PHYSICAL REVIEW B VOLUME 41, NUMBER 2 15 JANUARY 1990-I

Hydrogen adsorption on Si(100)-2 × 1 surfaces studied by elastic recoil detection analysis

Kenjiro Oura, Junji Yamane,[*] Kenji Umezawa,[†] Masamichi Naitoh,
Fumiya Shoji, and Teruo Hanawa[‡]
Electron Beam Laboratory, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

(Received 30 May 1989; revised manuscript received 31 July 1989)

Hydrogen adsorption on a clean Si(100)-2 × 1 surface has been studied by the high-energy ion-beam method (6-MeV F^{3+}) combined with low-energy electron diffraction. We report that (1) the saturation coverage of hydrogen on a clean Si(100)-2 × 1 surface kept at room temperature is 1.85±0.18 monolayers (ML), and (2) the first 1-ML hydrogen adsorbs rather quickly, leading to a 2 × 1-H phase, while adsorption of more hydrogen beyond 1 ML occurs very slowly, approaching a saturated structure of 1 × 1-H. The effect of substrate temperatures on adsorption is also studied.

Hydrogen adsorption is one of the most fundamental processes in adsorbate-substrate interactions, and various surface-sensitive techniques have been extensively applied.[1] However, owing to the difficulty in the detection of surface hydrogen by conventional electron-spectroscopic methods, absolute coverage information is usually lacking in such adsorption studies. In this paper we have applied, for the first time, elastic recoil detection analysis (ERDA) to a quantitative analysis of hydrogen adsorbed on clean Si(100)-2 × 1 surfaces. On the basis of the ERDA experiment using a 6-MeV F^{3+}-ion beam combined with low-energy electron-diffraction (LEED) observations, we report that (1) the saturation coverage of hydrogen on the clean Si(100)-2 × 1 surface kept at room temperature (RT) is 1.85+0.18 monolayers (ML), where 1 ML is defined to be 6.78×10^{14} cm^{-2}, the ideal Si density in the (100) plane, and (2) the first 1 ML hydrogen adsorbs rather quickly onto the clean Si surface, leading to a 2 × 1-H structure, while the adsorption of more hydrogen beyond 1 ML occurs very slowly, approaching a saturated adsorption structure of a 1 × 1-H phase. The effect of substrate temperatures on hydrogen coverage is also studied. The present method is simple, reliable, and nondestructive for a quantitative detection of surface hydrogen, and therefore can be applied to many kinds of more complicated adsorption systems in which absolute coverage information is desirable.

Quantitative analysis of adsorbed hydrogen or deuterium has so far been carried out by the use of high-energy ion beams.[2] Nuclear-reaction analysis (NRA) of a ^{3}He-ion beam (750-keV energy) with deuterium, D(^{3}He,*p*)^{4}He, has been applied to D/Ni(111),[3] D/Si(111)-7 × 7,[4] and D/Si(100)-2 × 1 (Refs. 5 and 6) systems. This nuclear reaction of ^{3}He, however, cannot be applied to the analysis of hydrogen. A resonant nuclear-reaction analysis (RNRA) of a ^{15}N-ion beam of 6.385-MeV energy, ^{1}H(^{15}N, $\alpha\gamma$)^{12}C, has been recently used[7] to detect hydrogen adsorbed on a clean W(100) surface.

As for a clean Si(111)-7 × 7 surface, Culbertson *et al.*[4] have investigated, using D(^{3}He,*p*)^{4}He, the deuterium coverage as a function of D_2 exposure and determined a correlation between the coverage and LEED patterns. A saturation coverage of 1.25±0.13 ML was also established by them. Much less is reported for the D/Si(100)-2 × 1 system, although only saturation coverages of 1.5 and 1.7±0.25 ML have been shown by Feldman *et al.*[5] and Narusawa and Gibson,[6] respectively. No correlation of the deuterium coverage and D_2 exposure has been established as yet. Furthermore, there seems to be no such study for hydrogen, or deuterium, on Si(100) and Si(111) surfaces. In this study, we have applied another well-known ion-beam technique of ERDA to determine the hydrogen coverage adsorbed on a clean Si(100)-2 × 1 surface.

ERDA has been widely used for depth profiling of hydrogen involved in thin films or subsurface regions of solids.[8] In ERDA, the number of hydrogen particles recoiled by the primary ion beam through a classical binary-collision process is directly measured. Since the recoil process caused by heavy ions can be quantitatively well described by the so-called Rutherford-scattering cross-section formula, ERDA is a simple and straightforward method for hydrogen analysis, and its analytical quantification is highly reliable for such analysis, just as Rutherford-backscattering spectrometry is in heavy-element analysis. Among several high-energy ion-beam techniques available for hydrogen detection, another strong point of ERDA is its large scattering cross section, which means that possible damage or desorption by the probe beam can be significantly reduced as described later. In spite of these strong points, so far ERDA has been applied only to the analysis of thin films, and not to the analysis of surface hydrogen. Our present study has proved ERDA as a powerful method of surface-hydrogen detection.

Experiments were performed in an ultrahigh-vacuum chamber (base pressure of 2×10^{-10} torr). A 6-MeV beam of F^{3+} ions from a tandem accelerator impinges on the specimen. The beam is collimated upstream to a size of 3 mm, and the current is about 3 particle nanoamperes (*p* nA). Particles recoiling or scattered from the specimen enter an Al film (thickness of 5.7 μm) placed just in front of a silicon surface barrier detector (SSBD). The SSBD is at 40° to the beam direction and 3 cm away from the specimen. Heavy particles other than recoiled hydrogen, i.e., scattered F and recoiled Si, are stopped in the Al film, and only H particles enter the SSBD. An absolute calibration of the system has been carefully carried out[9–11] through the use of standard specimens consisting of several calibrated concentrations of hydrogen and deuterium implanted at low energy (4 and 8 keV) into Si. In addition, a simultaneous measurement by ERDA and RNRA of ^{1}H(^{19}F,$\alpha\gamma$)^{16}O, both carried out using a F^{3+}-ion beam as reported before,[9,11] agrees well within experimental error. Thus, the overall accuracy of our present measurement of hydrogen coverage can be estimated to be less than 10%. Additional experimental details will be reported elsewhere.[12]

A P-doped, 8-Ω cm, $8\times20\times0.5$-mm^3 Si(100) wafer was preoxidized and cleaned *in situ* by direct current heating at 1000 °C under a base pressure of 3×10^{-10} torr. After the cleaning, a sharp 2×1 LEED pattern was observed. A 1800-°C tungsten filament, 12 cm from the Si surface, was used to dissociate molecular hydrogen ($P_{\mathrm{H2}}=1\times10^{-6}$ or 2×10^{-7} torr) during adsorption. Hydrogen coverages at various stages of adsorption were obtained at an incident charge of 2 μC, which corresponds an ion dose of 2.0×10^{13} F^{3+} ions/cm^2. The effect of the probe beam on the desorption of hydrogen was experimentally confirmed[12] to be about 2% for each coverage measurement.

Figure 1 is a measured concentration or coverage of adsorbed hydrogen atoms plotted against the exposure of hydrogen molecules for activated hydrogen adsorption onto a Si(100)-2×1 clean surface at RT. As we can see, the adsorption curve reveals a rather sharp break point at about 25 L (1 L=1 langmuir$\equiv10^{-6}$ torr sec) exposure, where the coverage is roughly 1 ML. In the initial stage of adsorption below 25 L exposure (or below 1 ML coverage), hydrogen adsorption takes place rather quickly and almost linearly, while adsorption over 1 ML occurs very slowly toward a saturation coverage of about 1.85±0.18 ML above 1200 L exposure. LEED patterns corresponding to the coverage of 1 ML [point (b) of Fig. 1] and the full coverage [point (c)] are 2×1 and 1×1 periodicity, as reproduced in Figs. 2(b) and 2(c), respectively. These observations strongly support a hydrogen-adsorption model which has been proposed by Sakurai and Hagstrum[13] and widely accepted in many studies.[1] Atomic hydrogen initially bonds to a dangling bond without changing the 2×1 superstructure. Since there is one dangling bond per surface Si atom in the generally accepted 2×1 dimer model,[14] bonding of H to all available bonds produces the Si(100)-2×1-H monohydride phase at a coverage of 1 ML just as observed here. Adsorption of more atomic hydrogen results in the break of the Si—Si dimer bond accompanied by the bonding of H atoms to each of additional dangling bonds thus formed, producing the Si(100)-1×1-H dihydride phase at a coverage of 2 ML. Our present study has generally supported the above model and has shown that the formation of the monohydride phase takes place more quickly than that of the dihydride phase and that the saturation coverage of the dihydride phase is 1.85±0.18 ML, a value slightly smaller than the expected value of 2 ML, but a little larger than those observed previously, 1.5 ML (Ref. 5) or 1.7±0.25 ML (Ref. 6).

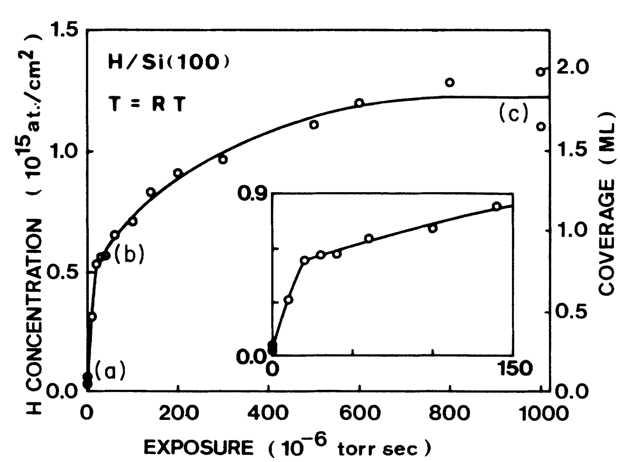

FIG. 1. Hydrogen concentration (coverage) on a Si(100)-2×1 surface kept at RT plotted against H_2-gas exposure. LEED patterns observed at points (a), (b), and (c) are reproduced in Figs. 2(a), 2(b), and 2(c), respectively.

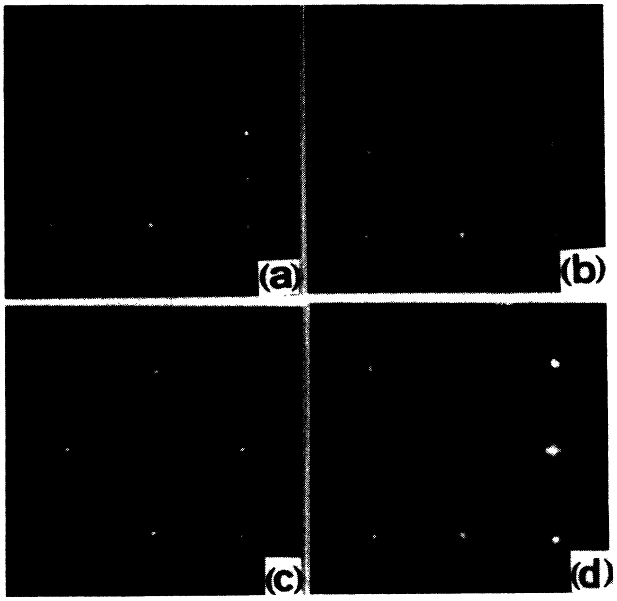

FIG. 2. LEED patterns taken from (a) clean Si(100)-2×1 (45 eV), (b) Si(100)-2×1-H (45 eV), (c) Si(100)-1×1-H (45 eV), and (d) Si(100)-3×1-H (57 eV).

Chabal and Raghavachari[15] have proposed, based on their high-resolution infrared data, that the so-called Si(100)-1×1-H dihydrized surface is in fact a disordered phase with roughly half of the H bonded in a monohydride configuration and half in a dihydride one. In addition, they have found a new ordered structure of the 3×1-H phase which involves alternating monohydride and dihydride units, giving a natural explanation for the

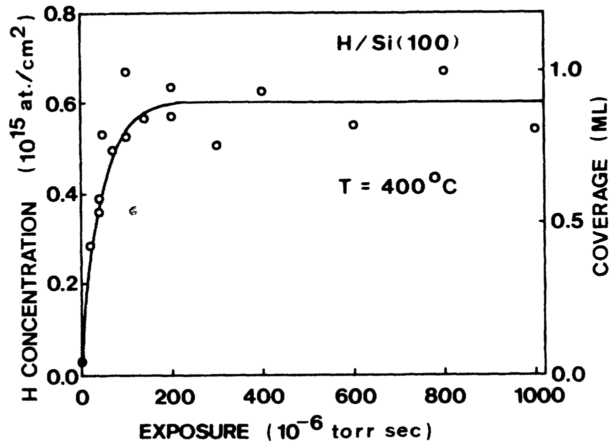

FIG. 3. Hydrogen concentration (coverage) as a function of H_2-gas exposure onto a heated Si(100) substrate at 400 °C. LEED pattern observed in the saturation stage is Si(100)-2×1–H [the same as Fig. 2(b)].

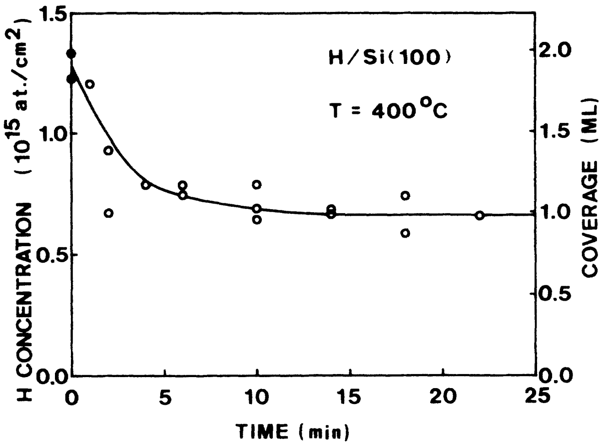

FIG. 4. Isothermal desorption of hydrogen from a Si(100) surface at 400 °C. The initial and final stages correspond to the Si(100)-1×1–H and Si(100)-2×1–H phases, respectively.

saturation coverage of 1.5 ML reported by Feldman, Silverman, and Stensgaard.[5] We have also obtained the 3×1-H phase upon saturation exposure at around 100 °C, as reproduced in Fig. 2(d). The hydrogen coverage for this surface has been determined to be about 1.7 ML. Thus, our present observation shows that the 3×1-H phase has less hydrogen than the so-called 1×1-H dihydride phase, and more detailed structural models are not yet attainable.

By assuming that all molecular hydrogen incident to the hot filament dissociates at 1800 °C and by knowing the filament area and the solid angle subtended by the sample, the flux of atomic hydrogen incident to the sample was estimated to be about 6×10^{13} atoms/L cm^2. Thus, the sticking coefficient of atomic hydrogen has been determined to be about 0.6 in the initial stage of adsorption below 25 L and then gradually decreases with the increase in the exposure, approaching values smaller than 0.1 above 300 L exposure.

Finally, we discuss the effect of substrate temperatures on the hydrogen adsorption. Shown in Fig. 3 is a result for adsorption at 400 °C, indicating the saturation coverage of 1 ML with the corresponding 2×1 LEED pattern. Stucki *et al.*[16] have shown, based on their high-resolution electron-energy-loss spectroscopy data, that adsorption at an elevated temperature (350 °C) results in only monohydride formation. Our present results, shown in Fig. 3, support the interpretation of Stucki *et al.* and reveal that all dangling bonds available for the monohydride phase are in fact occupied by atomic hydrogen, as expected. Figure 4 shows that heat treatment at 400 °C gives rise to the transformation from the 1×1-H dihydride phase initially saturated at RT to the 2×1-H monohydride phase. It is also found that thermal desorption of hydrogen in the 2×1-H monohydride phase takes place over 500 °C, in agreement with previous works.[1]

In summary, the adsorption of hydrogen on the clean Si(100)-2×1 surface was studied by ERDA and LEED. Absolute coverage was determined as a function of exposure and correlated with LEED patterns. It has been shown that about 1 ML hydrogen adsorption of the 2×1-H monohydride phase takes place more quickly than the subsequent adsorption of the 1×1-H dihydride phase, the saturation coverage being 1.85±0.18 ML. Since the ERDA method described in this paper is a simple, reliable, and nondestructive method for surface-hydrogen detection, it can be applied to many kinds of adsorption and coadsorption studies in which absolute coverage information is desirable. A coadsorption study of metal and hydrogen on clean Si surfaces is in progress in our laboratory and we plan to report results in the near future.

Part of this work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

---

[*] Present address: Sony Corporation, Atsugi, Kanagawa, Japan.

[†] Present address: College of Integrated Arts and Science, University of Osaka Prefecture, Sakai, Osaka, Japan.

[‡] Present address: Osaka Institute of Technology, Asahiku, Osaka, Japan.

[1] For example, see H. Froitzheim, in *The Chemical Physics of Solid Surface and Heterogeneous Catalysis*, edited by D. A. King and D. P. Woodruff (Elsevier, Amsterdam, 1988), Vol. 5.

[2] J. F. Ziegler, C. P. Wu, P. Williams, C. W. White, B. Terreault,

B. M. U. Scherzer, R. L. Schulte, E. J. Schneid, C. W. Magee, E. Ligeon, J. Lecuyer, W. A. Lanford, F. J. Kuehne, B. L. Cohen, G. L. Clark, W. K. Chu, C. Brassard, R. S. Blewer, R. Behrisch, B. R. Appleton, and D. D. Allred, Nucl. Instrum. Methods **149**, 19 (1978).

[3] K. Mortensen, F. Besenbacher, I. Stensgaard, and W. R. Wampler, Surf. Sci. **205**, 433 (1988).

[4] R. J. Culbertson, L. C. Feldman, P. J. Silverman, and R. Haight, J. Vac. Sci. Technol. **20**, 868 (1982).

[5] L. C. Feldman, P. J. Silverman, and I. Stensgaard, Nucl. Instrum. Methods **168**, 589 (1980).

[6] T. Narusawa and W. M. Gibson, J. Vac. Sci. Technol. **17**, 256 (1980).

[7] Y. Iwata, F. Fujimoto, E. Vilalta, A. Ohtsuka, K. Komaki, K. Kobayashi, H. Yamashita, and Y. Murata, Jpn. J. Appl. Phys. **26**, L1026 (1987).

[8] J. L'Ecuyer, C. Brassard, C. Cardinal, J. Chabbel, L. Deschenes, J. P. Labrie, B. Terreault, J. G. Martel, and R. G. St-Jacques, J. Appl. Phys. **47**, 381 (1976).

[9] K. Umezawa, A. Kitamura, and S. Yano, Nucl. Instrum. Methods B **28**, 377 (1987).

[10] K. Umezawa, T. Kuroi, J. Yamane, F. Shoji, K. Oura, T. Hanawa, and S. Yano, Nucl. Instrum. Methods B **33**, 634 (1988).

[11] K. Umezawa, J. Yamane, T. Kuroi, F. Shoji, K. Oura, and T. Hanawa, Nucl. Instrum. Methods B **33**, 638 (1988).

[12] K. Oura, K. Umezawa, J. Yamane, M. Naitoh, F. Shoji, and T. Hanawa (unpublished).

[13] T. Sakurai and H. D. Hagstrum, Phys. Rev. B **14**, 1593 (1976).

[14] J. D. Levine, Surf. Sci. **34**, 90 (1973).

[15] Y. J. Chabal and K. Raghavachari, Phys. Rev. Lett. **54**, 1055 (1985).

[16] F. Stucki, J. A. Schafer, J. R. Anderson, G. J. Lapeyre, and W. Göpel, Solid State Commun. **47**, 795 (1983).

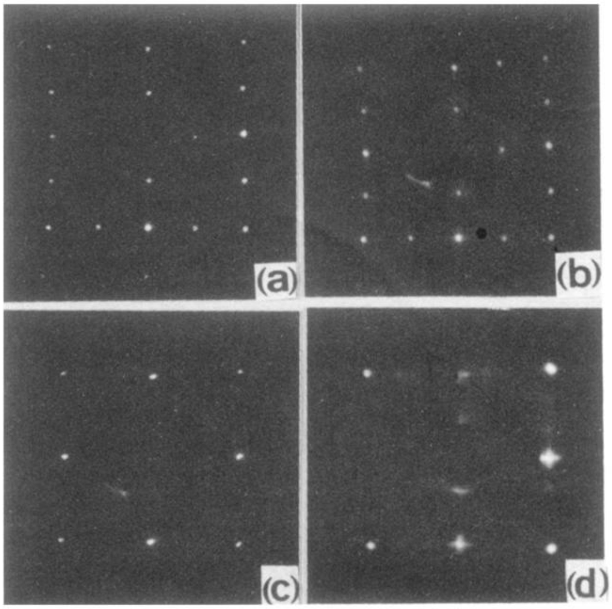

FIG. 2. LEED patterns taken from (a) clean Si(100)-2×1 (45 eV), (b) Si(100)-2×1–H (45 eV), (c) Si(100)-1×1–H (45 eV), and (d) Si(100)-3×1–H (57 eV).