Chemisorption of chlorine on Si(111) 7 × 7 and 1 × 1 surfaces *

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Using ultraviolet photoemission spectroscopy (UPS) in conjunction with theoretical calculations, we have studied the reaction of gaseous chlorine with Si(111) 7 × 7 and 1 × 1 surfaces. The UPS spectra of the two chlorine saturated surfaces are very similar and consist of four peaks, a sharp main peak at -10.7 eV and smaller ones at -7.5, -13.0, and -15.7 eV relative to vacuum level. Both the peak positions and their relative intensities are in quantitative agreement with a theoretical calculation for a structural model in which a single chlorine atom sits on top of each surface Si atom, indicating that Cl_2 decomposes at the surface to make strong covalent bonds with Si.

Recently Schlüter et al.[1] have studied the chemisorption of chlorine on the cleaved Si(111) 2 × 1 surface using ultraviolet photoemission spectroscopy (UPS) with a synchrotron radiation source and showed that the polarization effect of the incident photon could be utilized to determine the orbital characteristics of electronic states observed by UPS.[1] In this paper we present results for chlorine chemisorption on annealed Si(111) 7 × 7 and 1 × 1 surfaces using UPS with a conventional discharge lamp and we argue that it is possible to observe the photon polarization effect in UPS spectra by varying the photon incident angle using nonpolarized light. A theoretical spectrum calculated for a model system where each surface Si atom is bonded to a Cl atom is found to be in excellent agreement with experiment. The tight-binding approach used here enables us to make a simple symmetry-orbital assignment to the various peaks observed in UPS. These assignments are shown to be consistent with the observed polarization effects.

The vacuum system used for the present investigation has been described elsewhere in detail.[2] Briefly speaking the system consists of UPS, ion neutralization spectroscopy (INS), low-energy-electron diffraction (LEED), Auger electron spectroscopy (AES) and an arc-discharge sputtering device. The background pressure was approximately 2×10^{-11} Torr and experiments on gas chemisorption were carried out in a dynamic gas flow mode at pressures up to 1×10^{-3} Torr. Chlorine gas of research-grade purity was introduced to the Si(111) target surface through a leak valve using a retractable doser with a small orifice (1.25 mm diameter) that could be placed close to the sample surface.[3] In this way the effective chlorine exposure rate was kept at a high value (equivalent to a pressure of $\sim 1 \times 10^{-6}$ Torr) while

the main chamber remained at a much lower ambient pressure ($\leq 1 \times 10^{-8}$ Torr). The Si(111) 7 × 7 surface was prepared by sputter-etching, removing approximately 1000 atomic layers using 150-eV Ne^+ ions, followed by annealing at 600 °C for 10 min. The chemical purity of the surface was monitored by Auger electron spectroscopy. UPS spectra were obtained using a conventional He and Ne discharge lamp and a four-grid hemispherical energy analyzer which collects all the photo-emitted electrons, thus minimizing the multiple scattering or diffraction effects associated primarily with the final states. Angle integrated spectra thus obtained can be interpreted rather easily in terms of the density of occupied states near surface.

Figure 1 shows a family of He I ($h\nu = 21.2$ eV) UPS spectra for the Si(111) 7 × 7 surface with various exposures to chlorine gas (Cl_2). After an exposure of roughly 100 L (10^{-4} Torr sec in Cl_2), we obtain a chlorine-saturated surface (curve 6 in Fig. 1). For this saturation coverage, there are four Cl-associated peaks, the main peak at $E - E_{VAC} \sim -10.7$ and three smaller peaks at $E - E_{VAC} \sim -7.5$, -13.0, and -15.7 eV. Another significant change in the UPS spectrum caused by chlorine adsorption is the reduction in the emission intensity near the top of the valence band. This occurs because the Si dangling-bond surface states disappear upon chlorine adsorption and the adsorbed chlorine does not give rise to any appreciable emission intensity at these energies. Essentially identical UPS spectra were obtained when the clean Si(111) 1 × 1 surface was exposed to Cl_2. These observations were reproduced in the Ne I ($h\nu = 16.8$ eV) UPS spectra so that it is reasonable to assume that the structural changes in the UPS spectra represent changes in the electronic density of occupied states of the Si(111) surface during chlorine ex-

Si(111) + Cl
UPS He I (21.2 eV)

Cl SAT. (6)

6
5
4
3
2
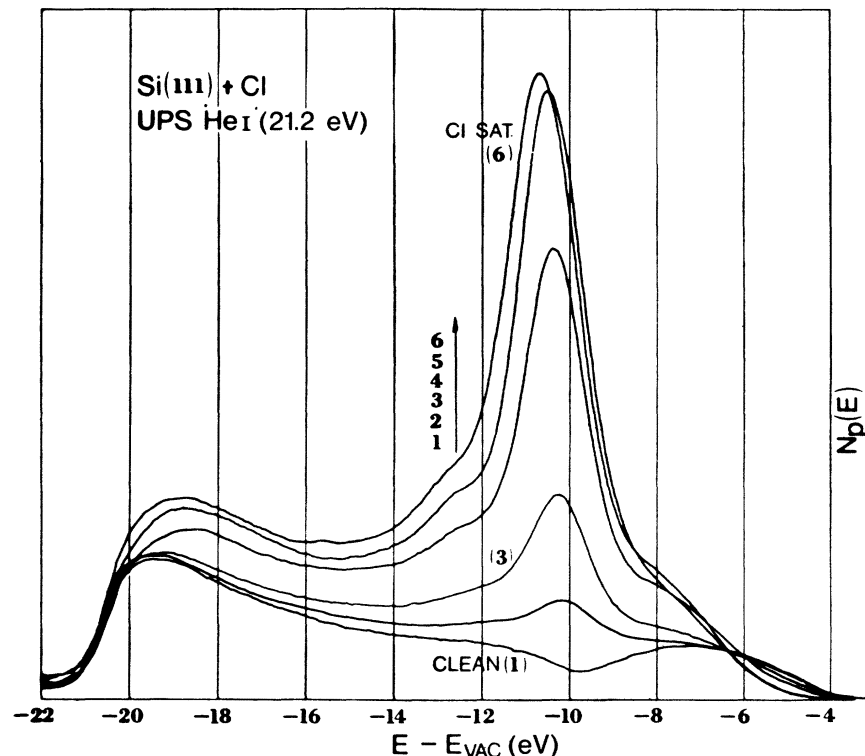1

(3)

CLEAN(1)

$N_p(E)$

$E - E_{VAC}$ (eV)

FIG. 1. UPS spectra $N_p(E)$ of Si(111) surface as a function of increasing chlorine coverage. Clean-surface spectrum shown by curve 1 and chlorine-saturated spectrum by curve 6. All spectra were taken using He I photons ($h\nu = 21.2$ eV) at normal light incidence.

posure. The main chlorine peak shifts its energy level $E - E_{VAC}$ from ~ −10.2 to −10.7 eV with chlorine coverage, as shown in Fig. 1, where the six spectra are aligned with respect to the vacuum level E_{VAC}. However, these peaks line up exactly at $E - E_F = -5.2$ eV when the spectra are aligned relative to the Fermi level E_F. During chlorine adsorption on the 7 × 7 surface the work function first increases monotonically by 1.1 eV and then subsequently decreases to a value 0.9 eV above the clean-surface value. Detailed results concerning the dependence of work function on chlorine coverage will be published elsewhere.[4]

The 7 × 7 LEED pattern which is characteristic of the clean Si(111) surface persists at all chlorine coverages. However, the intensity of nonintegral LEED spots decreases with increasing chlorine coverage. The 1 × 1 LEED pattern of the Si(111) 1 × 1 starting surface also persists on exposure to chlorine. As expected, the curves of the intensity I versus electron energy V of various diffracted beams on both Si(111) 7 × 7 and 1 × 1 change appreciably with exposure to chlorine.

In order to understand the change in electronic structure of the Si(111) surface caused by adsorbed chlorine, a theoretical calculation, using a tight-binding method,[5] was carried out for a model system in which a single chlorine atom sits on top of each Si atom of the ideal Si(111) 1 × 1 surface thus saturating all dangling orbitals to form normal

Si–Cl covalent bonds similar to those in $SiCl_4$. On chemical grounds, this is the simplest and most reasonable model. Even though this structural model assumes the ideal 1 × 1 periodicity and hence cannot be applied to the 7 × 7 surface, we will show that the central assumption of the model—that the covalent bonds are formed—is essentially true for both the 7 × 7 and 1 × 1 surfaces.

The semiempirical tight-binding model employed here to study chlorine chemisorption is similar to that used previously for the study of hydrogen chemisorption on Si and Ge surfaces[6] and is based on the concept of "bond transferability." The basic assumption underlying this model, which is based on the Hückel approximation (i.e., the basis functions consist of orthogonalized atomic orbitals), is that the local bond (i.e., the chemisorption bond) at the surface is similar to the corresponding bond in an appropriately chosen molecule. For chlorine chemisorption on the Si(111) surface such a molecule would be $SiCl_4$. Thus we assume that the Si–Cl bond length at the surface is the same as in $SiCl_4$ and the Hamiltonian matrix elements between different orbitals of Si and Cl are also the same in the two systems. The matrix elements between the various Si orbitals were assumed to be the same as in bulk Si and these have been determined previously[5] from the known bulk energy bands of Si. Because of the rather large number of matrix elements needed to describe the inter-
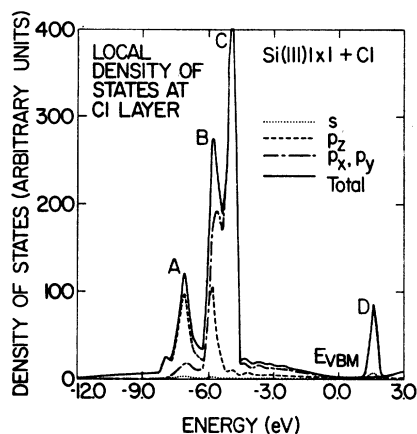
FIG. 2. Local density of states at the surface Cl layer and its decomposition into partial s, p_z and p_x, p_y components. Note that the peak A is mainly p_z-like in character while peaks B and C are mainly (p_x, p_y)-like.

action between Si and Cl orbitals we have used not only the molecular ionization potentials of SiCl$_4$ but also the ionization potentials of SiHCl$_3$, SiH$_2$Cl$_2$, and SiH$_3$Cl molecules for their determination.[7] All the molecular ionization potentials are known experimentally. The matrix elements between Si and H orbitals were determined previously[4] from the molecular levels of SiH$_4$ and Si$_2$H$_6$. Thus all the matrix elements needed in the present calculation are determined uniquely from molecular data.

The calculations of surface states were carried out using a slab geometry and two-dimensional periodicity.[5] All results were checked against the slab thickness so that the results did not depend on it. In the present calculation the slab consisted of 24 atomic layers of Si bounded on each side by a Cl layer. Local densities of states[5,6] for different atomic layers were calculated by numerical integration using a sample of 45 points in the irreducible section $\frac{1}{12}$ of the two-dimensional hexagonal surface Brillouin zone. This basic sample of 45 points was augmented by a factor of 100 by linear interpolation. Further details of the calculation including the interaction parameters etc. will be published elsewhere.[7]

Figure 2 shows the local density of states[5,6] at the surface chlorine atoms. Unlike the clean Si(111) surface, chlorine-covered Si(111) does not have any occupied surface state in the gap. This is expected since the dangling orbitals that give rise to these gap states are saturated, i.e., they are transformed into bonding orbitals giving rise to surface states at lower energies. There are three possible bonding states, one arising from the Cl- p_z orbital (z being surface normal) that makes a σ bond with the dangling sp_3 orbital of Si and the other two from the two Cl lone-pair orbit-

als, p_x and p_y. Because of the interaction between orbitals on the neighboring Cl atoms these lone-pair states are split. Due to the symmetry of the (111) surface one of the lone-pair orbitals hybridizes with the σ orbitals and lowers its energy, while the other does not. These states give rise to peaks in the local density of states (Fig. 2, energies measured relative to the valence-band maximum, E_{VBM}); A at -7.10 eV due to the σ bond and B and C at -5.75 and -4.95 eV, respectively, due to the lone-pair orbitals. To show clearly the nature of the states giving rise to these structures, Fig. 2 includes a decomposition of the local density of states into its partial s, p_z, and p_x, p_y components. In addition to these bonding states there is an empty state (peak D at 1.55 eV) of σ antibonding character. This empty state should be observable in electron-energy-loss spectroscopy. Note that, as a result of bonding, states from near the top of the valence band and in particular the dangling-bond states have been removed and the Fermi energy E_F is pinned at the top of the valence band.

In order to make a direct comparison between theory and experiment, a theoretical UPS spectrum[6] was obtained by superposition of the local densities of states of various layers weighted by an escape factor arising from the small escape depth of photoexcited electrons (assumed to be 5 Å). The resulting spectrum, broadened by a Lorentzian of half width 0.7 eV to simulate experimental broadening, is shown in Fig. 3 where it is compared with experiment. The theoretical spectrum obtained in this way represents the distribution of primary electrons only. The experimental
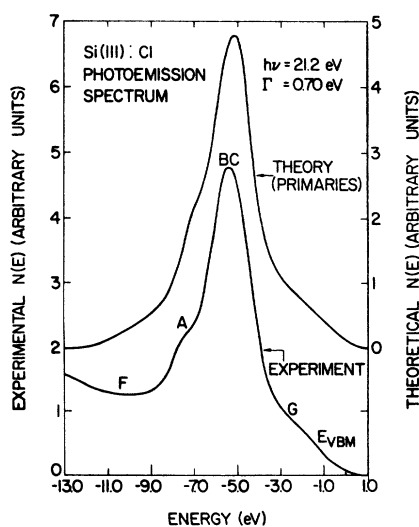

FIG. 3. Comparison between the experimental and theoretically simulated UPS spectra of chlorine saturated Si(111) surface. The experimental curve is for normal light incidence.

UPS spectrum includes a component of secondary electrons which raises the curve deep in the band, but does not alter the structure to be compared with the theoretical curve. The large peak labeled BC in Fig. 3 arises from the lone-pair peaks B and C of Fig. 2 which are now merged together due to resolution broadening. The shoulder A in Fig. 3 is due to the σ bonding peak, A, in Fig. 2. The small shoulders F and G at approximately −10.0 and −2.0 eV, respectively, are due to the under-lying Si layer which participates in bonding and whose local density of states is modified from that of bulk Si. In recent UPS measurements with better resolution,[1] the doubly split nature of the peak BC has clearly been demonstrated. It is clear that the two spectra in Fig. 3 are in very good agree-ment with each other, confirming the validity of the structural model. It also shows that the semiem-pirical tight-binding method for chemisorption studies, which has so far been applied to purely covalent cases only, can also be successfully em-ployed when the bonding is appreciably ionic.

A further test of our model, including the or-bital assignments of the various peaks, can be obtained from the dependence of the UPS spectra on the photon incidence angle θ_i. By changing the angle of incidence, the s vs p polarized component changes. At normal incidence the light is purely s polarized, i.e., there is no component of the electric vector normal to the surface which can excite electrons from a p_z-type orbital. Thus peak A in Fig. 3, which is due mainly to the p_z-type orbitals, should be small for normal incidence. Further, this peak should grow in intensity as we move away from normal incidence. That this is indeed the case is shown in Fig. 4, where the ratio of intensities of peaks A and BC, which can be measured more accurately than the absolute in-tensities, is plotted as a function of the incidence angle.

We also studied the effect of target temperature during chlorine exposure and found no significant
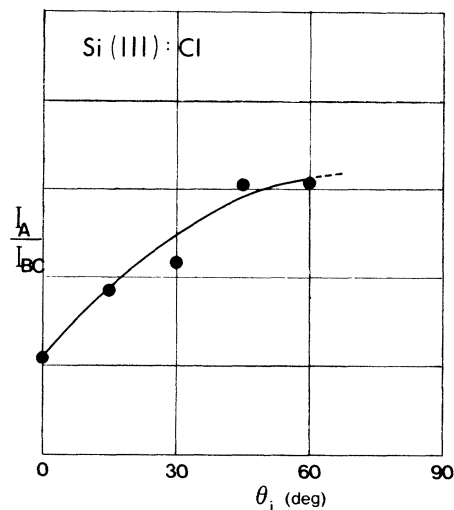

FIG. 4. Intensity ratio of peak A to peak BC as a func-tion of photon incidence angle θ_i.

change in the emission intensity due to heating ex-cept for some sharpening of the main peak, BC, at elevated temperatures (~400 °C) as a result of surface migration and island formation[8] of the sili-con-monochloride phase. The fact that there is no or very little temperature dependence suggests that dissociation of chlorine molecules into the chlorine atoms to form the monochloride phase on Si(111) occurs readily at room temperature.

We conclude that chlorine atoms make covalent bonds with the surface Si atoms on the two an-nealed surfaces, Si(111) 7 × 7 and 1 × 1, so as to saturate the surface dangling orbitals of Si. As shown by Schlüter et al.[1] similar local bonding oc-curs on the cleaved Si(111) 2 × 1 surface as well.

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