Chemisorption of atomic hydrogen on the silicon (111) 7×7 surface

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The chemisorption of atomic hydrogen on the silicon (111) 7 × 7 surface has been studied using ionneutralization spectroscopy and ultraviolet-photoemission spectroscopy with the help of low-energy electron diffraction and work-function measurement. Both spectroscopies showed that the dangling-bond surface state disappears when the clean surface is exposed to atomic hydrogen. Chemisorbed hydrogen produces two sharp peaks in the surface density of states at approximately -10 and -12 eV from the vacuum level. These results are in good quantitative agreement with the recent theoretical works by Appelbaum and Hamann and by Pandey.

I. INTRODUCTION

Silicon surfaces have been the subject of surface studies for many years, by low-energy electron diffraction (LEED) and various electron spectroscopies. Hydrogen chemisorption on silicon surfaces was also studied by a number of people^{1,2} since this system is simple and basic to the understanding of chemisorption both theoretically and experimentally. Ibach and Rowe³ were the first to apply ultraviolet-photoemission spectroscopy (UPS) to this system and obtained much basic information. They reported that exposure of the silicon (111) 7×7 surface to atomic hydrogen produces one fairly broad peak in the UPS spectra at -11.3 eV from the vacuum level. When Appelbaum and Hamann⁴ calculated the surface density of states in the Si (111)-H system by self-consistent quantum theory, it was found that their calculation did not agree with the experimental results in detail. The theory predicted two sharp peaks, while the experiment showed only a single broad peak.

It appeared to us that this might be a case where ion-neutralization spectroscopy⁵ (INS) could help to resolve the difference between theory and experiment. We have found that both INS and UPS show two resonance peaks separated by about 2 eV, in agreement with the theory. ^{4,6} In recent work, Rowe has shown that he can reproduce both the earlier result³ and that given here by use of differing preparation procedures. He reports that he can reproduce the single-peak spectrum by absorption at substrate temperatures below 100 °C and will publish these results presently.

This paper will deal primarily with our UPS result. In our INS study, hydrogen on Si (111) provides one of two recent examples in which it appears that relative wave-function magnitude varies sufficiently rapidly with distance outside the solid as to make necessary a modification of our usual data-reduction procedures. The reason for this is that variation of ion position at neutralization with ion incident kinetic energy mixes appreciable wave-function variation with change in energy broadening. The details of this will be published later.⁷

We also report some LEED observations in this work. Although it maintains basic features of the 7×7 pattern for the clean surface, the LEED pattern for the hydogenated surface displays a profound modification of intensities of nonintegral spots.

II. EXPERIMENTAL TECHNIQUES

The vacuum system used in this study has been described elsewhere.⁵ It consists of INS, UPS, LEED, and Auger electron spectroscopy(AES) for surface study and evaporation and sputtering devices for surface preparation. The base pressure is 5×10^{-11} Torr upon baking at 150 °C, and the working pressure is better than 1×10^{-10} Torr. The silicon (111) targets were cut from a lightly boron-doped single crystal in the U-shape form shown in Figs. 1-3 of Ref. 8. This shape of target enables us to sputter and anneal the surface to be studied uniformly and minimize introduction of undesirable impurities or contamination from its supporting legs. A two-axis sample-positioning mechanism is employed, with which it is possible to move the target from port to port of the apparatus and to vary the angle of incidence of light or ion beams from -15 to 70 deg.

The silicon target was sputtered with Ne⁺ ions for an hour, removing the order of 10^3 monolayers from its original surface. After annealing for 20 min. at 600 °C by resistance heating a sharp 7×7 pattern was observed. Then INS and UPS data were taken on this surface to check its chemical purity. The dangling-bond surface states on clean Si(111)7×7 are observed with both UPS and INS. We have found, however, that the surface-state evidence in the INS kinetic-energy distribution is more difficult to achieve than is that in the UPS distribution, because the transition probability for

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INS is believed to be smaller than that for UPS. We have consistently required that the surface exhibit the surface-state structure by INS as the more stringent requirement before we consider the surface to be clean. We also require that all AES signals of impurities be below the noise level. Peak-to-peak noise in the differential Auger spectrum is approximately 1800 times smaller than the peak to peak signal of the Si feature at 91 eV.

Once a clean surface is established background gases absorbed on the surface can be removed by heating to 400 °C for 10 sec. Exposure to atomic hydrogen was achieved by placing the target inside the sputtering device⁹ and heating the tungsten filaments. These filaments have been carefully outgassed and tested to be clean. Background pressure is less than 5×10^{-10} Torr with the filaments hot so that only negligible contamination could accumulate on the target surface during the time of the exposure. The rate of atomic-hydrogen exposure was controlled either by adjusting the partial pressure of molecular hydrogen introduced to the system or by adjusting the temperature of the tungsten filaments. Since we could not measure the partial pressure of atomic hydrogen near the target position, the exposure to atomic hydrogen is expressed in terms of the time the filaments were at a specific temperature in a specified pressure of molecular hydrogen. As a typical example, INS and UPS data were taken as a function of atomichydrogen exposure in the range 0-40 min. with the tungsten filaments at the temperature of 1710 °C in 3×10^{-6} Torr of H₂. Both spectra changed with H exposure during the first 20 min. and remained unchanged during the next 20 min. Thus we conclude that we had achieved a saturated monolayer coverage of atomic hydrogen on the Si (111) 7×7 clean surface. Indirect heating of the silicon sample used to dissociate H_2 to 2H raised the sample temperature to 150-200 °C during the H exposures.

It was found that the hydrogen-covered surface is fairly inert to contamination. It is unlikely that the surface is contaminated by other impurities during hydrogen exposure which may last 20-180min depending upon the partial pressure of hydrogen. However, it was observed that molecular hydrogen adsorbed on the surface could reduce the atomic-hydrogen peak slightly while producing no other change in the UPS spectra. Heating of the target for 10 sec at 300-400 °C was found to be sufficient to desorb molecular hydrogen without desorbing atomic hydrogen. Desorption of the adsorbed atomic hydrogen is accomplished by heating to 600 °C for 10 sec.

The change of work function of the target during the hydrogen exposure was measured by a criticalretarding-potential method¹⁰ using the He^{*} ion beam of INS or by the width of the UPS spectra ($\Delta E = \hbar \omega$



FIG. 1(a). UPS spectra $N_P(E)$ of HeI (21.2 eV) radiation for the Si (111) surfaces obtained during exposure to atomic hydrogen with W filaments at 1710 °C and H₂ partial pressure equal to 6.2×10^{-7} Torr. Exposure times in minutes are: curve 1, 0 (clean surface); curve 2, 10; curve 3, 20; curve 4, 40, and 60 (hydrogen-saturated surface). (b) Difference spectra ΔN_P between the hydrogencovered surfaces (curves 2, 4) and the clean surface (curve 1). Histogram $\Delta \rho$ is the difference between the local density of states at the adsorbed hydrogen on the Si (111) substrate and the bulk density of state of Si calculated by Appelbaum and Hamann (Ref. 4). It is normalized so that the height of a peak at -9 eV is the same as that of the experimental curve at -9.8 eV.

 $-\phi$). Both techniques yield similar results in all the cases studied although the magnitude of change in work function did differ by as much as a factor of two from one exposure to another.

III. EXPERIMENTAL RESULTS

A series of the photoemission spectra of He I $(\hbar\omega = 21.2 \text{ eV})$ with various hydrogen exposures are shown in Fig. 1(a) with the secondary electron emission peaks at the low-energy side normalized to the same height. The experimental difference spectra between the hydrogen-covered surfaces and the clean surface are given in Fig. 1(b) where they are compared with the theoretical result obtained by Appelbaum and Hamann.⁴ $\Delta \rho$ in Fig. 1(b) is the difference between the theoretical local density of states at the atomic hydrogen on the silicon (111) substrate and the bulk density of states of silicon. Assuming that these two densities of states correspond to the UPS spectra for the cases of the hydrogenated silicon (111) surface and the clean silicon (111) surface, $\Delta \rho$ is the quantity to be compared with the UPS experimental data of Fig. 1(b).

The two positive peaks at -9.8 and -12.0 eV are due to the local density of states near the hy-

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drogen atom, and are in a good agreement with the theory. The larger peak located at -9.8 eV arises from the Si-H bond, and the smaller one at -12.0eV reflects the enhancement of a s-like bulk band by hydrogen chemisorption on the surface layer. We observed some variability in the hydrogen peak heights such as that to be seen by comparing Figs. 1 and 3. However, the energy positions of the peaks were always accurately reproduced. The two broad negative peaks with their centers at approximately -6 and -16 eV are explained both by the disappearance of intrinsic surface states upon hydrogen chemisorption and by the suppression of near-surface bulk states due to hydrogen chemisorption. Thus it is meaningless to estimate the electron density of dangling-bond surface states simply by assuming that the negative peak near the Fermi surface is due to the surface dangling bond.¹¹ The fact that the hydrogen peak is more than four times the negative peak near the Fermi level implies that the oscillator strength of the Si-H bond is much larger than those of the nearsurface Si-Si and the Si dangling bonds in the photon energy range 16-21 eV, in agreement with a recent calculation by Pandey and Phillips.¹²

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The UPS spectrum of Ne I ($\hbar\omega = 16.8 \text{ eV}$) for the hydrogen-saturated Si (111) surface is shown in Fig. 2 with that calculated theoretically by Pandey.⁶ The relative normalization of these curves is arbitrary. Pandey's curve was obtained by



FIG. 2. UPS spectra $N_P(E)$ of Ne_I (16.8 eV) radiation for the hydrogen-saturated Si (111) surface compared with the calculated total density of state $\rho(E)$ obtained by Pandey (Ref. 6) in the case of Si(111)-H system.



FIG. 3. UPS spectra $N_P(E)$ for the hydrogen-saturated Si (111) surfaces obtained at two different photon energies, 21.2 and 16.8 eV, illustrating the invariance of the principal hydrogen features with respect to photon energy.

first calculating the local density of states for each surface layer and by summing these with weight functions characterizing the photoemission process. Thus this curve should be considered to be the theoretical UPS spectrum, without the peak of secondary electrons, if final-state effects and multiple scattering may be neglected. The agreement between these two spectra is very good both as regards peak position and peak height. When the two curves are placed such that the sharp hydrogen peaks line up exactly, the theoretical position of the valence-band top (E_V) lies 0.4 eV below the Fermi level determined experimentally. Thus the width of the filled surface state $(\Delta E = E_F - E_V)$ is 0.4 eV, in agreement with our result by INS.

In Fig. 3 two UPS spectra at photon energies $\hbar\omega = 16.8$ and 21.2 eV are placed on the energy scale $(E - E_{VAC})$. As is seen, the atomic-hydrogen peaks of the two curves line up very well, which suggests that there is no final-state effect involved in the photoemission process as far as the present Si-H system is concerned. This fact is considered significant since it justifies the simplifying assumptions made in the theoretical calculation.

An interesting difference between the He I and NeI spectra of Fig. 3 is that of the total emission intensity at -8 eV above the zero ordinate axis relative to the height of the hydrogen peak at -10 eVabove an assumed background due to the silicon substrate. The ratio of the total intensity at -8eV to the hydrogen peak increment at -10 eV is 3.7 in the NeI spectrum and 1.3 in the HeI spectrum. We believe that this results from the fact that the emission intensity at -8 eV comes largely



FIG. 4. Plot of the changes in work function of the Si (111) surface during the hydrogen exposure as a function of exposure time with W filaments at 1710 °C and H₂ partial pressure of 1.5×10^{-6} Torr.

from bulk excitations. These should be more strongly evident in the Ne I spectrum because the electron escape depth is greater for the 16.8 eV radiation than it is for the 21.2 eV radiation, although the fact that the oscillator strength for lowenergy states is greater at 21.2 eV than at 16.8 eV should be taken into account in a quantitative evaluation.

The change in work function with hydrogen exposure was found to vary in a manner far from the monotonic variation we had expected. The work function first increases by about 0.1 eV, then decreases to a value smaller than the original value, and finally increases again to reach a plateau $(\Delta \phi \approx 0.2 \text{ eV})$ as shown in Fig. 4. This suggests that atomic hydrogen, like chlorine, ¹³ can occupy more than one adsorption site on the Si (111) surface. Although it was found that the magnitude of work-function change differs by as much as a fac-

tor of two for different exposures, the structure of the curve (Fig. 4) is essentially invariant.

Contrary to the earlier work,³ we have observed an interesting change in the LEED pattern upon the hydrogen exposure, though we did not carry out quantitative measurements of intensity versus incident electron energy. The 7×7 LEED pattern does not change appreciably during H exposure corresponding to less than one-half of the saturation exposure, at which point the work-function change $\Delta \phi$ is near its minimum value. Beyond this point, the nonintegral spots become weak and finally disappear, except for certain spots near the integral spots (p,q) with p,q integral. These remaining nonintegral spots can be separated into two groups. (i) The six nearest spots around the integral spot with coordinates (p+k, q+l), where $k=0, \pm \frac{1}{7}$ and $l=0, \pm \frac{1}{7}$, and (ii) those along the line joining the integral spots with coordinates (p+k, q), (p, q+l), and (p+k, q+l), where $-k = l = \frac{1}{7}, \frac{2}{7}, \frac{3}{7}, \frac{4}{7}, \frac{5}{7}$, and $\frac{6}{7}$. These spots form a Y of threefold symmetry with integral order spots at its center and three extremities (Fig. 5). The sixfold symmetry of the Si (111) surface gives rise to a second Y with coordinates (p+k, q), (p, q+l), and (p+k, q+l), where k = -l $=\frac{1}{7}, \frac{2}{7}, \frac{3}{7}, \frac{4}{7}, \frac{5}{7}$, and $\frac{6}{7}$. The second Y is obtained from the first by the point-symmetry translation through their common central spot (p+q). Other nonintegral spots were never observed in the energy range we have studied, though it is difficult to eliminate the possibility that these may exist with intensity below our detection limit. It should be noted that these LEED data were obtained at the incidence angle of 36° which prevails in our apparatus when the sample face is kept normal to the port axis.⁵

It is interesting to note that when hydrogen is chemisorbed on the surface, the two Y configurations of LEED spots appear alternately as the incident electron energy increases in the range 30-



Si (111) 7 × 7



Si(111)-H

FIG. 5. LEED photos of the clean and the hydrogensaturated Si (111) surfaces at the electron energy of 40 eV.



FIG. 6. Series of kinetic-energy distribution $N_I(E)$ of Auger electrons from the neutralization of 10-eV He⁺ ions at the Si (111) surfaces obtained during exposure to hydrogen with W filaments at 1710 °C and H₂ partial pressure equal to 3.1×10^{-7} Torr. Exposure times in minutes are: curve 1, 0 (clean surface); curve 2, 5; curve 3, 10; curve 4, 20; curve 5; 35; curve 6, 65; curve 7, 120, and 180 (hydrogen-saturated surface). Arrows indicate the maxima P_1 and P_2 in the $N_I(E)$ distribution produced by the two peaks at ϵ_1 and ϵ_2 in the local density of states of the adsorbed hydrogen.

200 eV. This cycle repeats with a period of approximately 40 eV. This can be interpreted as due to an alternation in the relative contributions of the top and second layers to the diffraction pattern as discussed by others.^{14,15} The sixfold nonintegral spots near the integral spot remain visible throughout the entire energy range we have studied. In order to understand this LEED pattern in greater detail it will be necessary to make a careful study of its dependence upon hydrogen coverage, energy and incidence angle of the primary electrons, and annealing temperature of Si target.

Taking those results by LEED, and work-function measurement into account, it seems reasonable to conclude that in the earlier work of Ibach and Rowe³ the hydrogen coverage of the Si (111) surface was less than one-half monolayer.

Finally, we present some preliminary results by INS. The basic INS data, the kinetic energy distributions of Auger electrons ejected from the Si (111) surfaces during exposure to atomic hydrogen are given in Fig. 6 with hydrogen exposure time as a parameter using helium ions with kinetic energy of 10 eV. Here the striking fact is that upon hydrogen chemisorption the number of Auger electrons with higher kinetic energy (E > 6 eV) decreases drastically while the number of Auger electrons with lower kinetic energy $(E \approx 4 \text{ eV})$ increases by 20%. With atomic hydrogen present on the Si (111) surface, the ion-neutralization process occurs farther away from the Si surface than in the case of the clean surface. The wave-function components outside a surface fall off in intensity exponentially at rates which depends upon their symmetry character. A *p*-type function falls off more rapidly than does an *s*-type function. We take this to be the reason why the fraction of electrons coming from the higher *p*-type region of the valence band decreases relative to that of the deeper *s*-type region. The peak at $E - E_{VAC} \approx 8 \text{ eV}$ in the $N_I(E)$ distribution for the clean surface comes principally from the upper *p* band of silicon.

Without the data reduction needed to obtain the unfold function or transition density, it is also possible to estimate the rough structure of the density of states involved in the ion-neutralization process in the case of hydrogen-saturated surface. Since the highest peak (P_1) in this case lies at $E_{P_1} = E_{VAC}$ = 4.4 eV, the largest peak ϵ_1 in the density of states should be at $(E_{VAC} - \epsilon_1) = 9.2$ eV relative to the vacuum level according to the relation⁹ $E_{P_1} - E_{VAC}$ $=E'_n-2(E_{VAC}-\epsilon_1)$, where E'_n is the effective neutralization energy of the helium ion and is chosen to be 22.5 eV. The additional peak (P_2) lies at $E_{P_{o}} - E_{VAC} = 2.0 \text{ eV}$ in the kinetic-energy spectrum, that is, 2.4 eV below the main peak. It can be shown that the corresponding second peak ϵ_2 in the density of states will lie 2.4 eV below the main hydrogen peak at -9.1 eV, thus at -11.5 eV. Of course, these values are only approximate and can differ from the UPS values by virtue of our choice of E'_n and the effect of energy broadening. However, they are close to the results by UPS from which we conclude that INS and UPS both detect the two atomic-hydrogen peaks in a similar way.

IV. CONCLUSION

Using INS and UPS we have studied hydrogen chemisorption on the Si (111) surface and observed two sharp peaks in surface density of states due to atomic hydrogen on the surface. Our experimental results are in good agreement quantitatively with the theoretical calculations by Appelbaum and Hamann and by Pandey, although the calculations are based on the Si (111) 1×1 surface. Our work also shows the evidence of two surface states seen by others, one just below the Fermi level associated with the dangling-bond surface state and the other 16 eV below the vacuum level due to the back-bond surface state.

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Si(111)-H

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