PHYSICAL REVIEW B VOLUME 52, NUMBER 15 15 OCTOBER 1995-I

Hydrogen-adsorption-induced phase transitions on Pt(100)-hex and the surface structure of Pt(100)-(1×1)H

Xiaoming Hu* and Zhangda Lin
State Key Laboratory of Surface Physics, Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing, People's Republic of China

(Received 21 March 1995; revised manuscript received 9 June 1995)

While adsorption of 100 L (1 L$=10^{-6}$ Torr s) H_2 molecules at room temperature does not cause any phase transitions from a clean reconstructed Pt(100)-hex surface, a 10-L dose of dissociated H_2 can induce a phase transition from the Pt(100)-hex to an atomic-hydrogen-stabilized Pt(100)-(1×1) structure as observed using low-energy electron diffraction (LEED). This Pt(100)-(1×1) surface was subsequently cooled down using liquid nitrogen to a temperature around 80 K and LEED I-V (intensity vs electron energy) curves were measured at normal incidence. Dynamical tensor LEED calculations were performed using different surface structure models including neglecting hydrogen, ordered (1×1) hydrogen at atop, bridge, and fourfold hollow sites. It has been found that within the converging range of atomic displacements, the minimum overall Pendry R factors (R_p) for the above models are 0.28, 0.35, 0.31, and 0.28, respectively. For the first model, Pt(100) interlayer relaxations down to the fifth layer were calculated. The fourfold hollow site model which also gave an overall small R_p showed scattered R_p for different beams and it is likely that the surface contained disordered hydrogen.

I. INTRODUCTION

It is known that absorption of hydrogen on crystals can induce relaxation, reconstruction, and faceting of the surface structure.[1] The critical role of atomic hydrogen in an epitaxial diamond film growth requires a good understanding of the hydrogen absorption process on crystals, especially phase transitions and surface structure. For Pt(100), earlier studies have shown that intrinsic reconstructions take place on the surface and *result in a* quasihexagonal top layer on a square substrate lattice.[2] Two phases exist for clean reconstructed Pt(100): a metastable Pt(100)-hex phase and a stable Pt(100)-hex-$R0.7^\circ$ phase when the first phase is heated above 1100 K.[3] Hydrogen adsorption on platinum has been studied by numerous research groups. It has been reported that the hydrogen coverage on a Pt(100) surface remains small above room temperature and under conditions which can be realized in an UHV system. At lower temperatures, higher coverages of hydrogen can be attained, and the reconstructed surface transforms into a (1×1) phase.[4] Hydrogen adsorption at low temperatures on Pt(100) has been reported to form a disordered overlayer,[5] and the surface relaxation between the top two layers is small.[6] For Pt(111)-(1×1)H, it has been reported[7,8] that hydrogen occupies a threefold hollow site with a H—Pt bond length of about 1.93 Å. However, to our knowledge, no experiment has been reported for the phase transitions and surface structures resulting from dissociated hydrogen adsorption on a clean reconstructed Pt(100)-hex surface, and in this paper we shall show that predissociated hydrogen adsorption on Pt(100)-hex will result in a good Pt(100)-(1×1) low-energy electron-diffraction (LEED) pattern, and explore the possible ordered surface structures.

II. EXPERIMENT

The experimental setup has been described earlier.[9,10] Briefly, the vacuum chamber was equipped with a turbomolecular pump and an ion pump, and the base pressure for experiments was below 1×10^{-10} mbar. A Varian four-grid LEED system was used to observe the diffraction patterns. The sample with a NiCr-NiAl thermocouple attached to its back was mounted on a simple oven heated by a tungsten filament. For LEED I-V measurements, a dedicated video LEED analyzer (VLA) system from Data-Quire Co. was used. This VLA system was used successfully in an earlier experiment.[10] The system can automatically calculate and match the positions of the LEED spots on the screen at different electron energies, then digitize the intensities of each selected spot, and the whole process is under computer control. The initial electron energies for the I-V measurements of different diffraction beams were set at the points where spots begin to appear on the screen, and the maximum electron energy (250 eV) was limited by the output of the computer interface and amplifier. The experiment was started with a Pt(100) sample and, after conventional Ar^+ sputter and anneal at 800 °C, a Pt(100)-hex LEED pattern was observed, as shown in Fig. 1(a), indicating a clean metastable reconstructed Pt(100) surface[3] as confirmed by Auger electron spectroscopy (AES) using the same four-grid system as a retarding-field analyzer (RFA). Dosings of pure molecular hydrogen at room temperature in 10-L steps (1 L$=10^{-6}$ Torr s) up to 100 L does not cause any observable change to the Pt(100)-hex LEED pattern. However, when we used a tungsten filament placed about 10 cm away form the sample surface and heated up to about 2000 °C, dosing of hydrogen in 2-L steps up to 10 L resulted in the complete transforma-

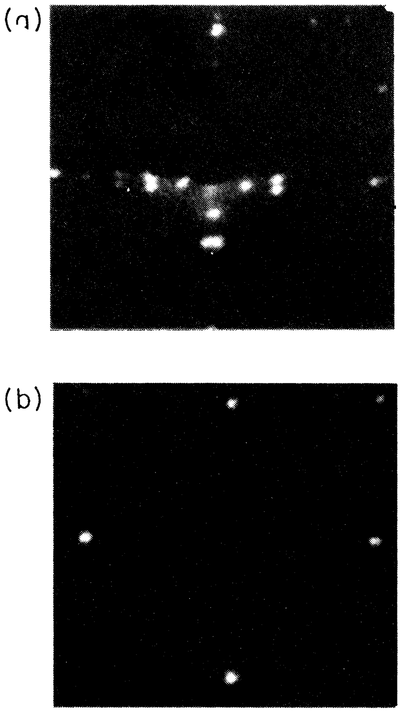

FIG. 1. (a) LEED pattern of Pt(100)-hex at 50 eV. (b) LEED pattern of Pt(100)-(1×1)H at 60 eV.

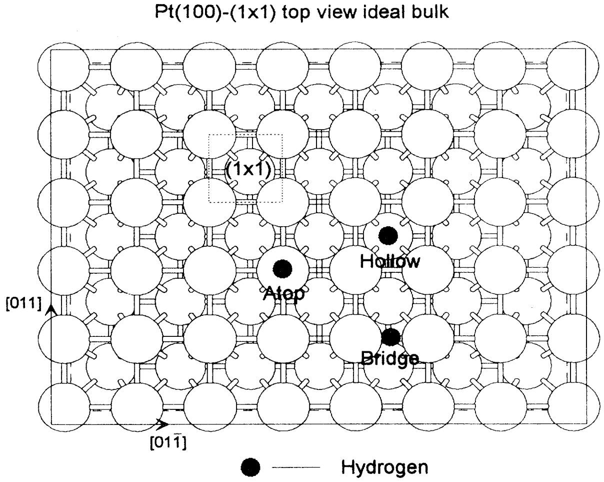

FIG. 2. Top view of Pt(100) ideal bulk showing a (1×1) unit cell and three atomic hydrogen positions—atop, bridge, and hollow—used in the dynamical LEED calculations.

tion of the Pt(100)-hex to a good Pt(100)-(1×1) LEED pattern, as shown in Fig. 1(b). The Pt(100)-(1×1) pattern showed no fractional spots at energies between 20 and 250 eV, while earlier studies[5] of hydrogen adsorption on reconstructed Pt(100) at low temperatures did not exhibit a perfect (1×1) periodicity but rather consisted of disordered derivatives of the initial, reconstructed structures. The sample was then annealed at 800 °C to desorb hydrogen on the surface and, after cooldown, this gave a Pt(100)-hex LEED pattern indicating that a reverse phase transition had occurred. Predissociated hydrogen was then redosed using the above conditions, and a total of 10-L dose again gave a good Pt(100)-(1×1) LEED pattern. The sample was subsequently cooled down using liquid nitrogen to a temperature around 80 K, and LEED *I-V* curves were measured at electron normal incidence. The condition of normal incidence was checked and confirmed by the result that equivalent beams such as (1,0), (0,−1), and (−1,0) give identical *I-V* curves. Since the surface has a fourfold symmetry, only beams (0,−1), (1,−1), and (2,0) were selected for comparison with theory. Higher-order beams only appeared near the edge of the LEED screen, and occupied too small an electron energy range to make reliable comparison with theory.

III. RESULTS AND DISCUSSIONS

The dynamical tensor LEED routines used in the calculation of the diffraction amplitudes (I-V curves) were constructed by the authors of Refs. 11 and 12. The running of the program contains two steps in determining a surface structure. In the first step, a reference model structure was calculated and a tensor collected for the top five layer atoms. The imaginary part of the potential representing electron damping due to inelastic processes was set to −4.25 eV, surface thermal vibrations were also considered, and Debye temperatures of 302 and 3358 K were used for platinum and hydrogen, respectively. The phase shifts used were provided by Van Hove, and the Pt phase shifts are relativistic. In the second step, the diffraction intensities for structures involving small deviations of the top five layer atoms were calculated using the tensor collected previously and the first-order perturbation theory, then the results were compared with the ex-

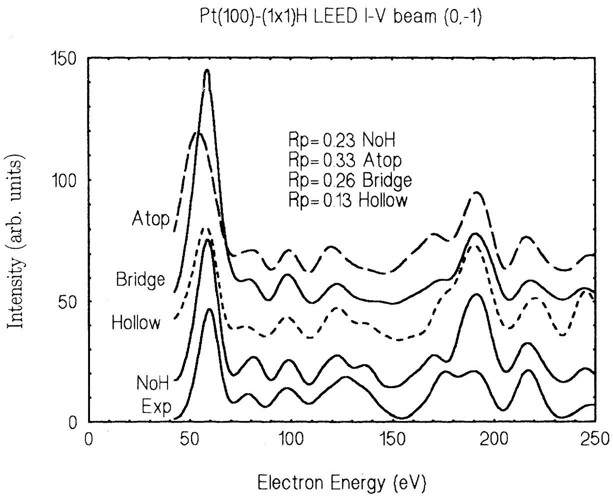

FIG. 3. Comparison of theoretical curves for the four different models with experiment for beam (0,−1) at the minimum of R_p.

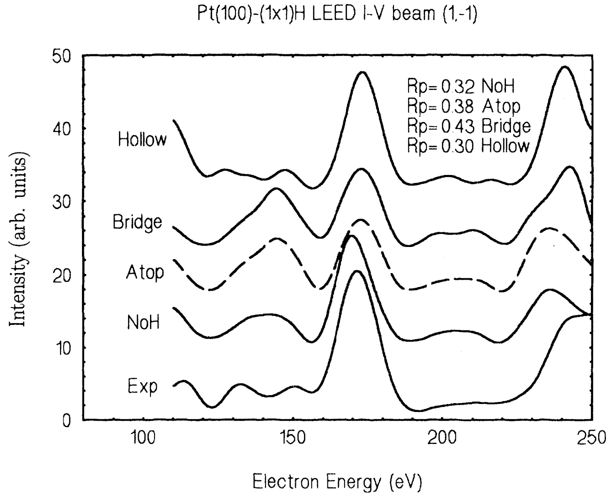

FIG. 4. Comparison of theoretical curves for the four different models with experiment for beam $(1,-1)$ at the minimum of R_p.

periment. The Pendry R factor (reliability factor)[13] R_p was used as a criterion for the comparison between theory and experiment. This factor is more sensitive to the positions of peaks and dips than the relative intensities. The optimum positions of atoms were searched automatically within a convergence radius (about 0.2 Å for Pt and larger than 0.4 Å for H), and the surface inner potential varied by the program until the minimum of R_p was found. The error introduced by the tensor LEED search was about 0.01 Å for each structural parameter. This is smaller than those caused by experimental errors, and inaccuracies in the theoretical models which are around 0.02–0.03 Å. Considering the total-energy range (460 eV, which is about half of the normal energy range) used for our comparison, we estimate an error for each fitting parameter of 0.05 Å, which is two times the mean value of 0.02 and 0.03. To explore the possible ordered or disordered surface structure, four different surface model structures were calculated in the first step. Considering the small scattering effects of hydrogen, model 1 neglects the hydrogen diffraction and assumes that the Pt(100) surface takes a form of an ideal bulk. Model 2 assumes an ordered (1×1) hydrogen at an atop site on an ideal Pt(100) surface, and an initial guess of a H—Pt bond length of 2.0 Å was used. Models 3 and 4 are similar to model 2, except that the hydrogen has been assumed to occupy the bridge and fourfold hollow sites, respectively. Figure 2 shows the top view of an ideal Pt(100)-(1×1) surface, and indicates the three different hydrogen positions used in the calculations. During the tensor LEED calculations, the full symmetry of the surface was retained and, as a result, the atoms were only allowed to deviate perpendicularly to the surface ([100] direction). The calculation results show that within the convergence range of atomic displacements, models 1 and 4 gives the equal smallest overall $R_p(0.28)$ among the four models. The other two models (atop and bridge) gave minimum overall R_p of 0.35 and 0.31, respectively. Results for the comparisons between theory and experiment for the four models are shown in Figs. 3, 4, and 5 for different diffraction beams $(0,-1)$, $(1,-1)$, and (2,0) (where NoH indicates model 1). Also shown in the figures are the individual R_p of each comparison between theoretical and experimental curves. It can be seen from the comparisons that visually all model calculations give good agreements with experiment. It also can be seen that model 1 (NoH) gave relatively uniform small Pendry R factors for all beams, while model 4 (the hollow site) gave a very small R_p (0.13) for beam $(0,-1)$ but a rather large R_p (0.54) for beam (2,0) due to the antiphase that occurred at 155 eV. The discontinuity of the R factors for different beams in model 4 indicates that this model is not a correct one, and we conclude that the surface is most likely a disordered atomic hydrogen-stabilized Pt(100)-(1×1) surface. The results justify the using of model 1, which neglects the influence of hydrogen in the calculation. Table I gives comparisons of interlayer distances between those obtained from calculations at the minimum R_p for model 1, with an optimum inner potential of 8.0 eV, and those of the ideal bulk of Pt(100). It shows small deviations or relaxations for the substrate

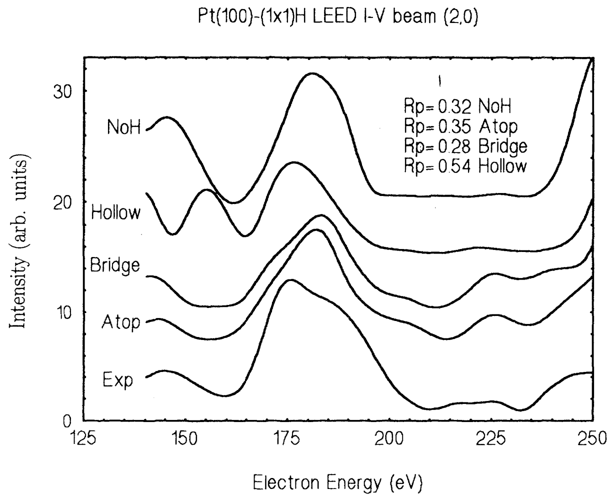

FIG. 5. Comparison of theoretical curves for the four different models with experiment for beam (2,0) at the minimum of R_p.

TABLE I. Comparison of interlayer distances between those obtained from calculations at the minimum of R_p using model 1, and those of the ideal bulk.

Interlayer distance (Å)	Ideal bulk d	At minimum R_p $D(\pm0.05$ Å)	Change $(D-d)$	Ratio $(D-d)/d(\pm2.6\%)$
d_{12}	1.96	2.02	0.06	3.1%
d_{23}	1.96	1.96	0.00	0.0%
d_{34}	1.96	2.03	0.07	3.6%
d_{45}	1.96	1.91	−0.05	−2.6%

Pt(100) interlayer spacings. We found that the spacing between the first and second Pt layers expanded 3.1%±2.6%, and this is in agreement with earlier studies[6] which gave an d_{12} increase of 0.8% for a hydrogen-saturated Pt(100)-(1×1) surface. The spacing between the second and third Pt layers (d_{23}) remained roughly unchanged, while the spacing between the third and fourth Pt layers (d_{34}) expanded 3.6%±2.6%, and finally the spacing between the fourth and fifth Pt layers (d_{45}) contracted 2.6%±2.6%.

IV. CONCLUSIONS

From the above discussions, it is clearly shown that dissociated hydrogen adsorption on a reconstructed Pt(100)-hex surface can induce a complete phase transition to a disordered atomic hydrogen-stabilized Pt(100)-(1×1) structure. The tensor LEED method can be used in determining the substrate surface relaxations, and we calculated the interlayer spacing changes down to the fifth layer.

ACKNOWLEDGMENTS

We would like to thank Professor M. A. Van Hove of the Lawrence Berkeley Laboratory for providing the tensor LEED routines and the phase shifts used in the calculation. This work was jointly supported by the State Educational Committee of China and the Natural National Science Foundation of China.

---

*Author to whom all correspondence should be addressed. Fax:(86-1)-2562605. Electronic address: usersf02@aphy01.iphy.ac.cn

[1] K. Christmann, Surf. Sci. Rep. **9**, 1 (1988).

[2] M. A. Van Hove, R. J. Koestner, P. C. Stair, J. P. Biberian, L. L. Kesmodel, I. Bartos, and G. A. Somorjai, Surf. Sci. **103**, 189 (1981).

[3] P. Heilmann, K. Heinz, and K. Müller, Surf. Sci. **83**, 487 (1979).

[4] B. Klötzer and E. Bechtold, Surf. Sci. **295**, 374 (1993).

[5] H. B. Nielsen and D. L. Adams, Surf. Sci. **97**, L351 (1980).

[6] J. A. Davies, T. E. Jackman, D. P. Jackson, and P. R. Norton, Surf. Sci. **109**, 20 (1981).

[7] C. M. Sayers, Surf. Sci. **143**, 411 (1984).

[8] I. P. Batra, J. A. Barker, and D. J. Auerbach, J. Vac. Sci. Technol. A **2**, 943 (1984).

[9] Xiamoming Hu and Zhangda Lin, Chin. Phys. Lett. **11**, 498 (1994).

[10] Xiaoming Hu and Zhangda Lin, Phys. Rev. B **51**, 10 164 (1995).

[11] P. J. Rous, M. A. Van Hove, and G. A. Somorjai, Surf. Sci. **226**, 15 (1990).

[12] A. Wander, M. A. Van Hove, and G. A. Somorjai, Phys. Rev. Lett. **67**, 626 (1991).

[13] J. B. Pendry, J. Phys. C **13**, 937 (1980).

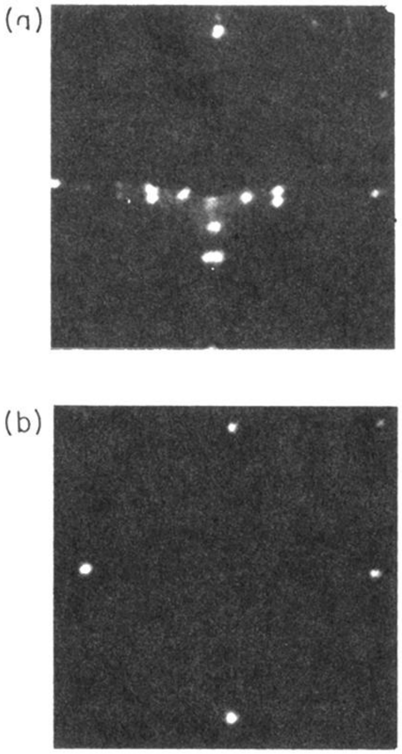

FIG. 1. (a) LEED pattern of Pt(100)-hex at 50 eV. (b) LEED pattern of Pt(100)-(1×1)H at 60 eV.