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Surface states and reactivity of H chemisorption on thermally cleaned Si(111) surfaces: New evidence for rough-surface models

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New experimental evidence supporting the surface-defect models for thermally cleaned Si(111) surfaces is presented. Photoemission spectral intensities for the two distinct surface states at 0.8 and 2.0 eV below Fermi level change dramatically, depending on detailed thermal preparation procedures. This implies different geometries and is correlated with the reactivity of H chemisorption. The enhancement of the defect-induced state at 2 eV on the quenched metastable surface and the formation of the trihydride phase suggest that vacancy-type defects can easily be incorporated on the Si(111) surface by thermal treatments.

Clean Si(111) surfaces exhibit a variety of surface reconstructions as seen in low-energy-electron-diffraction (LEED) patterns.[1,2] The cleaved Si(111) surface shows a 2×1 reconstruction, which is metastable and transformed irreversibly into the thermodynamically stable 7×7 surface upon annealing.[2] The clean Si(111) surface also exhibits an apparent 1×1 LEED pattern by quenching the high-temperature 1×1 phase[3] which is stable above 1140 K. The atomic and electronic structures of the 2×1 reconstruction are generally well understood, essentially based on the Haneman buckled model.[4] However, despite numerous LEED studies as well as other spectroscopic and theoretical investigations, the best model for the 7×7 or 1×1 surface still remains as a challenging problem.[5] To explain these thermally cleaned Si(111) surfaces, different structural models have been proposed so far, assuming the existence of vacancies,[1] adatoms,[6] bilayer atomic microdomains,[7] or a buckled[8] or rippled[9] model. Briefly speaking, these proposed models can be divided into two categories. Models in one category (the first three) suggest positions of the surface atoms to be strongly perturbed from the ideally truncated bulk (111) plane of Si due to missing or added surface atoms, and will be termed "the defect or rough-surface models." A second class of models (the last two) assumes only a small perturbation to a smooth (111) plane in which the surface atoms are electronically driven to buckle or ripple, and will be called "the smooth models."

In this paper, new experimental evidence in support of the defect models is presented by means of angle-integrated ultraviolet photoemission spectroscopy (UPS). It is shown that depending on the kinetics of surface preparation, the spectral intensities for intrinsic surface states are discernibly different between thermally cleaned Si(111) surfaces. This difference is interpreted as arising from microscopic changes of the surface atomic arrangement upon thermal agitation or annealing. If these changes are caused by the creation or order-disorder—type transition of surface atomic imperfections such as vacancies, adatoms, or bilayer atomic microdomains, significant differences should be expected in the reactivity and the bond character of various molecular or atomic adsorbates, depending on the amount of added surface radical centers. This is in fact observed here, and changes of the surface structures are correlated with the reactivity of H chemisorption as well as the final reaction products. These results provide us a crucial test for the discrimination of the surface structural models.

UPS measurements were performed in an ultrahigh-vacuum (UHV) system with the base pressure of 2×10^{-10} Torr (3×10^{-8} Pa). The light source was a differentially pumped glow-discharge He lamp operated at a photon energy $\hbar\omega = 21.2$ eV (He I). Kinetic energy distribution curves (EDC's) of the photoelectrons were obtained in an angle-averaged form with a spherical sector-type analyzer (the theoretical resolution $\Delta E/E$ of 0.01) and a pulse-counting system. The analyzer axis was in the plane of incidence of the photons and perpendicular to the photon beam line. The angle of incidence of the photon to the sample surface normal was kept at 45°. EDC's of the UPS spectra were measured relative to vacuum level E_{vac}, and 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.

Three different clean starting surfaces were prepared by indirectly heating the Si(111) samples up to 1500 K in UHV or Ar^+-ion bombardment and annealing procedures. One is the quenched metastable Si(111) surface *A* obtained by the instantaneous sublimation of the surface native oxide upon flashing at 1500 K or by Ar^+-ion bombardment followed by the flash pulse around 1500 K for about 30 sec. Another one is the well-annealed clean Si(111) surface *B*, which is thermodynamically most stable and could easily be confirmed to exhibit a sharp 7 × 7 LEED pattern in a separate chamber. Still another one is also the quenched metastable Si(111) surface *C* achieved by high-temperature annealing above 1200 K for 5 min and subsequent quenching to room temperature.[10] Cleanness of these Si(111) surfaces was checked *in situ* with Auger electron spectroscopy (AES) 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. The thermal transformation from the stable *B* to the metastable *C* surfaces or vice versa could alternatively be repeated, as judged by the UPS spectral features (to be discussed later).

Hydrogenation was achieved by introducing research-grade H_2 into the chamber by the controlled amount through a bakable leak valve, and by dissociation of H_2 to 2H at the hot filaments in the sputtering ion gun. As the arrival rate at the sample surface was not determined, the exposures were controlled by measuring the partial pressure of molecular hydrogen and the exposure time, preserving the dissociation conditions.

Figure 1 shows the UPS spectra for the thermally cleaned Si(111) surfaces prepared using three different preparation procedures, as described previously: (a) metastable *A*, (b) stable *B*, and (c) metastable *C*. EDC features common in these spectra are mostly attributed to the characteristics of bulk density of states of silicon,[11] as assigned in Fig. 1. Features observed near the top of the valence band are attributed to intrinsic dangling-bond surface states because of their sensitivities to gas adsorption and the surface cleaning procedures. These consist of a shoulder at 0.8 eV below E_F and a peak at 2.0 eV for the metastable *A* surface, while two shoulders at 0.8 and 2.0 eV for both the stable *B* and metastable *C* surfaces. Although the energy positions of the two most prominent surface states appear to be the same for each surface, it should be noted that there exist significant differences in their emission intensities between these three Si(111) surfaces. That is, an enhancement of the peak at 2.0 eV is observed only for the metastable *A* surface under the present experimental geometry. Differences are also seen in the structures around 4 eV between the UPS spectrum (a) and those for (b) and (c). In general, the spectral shapes of the intrinsic surface states for the spectra (b) and (c) appear to be the same, suggesting that the surface atomic structures for *B* and *C* have similar local bonding geometries. This trend is consistent with the previous observation for the 7 × 7 and 1 × 1 surfaces by Eastman *et al.*[12] However, it should be pointed out that there exists a discernible difference in the emission intensity between the surfaces *B* and *C*. That is, the emission for the quenched metastable *C* surface is always enhanced within the range roughly from 2 to 10 eV below E_F when compared with the stable *B* surface. This change in the emission intensity was alternatively reproducible over several cycles. I postulate that the change in the relative emission intensity of the UPS spectra is corresponding to the finding by Pandey *et al.*,[13] the filling of the valley at 10 eV below E_{vac} in going from the clean 7 × 7 to 1 × 1 surface. The photoemission results by Eastman *et al.*[12] also show a similar difference between the 7 × 7 and 1 × 1 surfaces in close agreement with the present results except for a metallic edge at E_F. The absence of a high density of surface states near E_F may be due to the experimental setup[14] (the photon

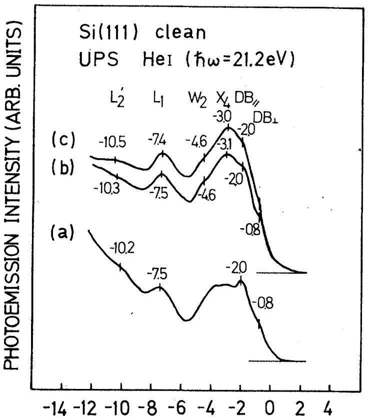

FIG. 1. UPS spectra of three Si(111) surfaces thermally cleaned with different surface preparation techniques: (a) after flash cleaning the surface to remove the surface native oxide, (b) after annealing around 900 K, (c) after high-temperature annealing above 1200 K and subsequently quenching to room temperature.

polarization and/or detection geometry) not being optimized for such a weak feature. The differences observed in the surface electronic density of states between these three Si(111) surfaces do not result from surface impurities, as can easily be checked with *in situ* AES measurements.

Figure 2 represents the UPS results of H chemisorption in the clean Si(111) surfaces as characterized in Fig. 1. When the stable *B* surface is exposed to atomic hydrogen at a pressure of 5×10^{-6} Torr H_2 for 15 min with the substrate temperature around 500 K, we obtained the H-saturated surface which reveals three new UPS peaks at 5.4, 7.4, and 10.1 eV below E_F, as indicated in Fig. 2(b). These H-related features are in excellent agreement with those of the monohydride phase, Si(111):H formed on the 7 × 7 surface.[15,16] On the other hand, the metastable *A* surface is found to be dramatically different from the stable *B* surface in the reactivity as well as the final reaction products after H exposures. Atomic hydrogen reacts most heavily to give the UPS spectrum, which reveals a giant peak at 6.7 eV and a peak at 10.9 eV after the exposure for 10 min at a pressure of 5×10^{-6} Torr H_2. After gentle annealing at 700 K two sharp peaks are observed at 6.7 and 10.0 eV, as shown in Fig. 2(a). These two H-related structures at 6.7 and 10.0 eV are ascribed to the trihydride phase, Si(111):SiH_3.[13] In contrast to this, the metastable *C* surface is found to be rather less active than the previous one, suggesting the lesser degree of the surface imperfection. Consequently, it is necessary to expose approximately 5 times more hydrogen atoms than the surface *A* in order to establish the trihydride phase, as shown in Fig. 2(c). This result is in accord with the previous observation by Pandey *et al.*[13] that the relatively large amount of H is required to produce the Si(111):SiH_3 on the metastable 1 × 1 surface.

The differences observed in the intrinsic surface state features among the thermally prepared clean Si(111) surfaces suggest that the surface will always be rough on an atomic scale. This is because of the difference in surface preparation, i.e., thermal roughening. Therefore, it is highly possible that the metastable quenched surfaces *A* and *C* may include many microscopic surface imperfections such as vacancy clusters, etc., but differ in their densities to a great extent. In fact, it has been reported by Ota[17] that prolonged heating at temperature higher than 1200 K in vacuum causes nonuniform sublimation resulting in thermal pits. Some of these imperfections are not evident with surface-sensitive techniques such as LEED.[18] Thus it could be said that the 7 × 7 diffraction pattern alone does not necessarily guarantee the perfect flatness for the thermodynamically stable Si(111) surface. The essentially important point is in the quantitative quality of the diffraction intensity reflecting the microscopic details of the surface atomic arrangement.

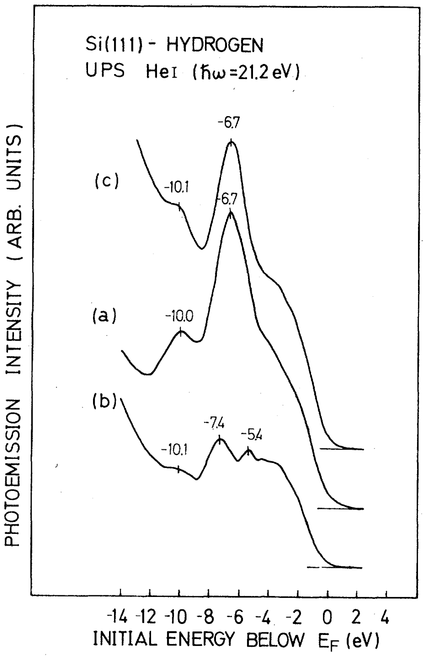

FIG. 2. UPS spectra after saturation with atomic hydrogen chemisorption for the three different clean Si(111) surfaces (see text), resulting in the monohydride (b) and the trihydride (a) and (c).

For the stable *B* and quenched metastable *C* surfaces, our UPS results as well as the previous ones[12,16] for the 7 × 7 and 1 × 1 surfaces find two distinct surface states at 0.8 and 2.0 eV below E_F. The surface state at 0.8 eV is attributed to the p_z-like dangling-bond surface state ($DB_\perp$).[19] This is because it possesses the strong p_z character (Λ_1 symmetry) as evidenced by the dependence on the polar angle of the emission as well as the polarization of the incident photon.[8,16] On the other hand, the surface state at 2.0 eV is predominantly ascribed to the vacancy-induced surface state (parallel dangling-bond state $DB_\parallel$) as suggested by Pandey.[19] Although Pandey has concluded that the UPS data by Rowe and Ibach[20] for the 7 × 7 surface is also consistent with a buckled surface model, our UPS result for the metastable *A* surface is significant. The observed big peak at 2 eV is not explained with the buckled model, and is attributed to the enhancement effect on the $DB_\parallel$ state upon surface damaging. This conclusion implies the importance of the short-range order in determining the intrinsic surface-state structures, which appears to be practically difficult to investigate by LEED intensity analysis. The higher reactivity of the surface A to H chemisorption and the easy formation of the trihydride phase as a final reaction product are taken as firm evidence for the presence of such microscopic surface imperfections as vacancies. It might be expected that the interpretation of the intrinsic surface-state feature at 2 eV is also correct for the other thermally cleaned Si(111) surfaces because of the localized nature of the bonding. Similar vacancy-induced surface states are also suggested independently by theoretical DV-$X\alpha$ cluster studies.[21] Recent investigations[16] of angular dependence and polarization dependence of this state show that the emission in the direction normal to the surface is most intense for s-polarized light (mainly Λ_3 symmetry). This result is also compatible with the vacancy model. The enhancement of the emission intensity between 2 and 10 eV below E_F in the UPS spectra in going from the stable B (7×7) to metastable C (1×1) surfaces should be associated with the vacancy disordering. Recent LEED studies of the relative magnitudes of diffuse and coherent scattering has suggested that the $7 \times 7 \leftrightarrow 1 \times 1$ phase transition at 1140 K is an order-disorder transition.[22]

When hydrogen atoms were chemisorbed on the clean Si(111) surfaces, they showed the drastic difference in the final reaction products, as demonstrated in Fig. 2. For the stable B surface, the terminal surface phase after saturation with H is corresponding to the monohydride Si(111):H. Therefore, the surface lattice is rigid against Si—Si bond breaking to form energetically favorable Si-H$_3$ units. On the contrary, the metastable A and C surfaces revealed a sharp contrast to the B surface, and exhibited the trihydride Si(111):SiH$_3$ after saturation with H. A plausible mechanism for the formation of the Si(111):SiH$_3$ phase has been proposed by Pandey *et al.*[13] In order to initiate the SiH$_3$ unit formation, they assumed disordered vacancies which are clustered on the metastable 1×1 surface. Based on their proposal, it is necessary to break the Si—Si bond and remove almost the entire surface monolayer of Si during the formation of the Si(111):SiH$_3$ phase. This means that retention of the reconstructed structure in the final Si—H bonding configurations is not implied. This reaction is found to be easiest on the most heavily damaged metastable surface A, as judged by the enhancement of the DB$_{\|}$ surface state. Higher reactivity of H chemisorption and the relatively smaller amount of H required to produce the trihydride phase on the metastable surface A than on the metastable surface C are consistent with this mechanism. Thus these experimental results give support for the presence of vacancy-type defects on the Si(111) surfaces.

In summary, it has been demonstrated that, depending on the kinetics of thermal preparation, three differently cleaned Si(111) surfaces exhibit definitely different surface electronic states, which give rise to drastically different atomic hydrogen chemisorption properties. These experimental results strongly support the defect models which may include vacancy-type surface imperfections for thermally cleaned Si(111) surfaces.

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