PHYSICAL REVIEW B VOLUME 27, NUMBER 7 1 APRIL 1983

Electronic structures of the monohydride (2×1):H and the dihydride (1×1)::2H Si(001) surfaces studied by angle-resolved electron-energy-loss spectroscopy

Shigemitsu Maruno, Hiroshi Iwasaki, Keiji Horioka, Sung-Te Li, and Shogo Nakamura
The Institute of Scientific and Industrial Research, Osaka University,
Mihogaoka, Ibaraki-shi, Osaka 567

(Received 11 June 1982)

We have identified the monohydride Si(001)-(2×1):H surface and the dihydride Si(001)-(1×1)::2H surface by angle-resolved electron-energy-loss spectroscopy and elastic low-energy electron diffraction. On the monohydride (2×1):H surface the S_3 transition from the back-bond surface state was distinctly observed although the S_1 transition from the dangling-bond surface state disappeared, while on the dihydride (1×1)::2H surface both the S_3 and the S_1 transitions completely disappeared. These facts show that on the monohydride surface the subsurface strain due to dimerization remains; on the other hand, on the dihydride surface the strain is healed out. The hydrogen-induced transitions for the two surfaces were clearly distinguished; the transition energy for the (2×1):H surface (SH_1) was 8.0 eV and that for the (1×1)::2H surface (SH_2) increased from 7.0 to 7.5 eV with increasing $|k_{\parallel}|$ due to dispersion. The present results support and develop the models for the monohydride and the dihydride surfaces proposed by Sakurai and Hagstrum.

I. INTRODUCTION

Since the early study of low energy electron diffraction (LEED) with a clean silicon (001) surface by Schlier and Farnsworth[1] the structural and electronic properties of such a surface have been investigated in a large number of experimental and theoretical studies. Recently it has been reported that a clean well-ordered Si(001) surface shows a reconstructed $c(4\times2)$ superstructure by LEED (Ref. 2) and atomic-beam diffraction.[3,4] However, quarter-order beams are very weak and the LEED pattern expected for the two-domain (2×1) reconstruction is usually observed. Appelbaum, Baraff, and Hamann[5] showed that dimerization of atoms on the surface layer associated with the subsurface strain in the first five layers gave a good account of the surface density of states observed by ultraviolet photoemission spectroscopy (UPS),[6] but their calculation led to the conclusion that the surface character is metallic. Chadi[7] has shown that deformation of the dimer increases the band gap between the surface states near the valence-band maximum, decreases the total energy, and makes the surface semiconductive. Verwoerd[8] also showed the possibility of the deformed dimerization by cluster calculation. Chadi[9,10] has shown that the additional relaxation of the first five layers lowered the total energy substantially.

So far, hydrogen-adsorbed silicon surfaces have been investigated to gain more insights into the structure of reconstructed silicon surfaces.[11-13] Ibach and Rowe[11] studied the adsorption of atomic hydrogen on a Si(001)-(2×1) surface by electron-loss spectroscopy (ELS). Sakurai and Hagstrum[12] reported that the adsorption of hydrogen on a Si(001) surface resulted in a surface which had a 1×1 LEED pattern. They also proposed models of the monohydride phase Si(001)-(2×1):H and the dihydride phase Si(001)-(1×1)::2H by UPS measurements.[12]

Moreover, hydrogen-covered silicon surfaces are interesting systems for investigating the role of hydrogen included in amorphous Si:H films.[14]

The angular distribution of elastically and inelastically diffracted electrons from a well-ordered surface include data on atomic and electronic structures of the surface.[15,16] Measurements of the angular dependence of energy-loss peaks due to plasmon losses and one-electron excitations give us the information of dispersion relations of plasmons and band structures, respectively.[15] Data on band structures available by angle-resolved electron-energy-loss spectroscopy (AR-ELS) include dispersion of empty states as well as filled states.

In this paper we investigate the adsorption of atomic hydrogen on the clean Si(001)-(2×1) surface. We identified the monohydride (2×1):H surface and the dihydride (1×1)::2H surface for the hydrogen-adsorbed Si(001) surfaces by measuring angle-resolved electron-energy-loss profiles and elastic low-energy electron diffraction.[17] These two surfaces could not be distinguished by angle-integrated electron-energy-loss spectroscopy.[11,18]

II. EXPERIMENTAL PROCEDURES

The experiments were performed in a diffusion-pumped stainless-steel system, the base pressure of which ranged below 1×10^{-8} Pa upon baking at 150 °C. It consists of two stages: The upper stage for LEED and Auger electron spectroscopy (AES) measurements and the lower stage for angle-resolved electron spectroscopy measurements. The samples used in this study were cut from a single crystal of a *p*-type (boron-doped semiconductor-device-grade silicon wafer ($4\times9\times0.4$ mm^3) with a resistivity of 20 Ω cm.

The samples were prepared by etching in a H_2O_2-NH_4OH mixture, dissolving the oxide layer so formed in HF, the etching in a H_2O_2-HCl mixture as described by Henderson.[19] In this study the sample was resistively heated by a dc current passing through it. The temperature of the samples was roughly estimated by an optical pyrometer for the higher-temperature range and by measuring the conductivity for the lower-temperature range; the temperature estimated by the measurement of conductivity was compared with the optical-pyrometer readings at intermediate temperatures. The sample surface was cleaned by heating to 1250 °C for a few minutes at pressure not greater than 1×10^{-7} Pa. After the heat treatment the ratio of the Auger-derivative peak-to-peak height of the carbon signal to that of the 92-eV Si-*LVV* signal could be reduced to 7×10^{-4} by AES using four-grid LEED optics. The surface flatness was assured by the eye.

AR-ELS measurements were performed using an angle-resolved electron-energy spectrometer of our own design. The electron-energy analyzer is a 157° spherical electrostatic deflector with a mean radius of 50.25 mm. The angular resolution in the plane of incidence is 0.5° and perpendicular to this direction is 2.0°. The halfwidth in energy ΔE of the elastically diffracted beam was 0.5 eV. The magnetic field was canceled by three pairs of Helmholtz coils below 10 mG.

Molecular hydrogen was introduced into the chamber by heating a palladium tube in 1-atm hydrogen gas. The hydrogen adsorption on the sample surface was attained by atomic hydrogen produced from molecular hydrogen dissociated at a tungsten filament heated to 1700 °C. The proportion of atomic hydrogen present in the adsorbing gas was unknown in this study. The rate of atomic-hydrogen exposure was controlled by adjusting the partial pressure of molecular hydrogen introduced to the system. The monohydride (2×1):H surface was produced by heating the sample to about 350 °C during atomic-hydrogen exposure in hydrogen at a pressure of 10^{-3} Pa for 6 min, while separating the filament from the sample surface by about 20 cm, and after evacuating the hydrogen the sample was quenched to room temperature. The dihydride (1×1)::2H surface was obtained by exposing the initial clean surface held at room temperature to atomic hydrogen in hydrogen at a pressure of 10^{-3} Pa for 30 min. In this study the monohydride (2×1):H surface was produced by exposing the clean surface heated to 350 °C to atomic hydrogen. We could not form the uniform monohydride (2×1):H surface by exposing the clean surface at room temperature to atomic hydrogen. In this case there exists a hydrogen-covered Si(001) surface which has a sharp (2×1) LEED pattern although the atomic and electronic structures of such a surface are different from the (2×1):H surface obtained by the method described above. The properties of the hydrogen-adsorbed Si(001) surface attained at room temperature will be reported elsewhere.

Mass spectra taken during hydrogen exposure showed that the largest impurity was H_2O, and it was typically below 2×10^{-7} Pa after the sufficient purge of the vacuum system by bleeding hydrogen into it while heating the tungsten filament to 1700 °C. Auger electron spectra taken after atomic-hydrogen adsorption in 2.6×10^{-3} Pa of H_2 for 30 min showed no oxygen signal but the carbon Auger peak-to-peak height was about twice as large as that on the clean surface. All measurements were made at room temperature and the pressure during measurements after the hydrogen exposure was 2.6×10^{-7} Pa where the residual gas was predominantly hydrogen. We could not detect a measurable change of the ELS spectra of the hydrogen-covered surfaces after prolonged measurements for about 0.5 h, probably due to the low sticking coefficient of molecular hydrogen on Si.

The elastic low energy electron diffraction was measured for the clean (2×1), the monohydride (2×1):H, and the dihydride (1×1)::2H surfaces, using the spherical energy analyzer described above. The Ewald construction enables one to determine the incident angle θ_i and exit angle θ_s, at which electrons leave the target measured from the surface normal within an accuracy of 0.5°. The elastic intensity profiles (*I-V* curves) for specularly reflected 00 beam were collected for the primary energy E ranging from 30 to 220 eV. The general shape of the curves for the clean Si(001) surface agrees with that reported by Ignatiev *et al.*[20] (very well at the same angle of incidence and azimuthal direction). The primary-beam current was about 0.06 nA for the elastic LEED measurements and below 0.1 μA for AR-ELS measurements. Electron-energy-loss spectra were taken as second-derivative loss spectra by modulating the deflection voltage ($1.1V_{p\text{-}p}$) and observing the second harmonic.

III. RESULTS AND DISCUSSIONS

Energy-loss profiles for the clean 2×1 surface are shown in Fig. 1. The incident angle $\theta_i=23.5°$ and the azimuth corresponds to the [110] crystallographic direction ($\phi=0°$). The primary-beam energy is adjusted at the 008 Bragg peak which is 77.9 eV for this incident angle. The Bragg peak is examined to be strong and relatively free from dynamical structure by I-V curve measurements. The incident condition with the primary energy at such a Bragg peak is suited for AR-ELS measurements because for the incident condition the inelastic diffraction process can be considered as the two-step process in the kinematical framework and the kinematical model analysis of the AR-ELS data is valid.[15,16] The energy positions and source identification of these features are given at the bottom of Fig. 1 according to the work of Rowe and Ibach.[21] The angular dependence of intensities and energy locations of loss peaks, which originate from one-electron exitations, is clearly seen in Fig. 1. The sharpest peak is the S_1 transition, the initial state of which has been ascribed to the dangling-bond state at energy near the top of the valence band.[21] The peaks S_2 and S_3 are due to transitions from back-bond surface states which originate from the subsurface strain. The S_3 peak is only seen as a shoulder of bulk plasmon in the angle-integrated ELS spectra of Rowe and Ibach.[11] E_1 and E_2 are bulk-band transitions near the surface in the selvedge of the crystal. The E_1 peak is stronger than the E_2 peak around the specular direction, but the former is weaker than the latter away from the specular direction. In addition to these facts the surface-plasmon dispersion is evident in Fig. 1 from the shift of the surface-plasmon loss peak. We have reported these results of AR-ELS from the clean (001)-(2×1) surface[15] and have shown that AR-ELS provide a useful method to survey the dispersions of the states between which one-electron transition occurs.

Figure 2 represents the angular distributions of elastically diffracted electrons for (a) the clean (b), the (2×1):H, and (c) the (1×1)::2H surfaces, respectively, with a primary energy of 100 eV and the incidence angle around 21°. The ratio of the $\frac{1}{2}$ 0-beam intensity to the 00-beam intensity on the monohydride (2×1):H surface is larger than that on the clean surface. The LEED pattern of the

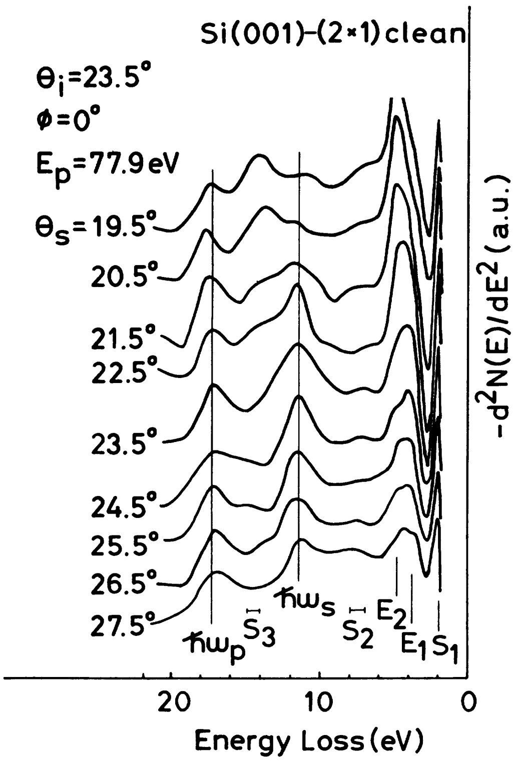

FIG. 1. Angle-resolved electron-energy-loss profiles for the clean Si(001)-(2×1) reconstructed surface measured at the 77.9-eV Bragg-type peak in the [110] azimuth ($\phi=0°$) at $\theta_i=23.5°$.

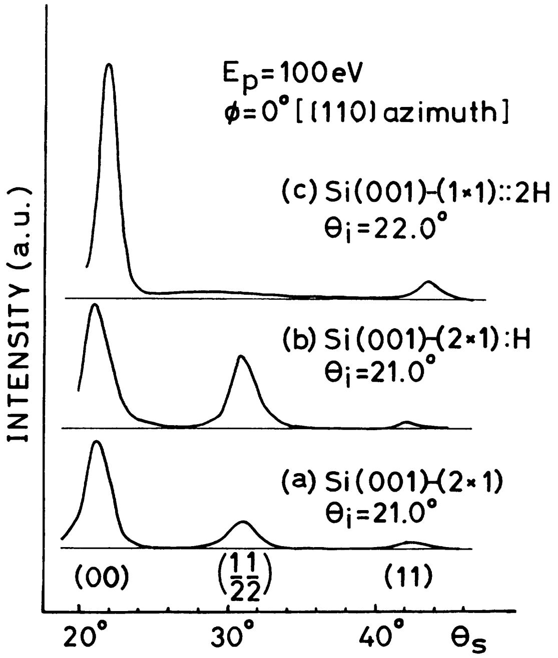

FIG. 2. Angular distribution of elastically diffracted electrons for (a) clean, (b) (2×1):H, and (c) (1×1)::2H surfaces. Primary-electron-beam energy is 100 eV.

(2×1):H surface was sharp and the half-order spots were indeed intensified at a primary-beam energy of 100 eV. We consider that the asymmetric dimer of the clean Si(001) surface, formed by superposition of a Jahn-Teller distortion and pair bonding,[8] is probably reconstructed to the symmetric dimer with hydrogen adsorption. The adsorption of hydrogen on the first-layer atoms, which results in a Si—H covalent bond,[22] would remove the driving force for the asymmetric dimer. From Fig. 2(c) it is evident that the $\frac{1}{2}$ 0 beam has completely disappeared and the hydrogen-induced unreconstructed structure has been built up. The LEED pattern of the (1×1)::2H surface was also sharp.

Figure 3 represents *I-V* curves of the 00 beam for (a) the clean, (b) the (2×1):H, and (c) the (1×1)::2H surfaces. As far as we know, we have, for the first time, obtained the *I-V* curve for the monohydride (2×1):H surface. The (2×1):H surface establishes a complicated *I-V* structure. Fractional-order peaks, which should be forbidden from the bulk space group of Si, are intensified compared with the clean surface. The 008 Bragg peak of the (2×1):H and the (1×1)::2H surfaces shifted to the higher-energy side of the clean (2×1) surface should be approximately the same amount. The *I-V* curve for the (1×1)::2H surface agrees well with the experimental results by White *et al.*[23–25] They concluded from their analysis of LEED *I-V* spectra that the Si(001)(1×1)::2H surface should be an unreconstructed bulklike structure. Tromp *et al.*[25] also find from their medium-energy-ion—scattering (MEIS) measurements that the (1×1)::2H surface is an isotropically ordered, but slightly inward, relaxed surface. In this study we could easily distinguish the clean (2×1) surface, the monohydride (2×1):H surface, and the 1(× 1)::2H surface by their characteristic *I-V* profiles.

The schematic models of the clean Si(001)-(2×1), the monohydride (2×1):H, and the dihydride (1×1)::2H surfaces are illustrated on the basis of the models proposed by Sakurai and Hagstrum[12] in Figs. 4(a)—4(c), respectively. The model of the (2×1) reconstructed surface is illustrated according to the asymmetric dimer model proposed by Chadi[7] in Fig. 4(a). We have suggested in the discussion of Fig. 2(b) that bonding of hydrogen atom to all available dangling orbitals results in the reconstruction of the initial asymmetric dimer to the symmetric dimer in the monohydride (2×1):H surface and Fig. 4(b) is drawn in accordance with such an idea. In Fig. 4(c) we show the model of the dihydride (1×1)::2H surface where two hydrogen atoms bond to one surface silicon atom.

The angle-resolved electron-energy-loss profiles for the (2×1):H and the (1×1)::2H saturated surfaces are represented in Figs. 5 and 6, respectively. In the spectra of the (2×1):H surface (Fig. 5) the S_1 peak ascribed to surface dangling bonds has disappeared and this fact indicates that the dangling bonds on the first silicon layer have been terminated by hydrogen atoms. A strong new peak is observed at 8.0±0.2 eV. This transition, which is located at

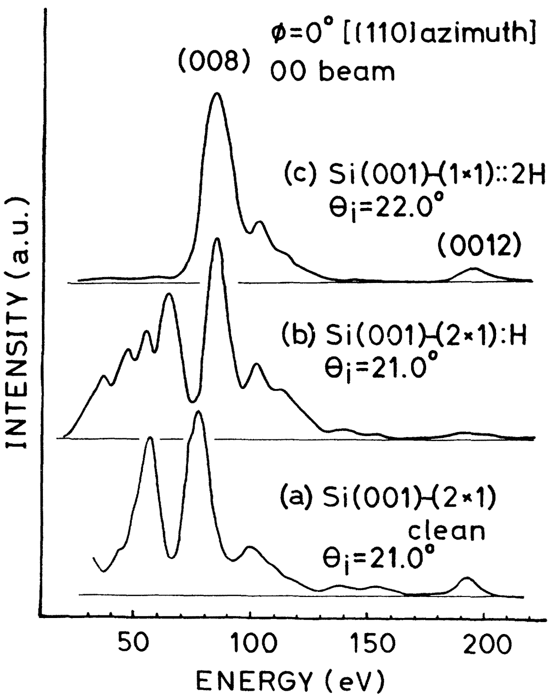

FIG. 3. *I-V* curves of the 00 beam for (a) clean, (b) (2×1):H, and (c) (1×1)::2H surfaces which are collected for the energy range from 30 to 220 eV.

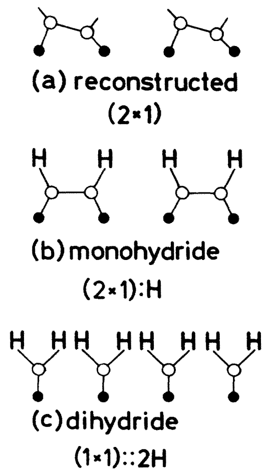

FIG. 4. Schematic models for (a) unreconstructed 2×1, (b) monohydride 2×1:H, and (c) dihydride (1×1)::2H surfaces.

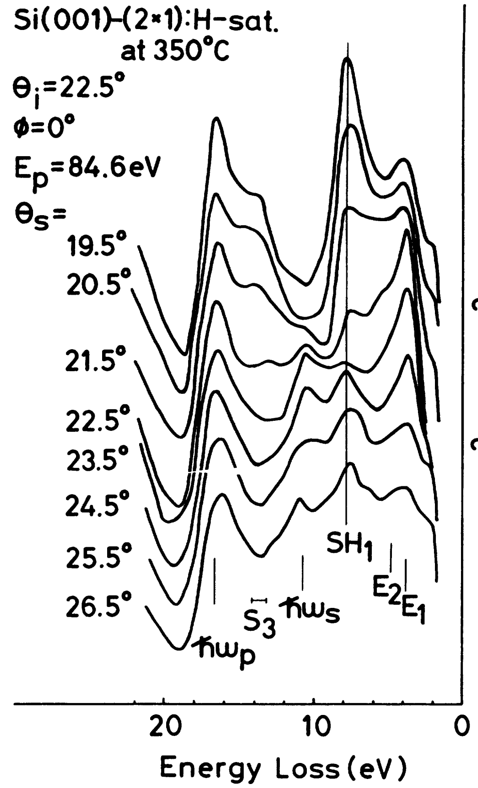

FIG. 5. Angle-resolved electron-energy-loss profiles for the monohydride (2×1):H surface measured at the 84.6-eV Bragg-type peak in the [110] azimuth at $\theta_i = 22.5°$.

nearly the same energy as the S_2 transition on the clean surface, is distinctly different from the S_2 transition because its intensity is weak even on the clean surface (see Fig. 1). The new peak at 8.0 eV can be ascribed to the transition from the state of the hydrogen—silicon bond. This hydrogen-induced transition (hereafter called SH_1) shows no dispersion within the experimental error from the angular dependence of the peak position of SH_1 shown in Fig. 5. The transition energy is in agreement with the result of Ibach and Rowe[11]: 8.5±1.0 eV. The S_3 peak ascribed to the back-bond surface state was observed distinctly in the spectra of the (2×1):H surface at nearly the same position in energy (14.0±0.2 eV) as for the clean surface. It is uncertain, however, whether another loss peak due to the back-bond surface state S_2 exists or not since the S_2 peak is weak even on the clean surface and is located close to the strong SH_1 peak in energy.

In contrast to the monohydride 2(×1):H surface, in the AR-ELS spectra of the Si(001)(1×1)::2H surface (Fig. 6) the S_3 peak completely disappeared. We confirm that on the (1×1)::2H surface the S_3 peak disappeared for various incident conditions. Therefore we considered that hydrogen adsorption

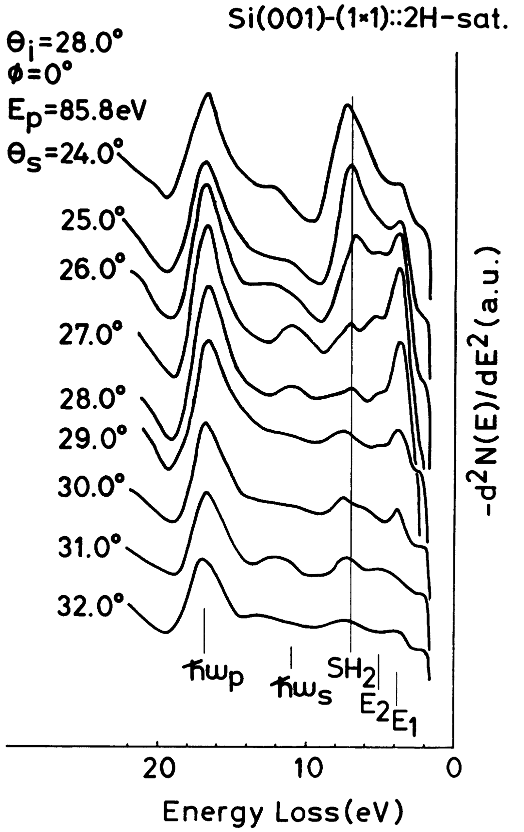

FIG. 6. Angle-resolved electron-energy-loss profiles for the dihydride (1×1)::2H surface measured at 84.8-eV Bragg-type peak in the [110] azimuth at $\theta_i = 28.0°$.

has removed the subsurface strain by breaking the lateral bond of the dimer on the (2×1) reconstruction surfaces. We found the new hydrogen-induced peak at 7.0±0.2 eV for the specular direction on the (1×1)::2H surface, indicated as SH_2 in Fig. 6. This SH_2 peak shifts systematically from 7.0 eV for the specular direction to 7.5 eV as the scattering θ_s deviates from the specular direction by 3° to both near- and off-surface normal sides. The magnitude of momentum transfer parallel to the surface $|k_{\parallel}|$ increases as the deviation of the scattering angle from the specular direction $|\theta_s - \theta_i|$ increases. Therefore the symmetrical shift of the SH_2 peak as increasing $|k_{\parallel}|$ indicates that the SH_2 peak disperses in contrast with the SH_1 peak.

Ibach and Rowe[11] could not observe this transition in their ELS spectra since they could not produce the (1×1) dihydride phase. The fact that the SH_2 transition disperses indicates that on the (1×1)::2H surface the interaction between the two Si—H bond states on a first silicon layer is stronger than on the (2×1):H surface (see Fig. 4).

Previously we have reported of the hydrogen-covered (1×1) surface which has a sharp (1×1)

LEED pattern in Fig. 4 in Ref. 17. On this surface we have observed a new peak in the place of the S_1 clean transition at slightly larger energy loss in ARELS spectra (hereafter called S'_1). On the other hand, the S'_1 peak disappears completely when the dihydride (1×1)::2H saturated surface has been produced as described in this study. Therefore we consider that the hydrogen-covered (1×1) surface in Ref. 17 has not been completely saturated by hydrogen atoms and we can ascribe the origin of this S'_1 peak to the newly produced dangling-bond surface state resulting from the rupture of the lateral bonds of dimers. These facts indicate that the formation of the dihydride (1×1)::2H surface progresses together with the rupture of the lateral Si—Si bonds on the first silicon layer. Details will be reported elsewhere.

By assuming a single final state for the SH_1 and SH_2 transitions we conclude that the energy of the initial state of the hydrogen-induced transition shifts by 1 eV toward the lower-binding-energy side from the (2×1):H(SH_1) state to the (1×1)::2H(SH_2) state. This is in reasonable agreement with the result of Sakurai and Hagstrum[12] by UPS: hydrogen-induced states are at -12 and -10 eV (referring to the vacuum level) for the $(2\times)1$:H and the (1×1)::2H surfaces, respectively. On the basis of this UPS result the final state of the hydrogen-induced surface transitions (SH_1 and SH_2) is around -3 eV (referring to the vacuum level).

IV. SUMMARY AND CONCLUSIONS

The hydrogen-covered Si(001) surface formed by moderately annealing the sample during atomic hydrogen exposure has a uniform monohydride phase (2×1):H where a hydrogen atom is bonded to one dangling bond per one surface silicon atom. The dangling-bond state is mixed strongly with the hydrogen state and so the S_1 transition is transferred to the SH_1 transition. On the monohydride (2×1):H surface the S_2 and the S_3 transitions observed on the clean (2×1) surface are also observed, and thus the subsurface strain has not been healed out. In addition the $(\frac{1}{2}0)$ spots are intensified on the (2×1):H surface. This fact indicates on the basis of the asymmetric dimer model of the clean surface that the hydrogen adsorption results in the reconstruction of the initial asymmetric dimer to the symmetric dimer.

The uniform dihydride phase (1×1)::2H was formed by heavily exposing the clean surface at room temperature to atomic hydrogen. On the dihydride (1×1)::2H surface two hydrogen atoms bond to one surface silicon atom associated with the breaking of the lateral bond of dimer. The destruction of the dimer results in the relaxation of the subsurface strain, and thus the back-bond surface states have disappeared. In the I-V curve only the Bragg reflections are intensified. This fact shows that the selvedge relaxes to have the periodicity of the bulk structure of Si. The energy of the hydrogen-induced transition SH_2 is different from that on the (2×1):H surface. In addition SH_2 shows dispersion as increasing $|k_{\parallel}|$. This fact indicates that since the neighboring Si—H bonds are close to each other the Si—H bond states interact strongly with each other.

ACKNOWLEDGMENTS

This work was partially supported by a Grant-in-Aid for a Special Research Program from the Ministry of Education Science and Culture of Japan.

---

[1] R. E. Schlier and H. E. Farnsworth, J. Chem. Phys. 30, 917 (1959).

[2] T. D. Poppendieck, T. C. Ngoc, and M. B. Webb, Surf. Sci. 75, 287 (1978).

[3] M. J. Cardillo and G. E. Becker, Phys. Rev. Lett. 40, 1148 (1978).

[4] M. J. Cardillo and G. E. Becker, Phys. Rev. B 21, 1497 (1980).

[5] J. A. Appelbaum, G. A. Baraff, and D. R. Hamann, Phys. Rev. B 14, 588 (1976).

[6] J. E. Rowe and H. Ibach, Phys. Rev. Lett. 32, 421 (1974).

[7] D. J. Chadi, J. Vac. Sci. Technol. 16, 1290 (1979).

[8] W. S. Verwoerd, Surf. Sci. 99, 581 (1980).

[9] D. J. Chadi, Phys. Rev. Lett. 43, 43 (1979).

[10] D. J. Chade, in Proceedings of the Fifteenth International Conference on the Physics of Semiconductors, Kyoto, 1980 [J. Phys. Soc. Jpn. 49, Suppl. A, 1035 (1980).]

[11] H. Ibach and J. E. Rowe, Surf. Sci. 43, 481 (1974).

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

[13] W. Mönch, P. Koke, and S. Krueger, J. Vac. Sci. Technol. 19, 313 (1981).

[14] J. C. Phillips, Phys. Rev. Lett. 42, 1151 (1979).

[15] H. Iwasaki, S. Maruno, K. Horioka, S. T. Li. and S. Nakamura, Jpn. J. Appl. Phys. 20, L745 (1981).

[16] K. Horioka, H. Iwasaki, A. Ichimiya, S. Maruno, S. T. Li, and S. Nakamura, Jpn. J. Appl. Phys. (in press).

[17] Some of the results have already been reported in S. Maruno, H. Iwasaki, K. Horioka, S. T. Li, and S. Nakamura, Jpn. J. Appl. Phys. 21, L263 (1982).

[18] H. H. Madden, Surf. Sci. 105, 129 (1981).

[19] R. C. Henderson, J. Electrochem. Soc. 119, 772 (1972).

[20] A. Ignatiev, F. Jona, M. Debe, D. E. Johnson, S. J. White, and D. P. Woodruff, J. Phys. C 10, 1109 (1977).

[21] J. E. Rowe and H. Ibach, Phys. Rev. Lett. 31, 102 (1973).

[22] J. A. Appelbaum, G. A. Baraff, D. R. Hamann, H. Hagstrum, and T. Sakurai, Surf. Sci. 70, 654 (1978).

[23] S. J. White and D. P. Woodruff, Surf. Sci. 63, 254 (1977).

[24] S. J. White, D. P. Woodruff, B. W. Holland, and R. S. Zimmer, Surf. Sci. 74, 34 (1978).

[25] R. M. Tromp, R. G. Smeenk, and F. W. Saris, Surf. Sci. 104, 13 (1981).