}^{-1}$  with 0.5-ML H, see Figs. 6(a) and 6(b)], while there are different variations in intensities. The absolute intensities of the elastic and inelastic peaks as a function of the scattering angle taken with all impact energies used in this study are plotted in Fig. 7. As the analyzer is moved away from the specular direction, the peak intensity of  $\sim 106$ -meV loss rapidly decreases, similar to the elastic peak, while that of  $\sim 87$ -meV loss remains almost unchanged for all impact energies used.

TABLE I. H-induced work function changes ( $\mu_0$  and  $\Delta\Phi_{\max}$ ) of the close-packed fcc(111) and open fcc(110) surfaces. W(110) and W(100) surfaces are included for comparison. The work functions of the clean surface ( $\Phi_{cl}$ ) and H-covered surface ( $\Phi_H = \Phi_{cl} + \Delta\Phi_{\max}$ ) are also listed.

Crystal surface	$\mu_0^a$ (debye)	$\Delta\Phi_{\max}$ (eV)	$\Phi_{cl}^b$ (eV)	$\Phi_H (= \Phi_{cl} + \Delta\Phi_{\max})$ (eV)
Ag(111)	+ 0.18 <sup>c</sup>	+ 0.32	4.74	5.06
Ag(110)		+ 0.22 <sup>d</sup>		
Ni(111)	+ 0.03	+ 0.17	5.2	5.37
Ni(110)		+ 0.53	5.0	5.53
Pd(111)		+ 0.18	5.55	5.73
Pd(110)	+ 0.07	+ 0.36		
Pt(111)	- 0.04	- 0.30	5.93	5.63
Pt(110)	+ 0.12	+ 0.17		
		/- 0.50		
W(110)		- 0.14 <sup>e</sup>	5.25	5.11
		- 0.50 <sup>f</sup>		4.75
W(100)	+ 0.21	+ 0.90 <sup>g</sup>	4.64	5.54

<sup>a</sup> $\mu_0$  and  $\Delta\Phi_{\max}$  are taken from Table 6 and Table 8 in Ref. 1, respectively, except where noted.

<sup>b</sup> $\Phi_{cl}$  are taken from Table I in Ref. 36, except for W.

<sup>c</sup>Present work.

<sup>d</sup>Reference 17.

<sup>e</sup>Reference 37.

<sup>f</sup>Reference 30.

<sup>g</sup>Reference 33.

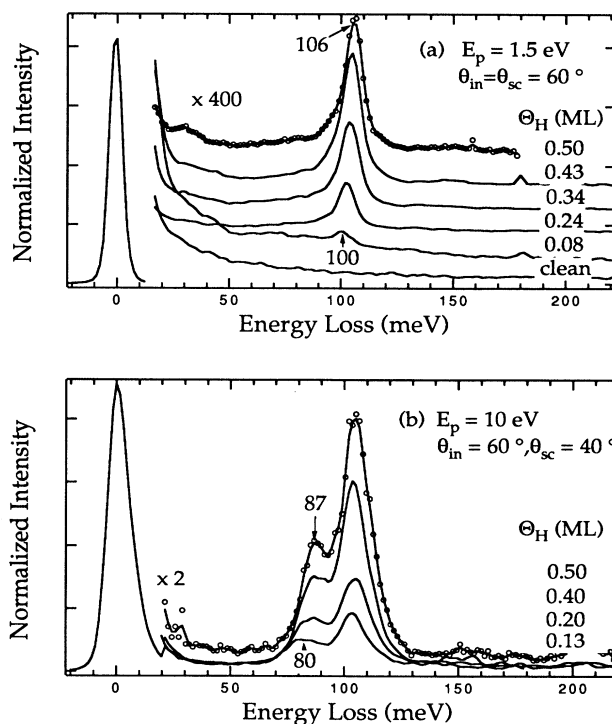


FIG. 6. Series of EELS spectra obtained as a function of H coverage. (a) Specular spectra with incident beam energy,  $E_p = 1.5$  eV and (b) off-specular ( $20^\circ$  off) spectra with  $E_p = 10$  eV. The elastic peak widths are  $\sim 6$  meV and  $\sim 10$  meV, respectively.

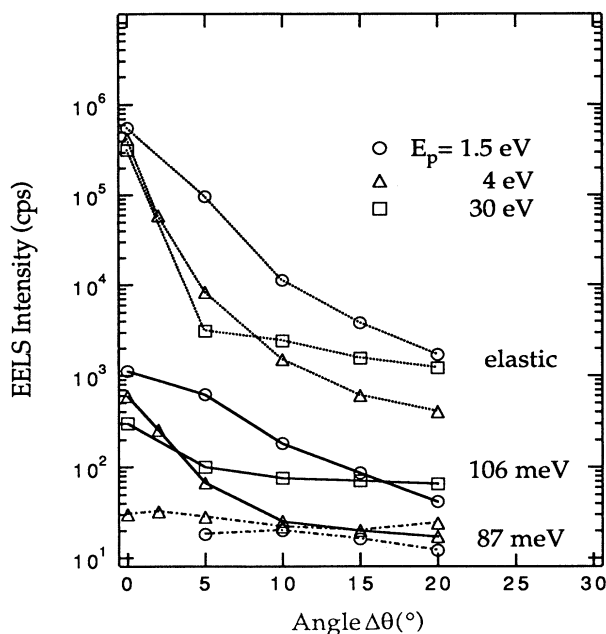


FIG. 7. The angular profiles for elastic and inelastic electron scattering intensities at different incident energies ( $E_p = 1.5, 4, \text{ and } 30 \text{ eV}$ ).

Therefore, the 106-meV loss manifests a strong “dipole” scattering contribution, while 87-meV loss peak intensity is governed by an “impact” scattering. This difference in angular dependence of the loss intensities allows us to assign unambiguously the observed losses at 87 meV and 106 meV as from asymmetric (parallel to the surface) and symmetric (normal to the surface) modes, respectively.

It has been very difficult in the case of H adsorption on metal surfaces to separate the dipole mode from the nondipole modes, due primarily to the weak intensity of the H modes.<sup>38</sup> Ag(111) is very different in that there is no experimental ambiguity. The high-energy loss ( $\sim 106 \text{ meV}$ ) assigned to the symmetric stretch mode, shows an exceptionally large intensity in the specular direction ( $I_{\text{loss}}/I_{\text{el}} \sim 1/300$  for  $E_p = 1.5 \text{ eV}$ ,  $\theta_{\text{in}} = 60^\circ$ ) among the close-packed surfaces and is obviously dipole active. The high intensity and dipole activity of this mode indicate that the effective charge and the oscillating dipole moment accompanying the excitation of vibration perpendicular to the surface is not as small as what is generally believed for H on close-packed surfaces. From the dipole contribution of the measured intensity relative to the elastic peak, the effective charge  $e^*$  associated with the hydrogen-metal stretch mode (106-meV peak) may be estimated using the cross-section formula for a dipole scattering.<sup>39</sup> A value of  $e^*/e \sim 0.1$  is estimated from the loss intensity for  $\Theta \sim 0.5 \text{ ML H/Ag(111)}$ . This value is significantly larger than those for fcc(111) transition metal surfaces, such as  $0.018e$  for H/Pt(111).<sup>40</sup> Therefore, H/Ag(111) is unique in that unequivocal mode assignment of H vibrational losses in HREELS is possible without resorting to any theoretical model.

As for the bonding site, the most consistent is the

threefold hollow site based on the observation of two loss peaks, one symmetric (perpendicular) and the other asymmetric (parallel) modes, in HREEL spectra for all incident energies and collection angles used in our study. In comparison, for H/Cu(111) where similar superstructures were reported, the adsorption of H at a bridge site rather than at a threefold hollow site was proposed.<sup>18</sup> The adsorption of H at the twofold bridge site on Cu(111) is in stark contrast to the general trend, acquired through the studies of mostly transition metal surfaces, that H adsorbs at the highest-coordinated site, i.e., a threefold site on the (111) surface and fourfold site on the (100) surface. In contrast, the theoretical calculations from both clusters<sup>41</sup> and slabs<sup>42,43</sup> for the hydrogen adsorbed on the unreconstructed Cu(111) surface preferred the threefold hollow site. For H/Ag(111), there are only a few cluster calculations published.<sup>15,41,44</sup> Because all calculations were performed for clusters simulating an unreconstructed structure of the Ag surface, they are unable to decide whether H occupies a threefold hollow or a bridge site on the (111) surfaces of Ag, especially when the surface is reconstructed. Our assignment of a bonding of H at a threefold hollow site on the Ag(111) surface is, therefore, based on the number of observed modes in HREELS (Ref. 45) and also consistent with the trend observed in most H/transition metal systems, rather than being exceptional. The large effective charge of the symmetric mode of the H/Ag(111) system is presumably related to the surface reconstruction, rather than being due to an adsorption at a bridge site which was claimed for H/Cu(111).

Though our HREEL spectra is interpreted as resulting from the harmonic motion of the hydrogen atoms adsorbed at well-localized sites, a different view on the motion of H on the surface exists in some H/metal systems. The large zero-point motion of H caused by its small mass being considered, the delocalized motion of H on the Ni surfaces has been proposed.<sup>5</sup> The theoretical calculation,<sup>2</sup> taking the quantum motion of H on the surface into account, shows that due to the overlap of the motion of H, the excited states can have bandwidths as large as several tens of meV depending on the face. In addition, both motions of H perpendicular and parallel to the surface may couple to each other through anharmonic potential and the delocalized motion, causing the deviation from the isotope shift in loss energies of H and D. As the coverage increases, the motion of H becomes highly localized because of strong H-H lateral interaction, resulting in the band narrowing, i.e., the decrease in the half width of the observed loss peak with H coverage. Experimentally, the HREEL spectra of H/Cu(110) (Ref. 3) and H/Rh(111) (Ref. 4) at low coverage have been interpreted as resulting from the delocalized motion of H on these surfaces. For H/Ag(111), however, there is no significant deviation from the isotope shift for both loss peaks observed when H is replaced by D. The loss peaks are quite narrow (the intrinsic widths are  $\sim 7$  and  $9 \text{ meV}$  for a symmetric and an asymmetric modes, respectively) and remain unbroadened as the coverage decreases as small as  $0.1 \text{ ML}$  where a  $(2 \times 2)$  LEED pattern has not yet been developed. Therefore, for the H

coverage as low as 0.1 ML, there is no evidence for the delocalized motion of H on the Ag(111) surface and the delocalized picture is invalid in the case of H/Ag(111).

The loss energies and linewidths (after deconvolution with the elastic peak) of both perpendicular and parallel modes as a function of H coverage are plotted in Fig. 8. The vibrational energies of both modes shift upwards as H coverage increases from dilute to dense layer, while the linewidths show little change or, if any, a very slight increase. The coverage-dependent energy shifts amount to 6 meV and 9 meV for the symmetric and the asymmetric modes of H, respectively. The coverage-dependent energy shifts of the loss peaks in HREELS have also been observed for other H/metal systems, such as H/Ru(0001)<sup>46</sup>, H/Pd(100),<sup>47</sup> H/Ni(100),<sup>48</sup> and H/Ag(110).<sup>17</sup> Similar to the observation of our study, the increase of vibrational energy of  $\sim 5$ –10 meV has been reported in all the sys-

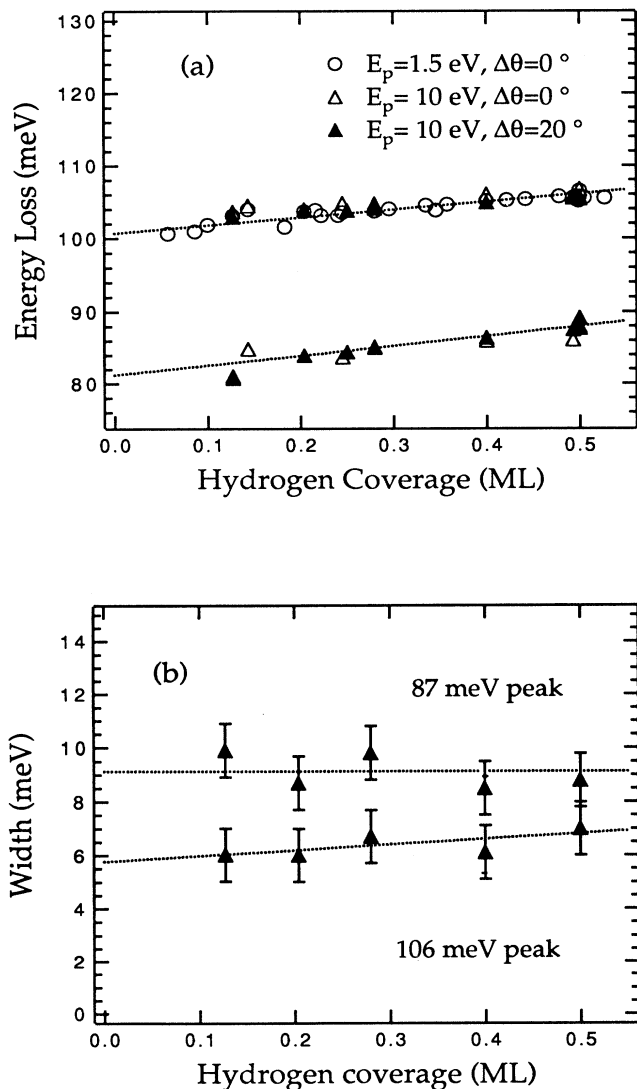


FIG. 8. (a) The energy and (b) the width (after deconvolution with elastic peak) of loss peaks observed in EELS spectra as a function of H coverage (lines are guides for eyes).

tems stated above, except for the case of H/Ag(110), where the energy of the dominant loss peak shifts down (from 64 meV to 58 meV) accompanied by a large increase in width as H coverage increases. In all cases, these shifts have been attributed to the H-H lateral interaction.

The lateral interaction between H on metal surfaces is a consequence of the indirect interaction mediated through the electronic disturbance in the metal surface by the adsorption because the H-H spacing is much larger than the size of atomic hydrogen. The increase in loss energy of the EELS peak for H/Pd(100) and H/Ni(100) with coverage has been analyzed in terms of the static and dynamic contributions of this interaction.<sup>49</sup> The former arises from the change in the H-metal bond strength as a function of coverage brought about by the presence of the other hydrogen atoms on the surface (chemical shift) whereas the latter arises from the dynamic coupling when the neighboring hydrogen atoms are also oscillating. The dynamic contribution results in the dispersion as well. While both contributions appear in the energy shift in the homogeneous adsorption, they can be separated by studying the isotopic mixture with identical total concentration but different relative concentrations, because the vibrational coupling between the isotope(s) is negligible due to the difference in vibrational energy. Figure 9 shows HREEL spectra in specular direction (i.e.,  $q_{\parallel} = 0$  mode) for (a) 0.5-ML H, (b) 0.1-ML H + 0.4-ML D (substitutional adsorption of isotopic mixture of H and D), and (c) 0.1-ML H. While the cases in Figs. 9(a) and 9(b) have the same total coverage of H+D and show the identical LEED structure [fully developed ( $2 \times 2$ )], the vi-

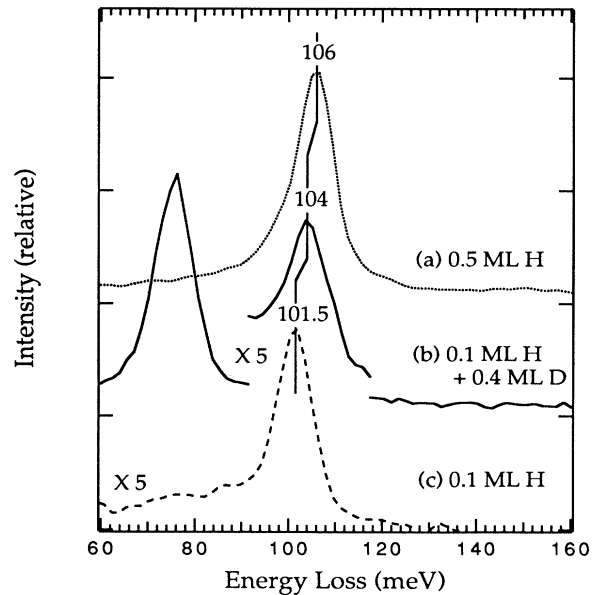


FIG. 9. Comparison of EELS spectra (energy of symmetric vibrational mode of H) at different absolute and relative concentration of H. (a) 0.5-ML H, (b) 0.1-ML H and 0.4-ML D (substitutional adsorption of isotope mixture of H and D), and (c) 0.1-ML H. The spectra are taken with  $E_p = 1.5$  eV in specular geometry.



brational energies of the symmetric modes of H differ by  $\sim 2$  meV. This shift is exclusively attributable to the dynamic contribution of H-H interaction, because the static configurations are identical. The rest of the total energy shift in homogeneous adsorption of H [ $\sim 4$  meV out of 6 meV as shown in Fig. 9(a)] results from the pure chemical shift. This is also reflected in the appreciable energy shift of the symmetric mode of H with and without coadsorption of D [compare Figs. 9(b) and 9(c)] because the dynamic coupling between H and D is negligible. The observation of small dispersion is also consistent with the small dynamic contribution ( $\sim 2$  meV for  $w_{\perp}$ ). Because of the exceptionally large effective charge for the symmetric mode of H/Ag(111), the dipole-dipole interaction may also contribute to the dynamic coupling. But it is small as shown in the small energy shift and dispersion caused by the dynamic contribution. It is concluded that most of the observed energy shifts of H/Ag(111) with coverage originates from the static contribution (i.e., chemical shift) of the lateral interaction mediated through the metal surface.

There is another obvious explanation of the shift, i.e., the conversion or the change of the relative population from one type of site to the other [the fcc(111) surface has two types of threefold hollow sites, fcc and hcp sites]. But it will not work because it would require a difference in the frequency of modes, resulting in a broader line shape, especially at 0.5 ML where fcc and hcp sites are equally populated [see Fig. 4(c)]. The linewidth as a function of coverage in Fig. 8(b) shows this possibility unlikely.

#### D. TDS and H-Ag bonding energy

The thermal desorption spectra of hydrogen or deuterium desorbing from the Ag(111) surface has already been reported elsewhere.<sup>14</sup> The spectra show only a single peak (with a small low-temperature shoulder at high coverage) at  $\sim 180$  K, in agreement with the previous study.<sup>16</sup> This desorption temperature is uncharacteristically low for most H/metal systems; for example, hydrogen desorbs from Al(111) at 320 K,<sup>50</sup> Cu(111) at 300 K,<sup>19</sup> Ni(111) at 380 K,<sup>5</sup> and Pd(111) at 380 K.<sup>10</sup> However, a similar low desorption temperature has recently been reported for Ag(110) (155–175 K),<sup>17</sup> as well as for H/Au(111) (110 K).<sup>51</sup>

Although there are some disparities in the kinetic order,<sup>52</sup> the activation energy for a recombinative desorption ( $E_{\text{des}}$ ) for H/Ag(111) has been determined to be 6–10 kcal/mole, which is also substantially smaller than those of hydrogen adsorbed on the transition metals and copper (typically  $\sim 20$  kcal/mole). Since there exists an activation barrier for the dissociative adsorption of hydrogen on silver, the desorption energy  $E_{\text{des}} = 6\text{--}10$  kcal/mole is an upper bound of the heat of adsorption  $E_{\text{ad}}$  when there is no adsorption barrier. While the activation barrier for adsorption of about 0.6 eV (14 kcal/mole) has been estimated for Cu surfaces both experimentally<sup>53</sup> and theoretically,<sup>54–56</sup> it is not known for Ag surfaces. If we assume that the activation barrier for adsorption on Ag is comparable to that of Cu

or at least larger than 6–10 kcal/mole, we end up with thermodynamically unstable chemisorption of atomic hydrogen on the silver surface ( $E_{\text{ad}} < 0$ ). This endothermic chemisorption of atomic hydrogen relative to molecular hydrogen was suggested in the theoretical calculation of binding energies of physisorbed and chemisorbed hydrogen using silver clusters, modeling the Ag(111) surface.<sup>15</sup>

It should be noted that the above argument is based on the assumption of a detailed balance between adsorption and desorption dynamics. If adsorption and desorption do not follow the same potential energy hyperspace, any argument based on a detailed balance is no longer valid.<sup>57</sup>

#### IV. DISCUSSION AND SUMMARY

While the interaction of hydrogen with transition metal surfaces has shown diversity in the details, there are some trends accumulated from the past studies. For the fcc(111) and the hcp(0001) surfaces of most transition metals, the adsorption of H *on the surface* is saturated with 1 ML, while the additional *bulk absorption* was observed for some systems.<sup>10,58</sup> Although there are variations in hydrogen phases at intermediate coverage (ordered or disordered), the LEED pattern finally reaches ( $1 \times 1$ ) at saturation coverage, consistent with 1 ML. The thermal desorption spectra of these systems show a typical double-peak structure ( $\beta_1, \beta_2$ ) at high coverage (typically  $> 0.5$  ML), starting from the single peak ( $\beta_2$ ) at higher temperature in the low coverage.<sup>59</sup> The multiple peaks in TDS are usually interpreted to be from the adsorption of adsorbate at different sites, either being locally different (*a priori*, different type of sites, e.g., threefold hollow versus bridge site, or overlayer versus underlayer) or being inequivalent by the lateral interaction, depending on the presence of adsorption at neighboring sites. The two are not easily differentiated by studying TDS alone. In the case of hydrogen on fcc(111) and hcp(111) transition metals, the latter is favored because there is no evidence of adsorption at multiple sites, as found in the vibrational spectra (HREELS), which is sensitive to the local adsorption geometry. Therefore, the repulsive H-H lateral interaction is considered to be responsible for the appearance of a double-peak structure in TDS for the close-packed surface. The decrease of the heat of adsorption above a certain coverage is also common in the H/transition metal system. The magnitude of the lateral interaction energy can be estimated from the decrease of the heat of adsorption that is related to the development of the second TDS peak. It ranges within 5–10 kcal/mole for the transition metals studied (Ni, Pt, Ru, Rh).

Compared to H/transition metal systems, H/Ag(111) shows different chemisorption properties. These include (1) a saturation coverage of 0.6 ML, which is less than 1 ML, (2) no appearance of a ( $1 \times 1$ ) LEED pattern at the saturation, (3) a single peak (possibly with small additional shoulder) in TDS, (4) characteristically low heat of adsorption and Ag-H binding energy, and (5) a hydrogen-induced substrate reconstruction stronger than usual. Table II summarizes the experimental observa-

tions on H/Ag(111) presented in the previous sections and compares them with those reported for H/Cu(111) and H/Ni(111). Ni is chosen as a prototype of a transition metal because it is the most studied system and also shows a similar LEED superstructure. As shown in Table II, H/Cu(111) seems to share those chemisorption properties listed above with H/Ag(111), although some differences are found in detail. When compared with H/Ni(111), the interaction of hydrogen with noble metal surfaces is very different. On Ag(111), there is a great reduction in bonding strength and an increase in surface reconstruction. Although the superstructures in LEED of H/Cu(111) were assumed to be from the overlayer in the past study, the Cu(111) surface is presumably reconstructed (see Fig. 1 of Ref. 18, the fractional order spots are not so weak). While it has been recently reported<sup>8</sup> that the Ni(111) surface is also reconstructed by H adsorption, the degree of reconstruction of noble metals seems much larger than that of Ni(111)—the relative beam intensity of fractional-order spots in  $(2 \times 2)$  LEED of H/Ag(111) ( $\sim 10\%$ ) is much larger than that of H/Ni(111) ( $< 3\%$ ).

The distinct adsorption properties of noble metals, observed in saturation coverage, LEED, and TDS, seems to be all related to the low hydrogen-metal binding energies relative to those of transition metals. The trends in chemisorption energy of H binding on the transition metal surfaces have been investigated in theoretical studies using the effective medium theory<sup>12</sup> and the em-

bedded cluster calculation.<sup>13</sup> These calculations showed that, while most of the chemisorption energy stems from the interaction of a hydrogen atom with  $s$ - $p$  electrons (treated as jellium), the interaction (i.e., hybridization) with  $d$  electrons of transition and noble metals explains the trends in these series. The theories predicted that the binding of H on noble metals is much weaker than on transition metals due to the filling of antibonding states, located above or at the upper part of the  $d$  bands that are not or less occupied for transition metals. The low chemisorption energy of H on Ag is consistent with these predictions. In fact, the occupation of the Ag-H antibonding state induced by H adsorption on the Ag(111) surface has been observed experimentally in angle-resolved photoemission.<sup>61</sup>

The saturation of the surface below a monolayer of H is presumably caused by the interplay of low heat of adsorption and the lateral H-H interaction on the noble metal surfaces. If the repulsive H-H interaction becomes sufficiently large and comparable with heat of adsorption above a certain coverage, it is likely to limit the additional adsorption of H and give rise to the saturation below a monolayer. Though it is only one possibility, it is consistent with other observations in LEED and TDS of H/Ag(111) and H/Cu(111); the LEED pattern does not evolve into a  $(1 \times 1)$  pattern and the low temperature second peak ( $\beta_1$ ) in TDS is not fully developed even at the highest coverage. For comparison, the  $(2 \times 2)$  LEED of H/Ni(111) at 0.5 ML, which is similar to H/Ag(111),

TABLE II. The summary of the experimental observation on H/Ag(111) in this study and the comparison with H/Cu(111) and H/Ni(111) (Ni is chosen as a representative of transition metal for comparison). The results for Ni(111) are with the dissociative adsorption of  $H_2$  molecules.

	H/Ag(111)	H/Cu(111) <sup>a</sup>	H/Ni(111) <sup>b</sup>
$\Theta_{\text{sat}}$	$0.6 \pm 0.1$ ML $0.82 \times 10^{15} \text{ cm}^{-2}$	$< 1$ ML ? <sup>c</sup> $(1.77 \times 10^{15} \text{ cm}^{-2}/1 \text{ ML})$	1 ML (surface adsorption) $1.86 \times 10^{15} \text{ cm}^{-2}$
LEED	$\rightarrow (2 \times 2)$ (0.5 ML) $\rightarrow (2 \times 2) + (3 \times 3)$ (sat)	$\rightarrow (2 \times 2)$ $\rightarrow (3 \times 3)$ (sat)	$\rightarrow (2 \times 2)$ (0.5 ML) $\rightarrow (1 \times 1)$ (sat)
e-beam effect	yes $(2 \times 2) \rightarrow (2 \times 2) + (3 \times 3)$	yes $(3 \times 3) \rightarrow (2 \times 2) + (3 \times 3)$	no
$\Delta\Phi_{\text{max}}$	+ 0.32 eV $\Delta\Phi_{\text{max}(111)} > \Delta\Phi_{\text{max}(110)}$		+ 0.17 eV $\Delta\Phi_{\text{max}(111)} < \Delta\Phi_{\text{max}(110)}$
TDS			
$T_{\text{des}}$ peaks	$\sim 180$ K ( $\beta_2$ ), [ $\sim 160$ K ( $\beta_1$ )] single peak ( $\beta_2$ ) with a very small shoulder ( $\beta_1$ )	$\sim 300$ K ( $\beta_2$ ), $\sim 220$ K ( $\beta_1$ ) <sup>d</sup> double peaks with different areas ( $\beta_2 : \beta_1 \sim 5 : 2$ in area)	$\sim 380$ K ( $\beta_2$ ), $\sim 350$ K ( $\beta_1$ ) double peaks with equal areas ( $\beta_2 : \beta_1 \sim 1 : 1$ in area)
$E_{\text{des}}$ <sup>e</sup> $E_{\text{M-H}}$ , $E_{\text{ad}}$ <sup>f</sup>	6 $\sim$ 10 kcal/mole < 53 kcal/mole, ( $< 0$ )	$\sim 18$ kcal/mole 56 kcal/mole, ( $\sim 6$ kcal/mole)	18 $\sim$ 22 kcal/mole 63 kcal/mole, ( $\sim 20$ kcal/mole)
HREELS			
vibrational modes	106 meV ( $\omega_{\perp}$ : dipole) 87 meV ( $\omega_{\parallel}$ : nondipole)	129 meV ( $\omega_{\perp}$ : dipole) 143 meV ( $2\omega_{\parallel}$ : dipole) <sup>g</sup>	139 meV ( $\omega_{\perp}$ : nondipole) 89 meV ( $\omega_{\parallel}$ : nondipole)
adsorption site	threefold hollow	bridge site	threefold hollow <sup>h</sup>

<sup>a</sup>Reference 18.

<sup>b</sup>Reference 5.

<sup>c</sup>No absolute measurement.

<sup>d</sup>Reference 19.

<sup>e</sup>At low coverage regime.

<sup>f</sup>Metal-hydrogen binding energy, Ref. 60.

<sup>g</sup>This was observed in reflection-absorption infrared spectroscopy (RAIRS) but not in HREELS.

<sup>h</sup>Reference 38.

finally converts into a  $(1 \times 1)$  LEED and the  $\beta 1$  peak is fully developed with equal area to that of  $\beta 2$  in TDS, reaching 1 ML at saturation.

The relation of the H-induced reconstruction of the (111) surface of noble metals with other chemisorption properties is not clear. The driving force of the adsorbate-induced reconstruction of the metal surface is considered to be either the inherent instability of a clean surface [e.g.,  $(1 \times 2)$  missing row reconstruction of Ag(110) surface upon small amounts of alkali-metal adsorption] or the reduction of bond strength between metal atoms (e.g., surface relaxation with possible displacement of surface atoms). The reconstruction of the (111) surface of noble and transition metals upon atomic and molecular adsorption has been reported and interpreted to be from the latter.<sup>21,62</sup> The H-induced reconstruction of the Ag(111) [and possibly Cu(111)] surface is not unique, but the degree of the reconstruction is much

larger than of H/Ni(111). This seems to be quite contradictory to the fact that the bonding strengths of hydrogen with Ag and Cu are weaker than with transition metals. Further experimental and theoretical studies are needed to understand the driving force of the reconstruction of the (111) surface of noble metals by adsorption of H.

#### ACKNOWLEDGMENTS

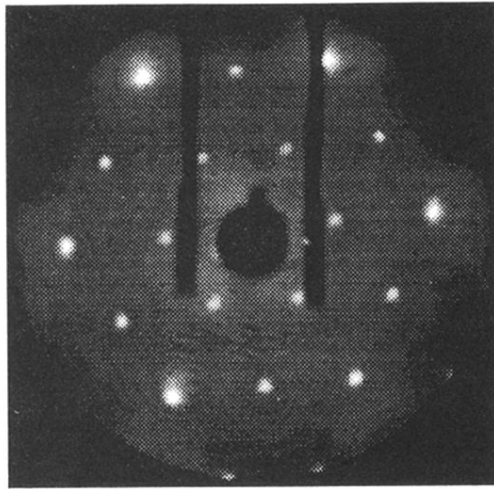
One of us (G.L.) wishes to thank P. T. Sprunger for his assistance in the beginning of this work. The primary support for this work came from the National Science Foundation under Grant No. DMR-93-96059. Part of this research was carried out at ORNL, supported by the Division of Materials Sciences, U.S. DOE, under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

\* Present address: Oak Ridge National Laboratory, Oak Ridge, TN 37831-6032.

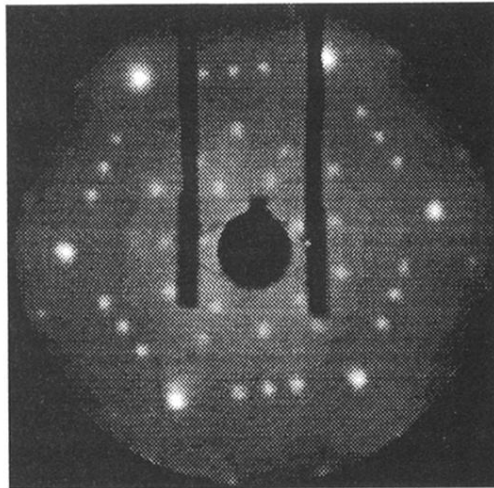
Electronic address: glee@solid.ssd.ornl.gov

- <sup>1</sup> K. Christmann, *Surf. Sci. Rep.* **9**, 1 (1988), and references therein.
- <sup>2</sup> M. J. Puska and R. M. Nieminen, *Surf. Sci.* **157**, 413 (1985).
- <sup>3</sup> C. Astaldi, A. Bianco, S. Modesti, and E. Tosatti, *Phys. Rev. Lett.* **68**, 90 (1992).
- <sup>4</sup> C. M. Mate and G. A. Somorjai, *Phys. Rev. B* **34**, 7417 (1986).
- <sup>5</sup> K. Christmann, R. J. Behm, G. Ertl, M. A. Van Hove, and W. H. Weinberg, *J. Chem. Phys.* **70**, 4168 (1979).
- <sup>6</sup> T. E. Felter, S. M. Foiles, M. S. Daw, and R. H. Stulen, *Surf. Sci.* **171**, L379 (1986).
- <sup>7</sup> K. Christmann, *Z. Phys. Chem.* **154**, 145 (1987), and references cited therein.
- <sup>8</sup> L. Hammer, H. Landskron, W. Nichtl-Pecher, A. Fricke, K. Heinz, and K. Müller, *Phys. Rev. B* **47**, 15969 (1993).
- <sup>9</sup> W. Eberhardt, F. Greuter, and E. W. Plummer, *Phys. Rev. Lett.* **46**, 1085 (1981).
- <sup>10</sup> G. E. Gdowski, T. E. Felter, and R. H. Stulen, *Surf. Sci.* **181**, L147 (1987).
- <sup>11</sup> J. Harris, S. Andersson, C. Holmberg, and P. Nordlander, *Phys. Scr.* **T13**, 155 (1986).
- <sup>12</sup> P. Nordlander, S. Holloway, and J. K. Nørskov, *Surf. Sci.* **136**, 59 (1984).
- <sup>13</sup> J. P. Muscat, *Surf. Sci.* **110**, 389 (1981).
- <sup>14</sup> G. Lee, P. T. Sprunger, M. Okada, D. B. Poker, D. M. Zehner, and E. W. Plummer, *J. Vac. Sci. Technol.* **A12**, 2119 (1994).
- <sup>15</sup> C. Mijoule and V. Russier, *Surf. Sci.* **254**, 329 (1991).
- <sup>16</sup> X.-L. Zhou, J. M. White, and B. E. Koel, *Surf. Sci.* **218**, 201 (1989).
- <sup>17</sup> P. T. Sprunger and E. W. Plummer, *Phys. Rev. B* **48**, 14436 (1993).
- <sup>18</sup> E. M. McCash, S. F. Parker, J. Pritchard, and M. A. Chesters, *Surf. Sci.* **215**, 363 (1989).
- <sup>19</sup> F. Greuter and E. W. Plummer, *Solid State Commun.* **48**, 37 (1983).
- <sup>20</sup> S. J. White, D. P. Woodruff, B. W. Holland, and R. S. Zimmer, *Surf. Sci.* **74**, 34 (1978).
- <sup>21</sup> A. Wander, M. A. Van Hove, and G. A. Somorjai, *Phys. Rev. Lett.* **67**, 626 (1991).
- <sup>22</sup> A. P. Baddorf, I. W. Lyo, E. W. Plummer, and H. Davis, *J. Vac. Sci. Technol.* **A5**, 782 (1987).
- <sup>23</sup> G. Gross and K. H. Rieder, *Surf. Sci.* **241**, 33 (1991).
- <sup>24</sup> LEED-IV of the diffraction spots (10), (01), (11) (integer order),  $(1/2\ 0)$ ,  $(0\ 1/2)$ , and  $(1/2\ 1/2)$  (fractional order) in the beam energy range of 50–150 eV were used in the calculation. For simplicity, the surface Debye temperatures corresponding to the integer and fractional order spots were assumed to be equal.
- <sup>25</sup> For example, the corresponding intensities are 14% for  $(1 \times 3)$ -H/Ag(110) (Ref. 17), 10% for  $(1 \times 2)$ -H/Rh(110) [W. Puchta, W. Nichtl, W. Oed, N. Bickel, K. Heinz, and K. Müller, *Phys. Rev. B* **39**, 1020 (1989)] and 5% for  $(1 \times 3)$ -H/Rh(110) [K. Lehnberger, W. Nichtl-Pecher, W. Oed, K. Heinz, and K. Müller, *Surf. Sci.* **217**, 511 (1989)], averaged over the range of 50–200 eV.
- <sup>26</sup> K. Mortensen, F. Besenbacher, I. Stensgaard, and W. R. Wampler, *Surf. Sci.* **205**, 433 (1988).
- <sup>27</sup> P. A. Thiel and T. E. Madey, *Surf. Sci. Rep.* **7**, 211 (1987).
- <sup>28</sup> K. Christmann, G. Ertl, and T. Pignet, *Surf. Sci.* **54**, 365 (1976).
- <sup>29</sup> F. Bozso, G. Ertl, M. Grunze, and M. Weiss, *Appl. Surf. Sci.* **1**, 103 (1977).
- <sup>30</sup> E. W. Plummer and A. E. Bell, *J. Vac. Sci. Technol.* **9**, 583 (1972).
- <sup>31</sup> K. B. Ray, J. B. Hannon, and E. W. Plummer, *Chem. Phys. Lett.* **171**, 469 (1990).
- <sup>32</sup> A. P. Baddorf, Ph.D. thesis, University of Pennsylvania, 1987.
- <sup>33</sup> P. J. Estrup and J. Anderson, *J. Chem. Phys.* **45**, 2254 (1966).
- <sup>34</sup> P. Feulner and D. Menzel, *Surf. Sci.* **154**, 465 (1985).
- <sup>35</sup> I. Stensgaard, K. G. Purcell, and D. A. King, *Phys. Rev. B* **39**, 897 (1989).
- <sup>36</sup> D. Straub and F. J. Himpsel, *Phys. Rev. B* **33**, 2256 (1986).
- <sup>37</sup> B. J. Hopkins and K. R. Pender, *Surf. Sci.* **5**, 316 (1966).
- <sup>38</sup> W. Ho, N. J. DiNardo, and E. W. Plummer, *J. Vac. Sci. Technol.* **17**, 134 (1980).

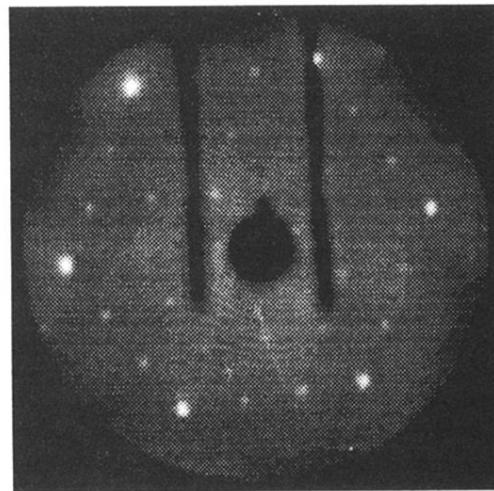
- <sup>39</sup> H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic Press, New York, 1982).
- <sup>40</sup> J. E. Reutt, Y. J. Chabal, and S. B. Christman, *J. Electron Spectrosc. Relat Phenom.* **44**, 325 (1987).
- <sup>41</sup> J. Flad, G. Igel-Mann, M. Dolg, H. Preuss, and H. Stoll, *Surf. Sci.* **163**, 285 (1985).
- <sup>42</sup> P. J. Feibleman and D. R. Hamann, *Surf. Sci.* **173**, L582 (1986).
- <sup>43</sup> K. Gunderson, B. Hammer, K. W. Jacobsen, J. K. Nørskov, J. S. Lin, and V. Milman, *Surf. Sci.* **285**, 27 (1993).
- <sup>44</sup> E. A. Carter and W. A. Goddard III, *Surf. Sci.* **209**, 243 (1989).
- <sup>45</sup> In the case of a bridge site, three losses (one perpendicular and two nondegenerate parallel modes) are expected to be seen in the off-specular EELS spectra. This is not the case in our observation. However, the possibility of bridge-site adsorption is not completely ruled out because one of the nondipole active modes may not be detected due to either its low energy or very small cross section.
- <sup>46</sup> H. Conrad, R. Scalar, W. Stenzel, and R. Unwin, *J. Chem. Phys.* **81**, 6371 (1984).
- <sup>47</sup> C. Nyberg and C. G. Tenstal, *Phys. Rev. Lett.* **50**, 1680 (1983).
- <sup>48</sup> P.-A. Karlsson, A.-S. Martensson, S. Andersson, and P. Nordlander, *Surf. Sci.* **175**, L759 (1986).
- <sup>49</sup> P. Nordlander and S. Holmström, *Surf. Sci.* **159**, L443 (1985).
- <sup>50</sup> A. Winkler, G. Poägainer, and K. D. Rendulic, *Surf. Sci.* **251/252**, 886 (1992).
- <sup>51</sup> L. Stobinski and R. Dus, *Surf. Sci.* **269/270**, 383 (1992).
- <sup>52</sup> D. H. Parker, M. E. Jones, and B. E. Koel, *Surf. Sci.* **233**, 65 (1990).
- <sup>53</sup> G. Comsa and R. David, *Surf. Sci.* **117**, 77 (1981).
- <sup>54</sup> J. Harris and S. Andersson, *Phys. Rev. Lett.* **55**, 1583 (1985).
- <sup>55</sup> J. A. White, D. M. Bird, M. C. Paync, and I. Stich, *Phys. Rev. Lett.* **73**, 1404 (1994).
- <sup>56</sup> B. Hammer, M. Scheffler, K. W. Jacobsen, and J. K. Nørskov, *Phys. Rev. Lett.* **73**, 1400 (1994).
- <sup>57</sup> E. Pehlke and M. Scheffler (unpublished).
- <sup>58</sup> A. D. Johnson, K. J. Maynard, S. P. Daley, Q. Y. Yang, and S. T. Ceyer, *Phys. Rev. Lett.* **67**, 927 (1991).
- <sup>59</sup> H/Pd(111) seems to be the only exception that maintains a single-peak structure in TDS through all coverage up to 1-ML surface saturation. In addition to  $\beta$  peak(s), an additional peak ( $\alpha$ ) at lower temperature is observed for H/Pd(111) and H/Ni(111). But this additional peak corresponds to the desorption from the absorbed hydrogen from subsurface or bulk over 1-ML hydrogen and is not relevant for our discussion.
- <sup>60</sup> G. Ertl, in *The Nature of the Surface Chemical Bond*, edited by T. N. Rhodin and G. Ertl (North-Holland, Amsterdam, 1979).
- <sup>61</sup> Geunseop Lee and E. W. Plummer (unpublished).
- <sup>62</sup> D. T. Grimsby, Y. K. Wu, and K. A. R. Mitchell, *Surf. Sci.* **232**, 51 (1990).



(a)



(b)



(c)

FIG. 2. LEED patterns of superstructures observed for H/Ag(111) with a beam energy of 57 eV. (a)  $(2 \times 2)$  at 0.5-ML hydrogen at 100 K, (b)  $(2 \times 2) + (3 \times 3)$  at saturation ( $\sim 0.6$  ML) at 100 K, and (c)  $(3 \times 3)$  [with very weak  $(2 \times 2)$ ] after annealing at 140 K, starting from (b).