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Hydrogen interactions with Si(111) and Si(100) surfaces studied by ultraviolet photoemission spectroscopy

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H interactions with thermally cleaned Si(111) and Si(100) surfaces at 300–650 K have been studied by ultraviolet photoemission spectroscopy. Experimental results are consistent with the existence of weakly adsorbed H atoms at 300 K, which revealed surface resonance states around 7 eV below Fermi level. The weakly adsorbed H atoms desorb around 500 K from the Si(100) surface to form the monohydride phase, while they are irreversibly transformed into the trihydride phase by annealing at 650 K on the Si(111) surface. This indicates the different natures of Si-H chemical reactions on the two surfaces.

I. INTRODUCTION

The origin of the surface reconstructions on the low-index silicon surfaces has been the subject of many recent studies.[1] Qualitatively, the reconstruction on the Si(100)-(2×1) surface appears to be well described by the asymmetric dimer model.[2,3] However, the best model for the thermodynamically stable Si(111)-(7×7) surface still remains as a challenging problem. Hydrogenation of these surfaces provides a certain means of investigating the reconstructions upon which various Si–H bonding configurations are formed. The disappearance of fractional order diffraction spots upon roon-temperature H chemisorption[4,5] is consistently explained with the proposed model for the Si(100)-(2×1) surface, while the persistence of seventh-order diffraction spots upon H chemisorption[6,7] indicates more complex rearrangements which must occur on the Si(111) surface or its subsurface atomic layers.

In this paper, H interactions with thermally cleaned Si(111) and Si(100) surfaces have been investigated by angle-integrated ultraviolet photoemission spectroscopy (UPS). Detailed changes have been examined of the UPS spectra upon hydrogenation of the surfaces and their dependence on substrate temperatures. It is found that the natures of Si-H chemical reactions are essentially different for the two surfaces. From comparison with the theoretical local density of states (LDOS) of the adsorbed H atoms,[8–12] the experimental results are interpreted to show that in addition to the conventional tetrahedral Si–H bonds, H atoms are also weakly adsorbed on both surfaces forming unconventional bonds. It is observed that these H atoms desorb by annealing around 500 K from the Si(100) surface to form the monohydride phase, while they are irreversibly transformed into the trihydride by annealing around 650 K on the Si(111) surface. The striking differences observed in the H reactivity and the reaction products are discussed in relation to H-induced rearrangements of the atomic structure.

II. EXPERIMENTAL

The experimental apparatus used in the present work has been described in detail elsewhere.[13] Briefly it consists of an ultrahigh vacuum (UHV) chamber provided with a UPS spectrometer, the base pressure of which was 2×10^{-10} Torr (3×10^{-8} Pa). The initial energy was determined by a measurement of the spectrum from the tantalum holder which was used to locate the silicon Fermi level E_F. The work-function change was obtained from the displacement of the low-energy cutoff of the secondary electrons.

Atomically clean Si(111)-(7×7) and Si(100) surfaces were prepared by indirectly heating the samples up to 1500 K and annealing around 900 K in UHV.[13] Cleanness of these surfaces was checked *in situ* with Auger measurements, and confirmed that there were no detectable impurities such as carbon and oxygen on the surfaces. Typically, the noise level was of the order of 10^{-3} of the Si LVV peak intensity at 91 eV. Hydrogenation was achieved by introducing research grade H_2 into the chamber, in the controlled amount, through a bakable leak valve. Since hydrogen molecules do not have an appreciable sticking probability on the surfaces, dissociation of H_2 to 2H was made at the hot filaments in the sputter-ion gun. The arrival

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rate at the sample surface was not determined, but the exposures were controlled by measuring the partial pressure of molecular hydrogen and the exposure time, preserving the dissociation conditions.

III. RESULTS

Figure 1 shows the UPS spectra for the thermally cleaned Si(111) surface and the surfaces after hydrogenation. For the clean annealed Si(111)-(7$\times$7) surface as shown in Fig. 1(a), prominent surface state features observed at 0.8 and 2.0 eV below E_F are in agreement with the previous results.[14] These features at 0.8 and 2.0 eV are attributed to the intrinsic dangling-bond surface states and others are mostly attributed to the bulk states.[14,15] When the clean Si(111)-(7$\times$7) surface was exposed to H atoms with the substrate temperature around 500 K, the H-saturated surface was obtained after 4500 L (1 L$=10^{-6}$ Torr sec) H_2 exposures. This surface chiefly revealed two new UPS peaks at 5.4 and 7.4 eV below E_F, as shown in Fig. 1(b). Weak shoulders or peaks were also seen at -3.3, -4.2, and -10.1 eV. No significant changes of the work function were observed in this case. In contrast to these data shown in Fig. 1(b), different spectral features appeared when H atoms were exposed at room temperature. The experimental result is shown in Fig. 1(c) for the surface after 1500-L H_2 exposures at room temperature. The UPS spectrum showed an enhancement in the photoemission around 7 eV in spite of the fact that smaller amounts of H exposures were used than in case (b). In addition, the work function decreased by 0.2 eV. The broad peak around 7 eV in Fig. 1(c) exhibits an asymmetric line shape, tailing to the higher energy. On the other hand, annealing at 650 K changed the spectral features irreversibly, as shown in Fig. 1(d). The spectrum shows a prominent peak at -6.9 eV with a symmetric line shape and peaks at -4.1 and -10.4 eV. Then the work function increased by 0.2 eV.

A UPS spectrum for the thermally cleaned Si(100) surface is given in Fig. 2(a). This surface was stable and the UPS spectrum was reproduced repeatedly. The shoulder at -1.1 eV near the top of the valence band in the spectrum is attributed to the emission from the intrinsic surface states.[2] Very small or no photoemission seen at E_F suggests semiconductor surface bands. The peak around -4 eV always showed a triangular shape.

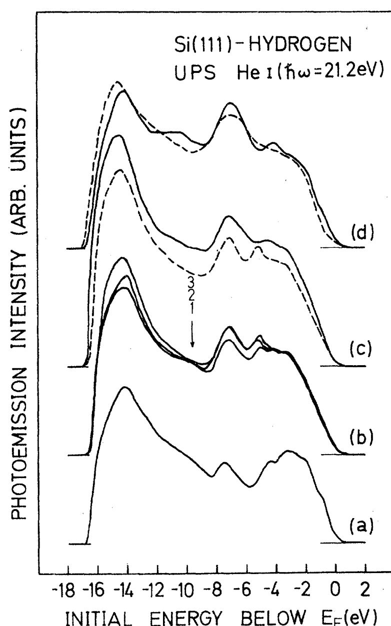

FIG. 1. UPS spectra for the thermally cleaned Si(111)-(7$\times$7) surface and the surfaces after H adsorption: (a) clean, (b) after exposures at 500 K (curves 1, 2, and 3 obtained by 1500-, 3000-, and 4500-L exposures, respectively), (c) after 1500-L exposures at 300 K (solid curve) and 4500-L exposures at 500 K (dashed curve), and (d) after 12 000-L exposures at 300 K (dashed curve) and subsequent annealing at 650 K (solid curve).

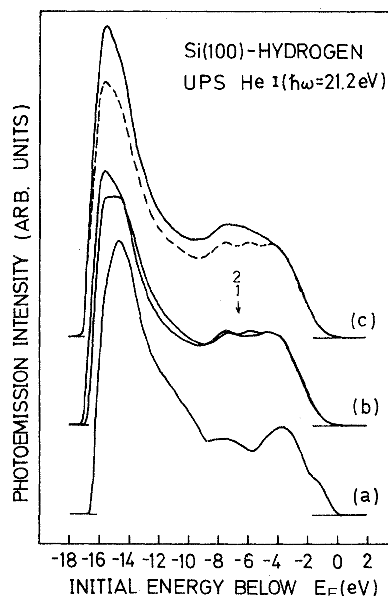

FIG. 2. UPS spectra for the thermally cleaned Si(100) surface and the sufaces after H adsorption: (a) clean, (b) after exposures at 500 K (curves 1 and 2 obtained by 6000- and 18 000-L exposures, respectively), and (c) after 18 000-L exposures at 500 K (dashed curve) and subsequent 12 000-L exposures at 300 K (solid curve).

These are in good agreement with the previous UPS results for the Si(100)-(2$\times$1) surface,[2] and they are interpreted as demonstrating the characteristics of the asymmetric dimer bonds.[16] Peaks or shoulders around 4, 7, and 11 eV below E_F in Fig. 2(a) are mostly attributed to the emission from the silicon bulk states. The back bond surface states might also contribute to the feature around 11 eV.[16] When this clean Si(100) surface was exposed to H atoms, UPS spectra revealed that the electronic structure of the surface was changing from that of the clean surface, as demonstrated in Fig. 2(b). Two spectra in Fig. 2(b) correspond to the surfaces after 6000- and 18 000-L H_2 exposures with the substrate temperature around 500 K. New peaks were developed at 4.5, 5.9, and 7.4 eV below E_F while the surface state features were eliminated. The work function decreased by 0.4 eV. No significant changes of the adsorbate-induced features were observed with further H exposures as long as the substrate temperature was kept around 500 K. However, changes were observed in the UPS spectral features when hydrogenation was made with the substrate at 300 K. Additional 12 000-L H_2 exposures at 300 K resulted in an enhancement of the emission around 7 eV in the UPS spectrum as shown in Fig. 2(c). These changes could also be pursued with only the room temperature adsorption. On the other hand, the spectrum in Fig. 2(c) was converted into the intermediate one in Fig. 2(b) after moderate annealing around 600 K without any notable work function changes. These results indicate that some of the H atoms adsorbed at room temperature were bound more weakly than those remaining at 500 K, and that they could easily be desorbed from the surface at 600 K.

IV. DISCUSSION

When the clean Si(111)-(7$\times$7) surface was exposed to H atoms, two different UPS spectra were obtained, depending on the substrate temperature. This means that at least more than two H adsorption states are involved at different substrate temperatures. The H adsorption around 500 K principally produced a double-peaked H-related structure at -5.4 and -7.4 eV in the UPS spectrum [Fig. 1(b)], while a single asymmetric peak was observed around -7 eV with the room-temperature H adsorption [Fig. 1(c)]. The double-peak structure is in excellent agreement with that reported previously,[7,14] and that predicted in the calculated photoemission spectrum[8,9] for the monohydride chemisorption phase, Si(111)-(1$\times$1):H, hydrogen bonded to the unreconstructed Si(111)-(1$\times$1) surface. Therefore, the UPS spectrum of Fig. 1(b) is interpreted in terms of SiH covalent bond formation, where H atoms are directly bonded to the surface silicon atoms. It should be noted, however, that the surface atomic structure persists in showing the seventh-order diffraction spots, i.e., the Si(111)-(7$\times$7):H instead of the Si(111)-(1$\times$1):H structure.[6,7] This fact is consistent with only the so called rough-surface model[14] among the proposed models for the (7$\times$7) structure. If we specifically assume a recently proposed structural model of double-layer islands by Cardillo[17] and the rigid-surface lattice model[18] against Si—Si bond breaking, the Si(111)-(7$\times$7):H structure is consistent with the monohydride phase, since most of Si—H bonds have the similar local bonding configurations to those for the Si(111)-(1$\times$1):H.

The UPS result of the room-temperature H adsorption on the clean Si(111)-(7$\times$7) surface is puzzling. The observation of a single broad peak at 7 eV in the UPS spectrum agrees with the previous result for the Si(111)-(7$\times$7):H by Ibach and Rowe,[6] but disagrees with Sakurai and Hagstrum.[7] The retention of the seventh-order diffraction spots for both cases indicates that the effect of H atoms on the low-energy electron diffraction (LEED) pattern should be small as long as the original (7$\times$7) atomic structures were preserved. However, differences in the amount and the chemical nature of H atoms adsorbed would be expected to change the surface LDOS greatly. The UPS spectral feature observed around -7 eV is therefore attributed to other H adsorption states than the monohydride. Recently, Wagner *et al.*[19] reported by their vibrational loss spectroscopy that SiH_2 and/or SiH_3 complexes are formed in the early stages of H adsorption on the Si(111)-(7$\times$7) surface especially at lower substrate temperatures. If the UPS feature around -7 eV was compared with the LDOS corresponding to various SiH_x configurations such as SiH_2 and SiH_3,[9,10] some of the spectral features might be explained with the coexistence of SiH_2 and/or SiH_3 configurations. However, the asymmetric line shape of the peak is distinct from that of the trihydride phase, Si(111):SiH_3, which possesses a dominant peak at -6.7 eV with a symmetric line shape.[14] In view of the strict difference in the UPS spectral features between Figs. 1(b) and 1(c) in detail, the mixture model of the various SiH_x tetrahedral bonding configurations is inadequate to explain the experimental results. This im-

plies the presence of weakly bound H atoms. Therefore, it seems probable to attribute the enhancement of the peak at -7 eV due to the resonance states as proposed by Lang and Williams.[11] The long-range character of the resonance states associated with the peak is also consistent with the conclusion reached by the cluster Bethe lattice calculations.[20]

The UPS results for the hydrogenation of the Si(100) surface are in general agreement with the previous observations by Sakurai and Hagstrum.[5] The spectral features at -4.5, -5.9, and -7.4 eV in Fig. 2(b) are attributed to the monohydridelike Si–H bond formation. The surface was relatively stable to moderate annealing at 500 K, and has previously been identified to be reconstructed as Si(100)-(2×1):H.[5] For the asymmetric dimer model, each surface silicon atom has bonded to three silicon atoms (two back bonds and one dimer bond) so that the local bonding site for the H adsorption is expected to be similar to what is expected on the unreconstructed Si(111)-(1×1) surface. I attributed this reason to the similarity between the LDOS features in the photoemission spectrum of Fig. 2(b) and those for the monohydride phase, Si(111)-(1×1):H. However, the experimental results are in disagreement with the existing LDOS calculation so far for the unreconstructed Si(100):2H surface.[21] On the other hand, the decrease of the work function by 0.4 eV upon hydrogenation has consistently been explained, based on the asymmetric dimer model.[22]

Additional evidence for the existence of weakly adsorbed H atoms is also given by studying annealing effects on the room-temperature H adsorption state, as discussed in the following. Room temperature H adsorption on the Si(100)-(2×1):H surface resulted in the enhancement of the photoemission intensity around 7 eV which coincides with the energy of the resonance states.[11] This means that weakly adsorbed H atoms are also incorporated on the Si(100) surface as well. The existence of nontetrahedral subsurface sites for such additional H atoms is in fact predicted theoretically on the Si(100) surface by using the Hellman-Feynman theorem.[12] Annealing effects on the adsorption state clearly demonstrated that the weakly adsorbed H atoms could easily be desorbed, as seen in the reversible changes of the H-related spectral features. I postulate that this reversible H bonding interaction is due to the stronger dimer bond characteristic of the Si(100) surface. However, it should be pointed out that the coexistence of SiH_2 bonding configuration is also possible since the (2×1) structure is transformed into the (1×1) structure after the room-temperature H adsorption.[4,5]

In contrast to the effects of annealing on the hydrogenated Si(100) surface, the case of the Si(111)-(7×7) surface is more dramatic. The irreversible change observed in the UPS spectral features in Fig. 1(d) is attributed to the formation of the trihydride phase, Si(111):SiH_3. The features at -4.1, -6.9, and -10.4 eV in the surface LDOS are in close agreement with those for the trihydride.[8,14] This implies that a corrosive process takes place on the Si(111)-(7×7) surface during the annealing, and that the Si(111):SiH_3 phase is the most stable surface phase for the Si(111) surface. Therefore, it is concluded that the nature of the surface rearrangements as well as the surface reactivities are entirely different from those of the Si(100) surface. In relation to the corrosive property of the Si(111) surface, it should be noted that the existence of weakly adsorbed H atoms as a precursor state is important to break the Si–Si bond and to form the tetrahedral SiH_3 configurations on the surface. Furthermore, in order to initiate the SiH_3 unit formation, it is inevitably necessary to postulate the existence of surface atomic imperfections such as vacancies, adatoms, and bilayer atomic microdomains. Thus the formation of the trihydride phase, Si(111):SiH_3, after moderate annealing also gives support for the rough-surface models as a structural model for the Si(111)-(7×7) surface.

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