Enhanced conductance of chlorine-terminated Si(111) surfaces: Formation of a two-dimensional hole gas via chemical modification

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Chlorine termination of low-doped, *n*-type Si(111) is found to lead to an increase in conductance relative to the hydrogen-terminated surface. This increase is attributed to formation of an inversion layer due to the strongly electron withdrawing character of the chemisorbed chlorine. The presence of this inversion layer is confirmed by high resolution electron energy loss spectroscopy and Hall effect measurements. Electron beam irradiation destroys the inversion layer, suggesting a route to nanoscale patterning of this 2D hole gas.

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Chemical modification can strongly modulate the conductivity of semiconductor surfaces by inducing surface states of acceptor or donor character, resulting in band bending. Although there are many reports of adsorbate-induced band bending in the literature,[1–5] the exploitation of this effect to tailor the conductivity of surfaces has remained largely unexplored. Previous surface conductivity studies on semiconductors have focused on clean and adsorbate-covered surfaces prepared under ultrahigh vacuum (UHV) conditions, facilitating observation of conduction through surface state bands.[6–10] Recently there has been considerable progress in the development of wet chemical methods for controllably modifying silicon surfaces in ways that cannot be achieved through UHV approaches.[11,12] The starting point for these modifications is usually the atomically flat H-terminated Si(111) surface produced by a wet etching procedure and exhibiting remarkably low surface state densities.[13–15] Replacing hydrogen with functional groups of electron donating or withdrawing character offers the possibility of systematically altering band bending and hence surface conductivities.

In this paper, we show that photoinduced (UV) chlorination of H-Si(111) surfaces is found to significantly enhance the surface conductance. This somewhat surprising result can be explained in terms of the formation of an inversion layer resulting from the strongly electron withdrawing nature of the chemisorbed chlorine. The presence of the minority carrier channel is confirmed via Hall effect measurements. Furthermore, *in situ* conductivity measurements are used to observe a spontaneous room temperature dark reaction of molecular chlorine with the H-terminated surface, demonstrating the utility of adsorbate-induced conductivity changes in monitoring adsorption events and reactions on semiconductor surfaces.

Samples used in these studies were cut from *n*(phosphorous)-doped silicon wafers (Virginia Semiconductor) with resistivities of 10–1000 Ω cm, corresponding to doping densities in the range of 10^{13}–10^{14} cm^{-3}. Atomically flat, hydrogen-terminated Si(111) surfaces were prepared by chemical cleaning followed by etching in 40% NH_4F as previously described.[14,15] Initially, chlorine-terminated surfaces [Cl/Si(111)] were produced by exposing the H-terminated surface [H/Si(111)] to ~20 torr of molecular chlorine (2% Cl_2 in Ar) in a quartz Schlenk tube under UV irradiation in a photoreactor for 5 min.[16,17]

Ultrahigh vacuum (UHV) scanning tunneling microscopy (STM) images of freshly chlorinated surfaces (shown in the inset of Fig. 1) indicate that they are atomically flat with an average terrace width of ~50 nm, reflecting the morphology of the initial H/Si(111) surface. However, an increased density of etch pits is noted, indicating that the chlorination step has caused additional etching. Atomic resolution images clearly show the expected (1×1) hexagonal structure. Auger electron spectroscopy shows substantial Cl and Si signals with no detectable oxygen or carbon peaks. From the measured Cl/Si signal ratio the Cl coverage is estimated at 0.9±0.1 ML. High-resolution electron energy loss spectroscopy (HREELS), discussed in more detail below, indicates the chlorination reaction has gone to completion, with evidence of a small amount of oxidation and hydrocarbon contamination of the surface.

Surface conductivity of these Cl/Si(111) surfaces was measured via *ex situ* four-probe measurements in the van der Pauw geometry. Several methods of making electrical contact to the sample were employed including direct contact of tungsten probes as well as contact pads of InGa eutectic and

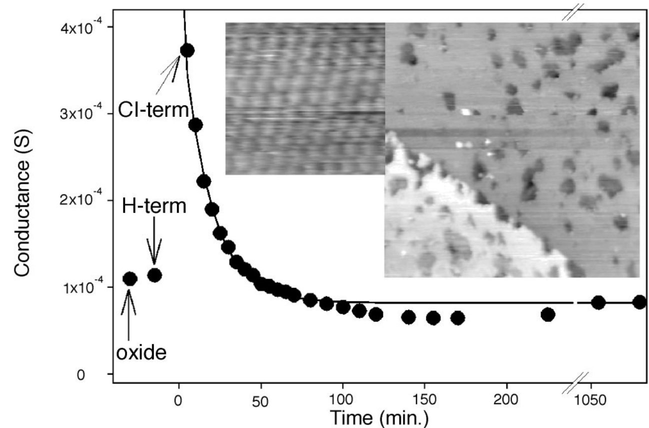

FIG. 1. Sheet conductance versus time in ambient for a chlorine-terminated surface prepared by UV irradiation of H/Si(111) in the photoreactor for 5 min. The solid line is a fit to an exponential decay with a time constant of 17 min. The inset shows STM images of Cl/Si(111): an atomic resolution image (2.5×2.5 nm, –2.1 V, 180 pA) and a wider area scan (100×100 nm, +2.9 V, 50 pA).

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$TiSi_2$ with all methods yielding similar results. The measured sheet conductance as a function of time in air is shown in Fig. 1. Although the conductance does not change significantly upon removal of the oxide and hydrogen termination, the chlorination step causes a dramatic conductance increase. This enhanced conductance decreases exponentially with time, eventually returning to a value slightly below that of the initial H/Si(111). Time constants for this decay range from ~15 min. to 1 h and increase as the humidity level in the laboratory decreases, suggesting that water-induced oxidation of the surface is responsible for the degradation. In a dry N_2 purge the time constant increased to >5 h. The measured conductance can be considered to be a sum of surface and bulk terms ($G_m = G_b + G_s$). The H/Si(111) surface has a low density of surface states and minimal band bending, implying $G_s = 0$. Using H/Si(111) as a measure of the "bulk" conductance (G_b) the surface conductance for the Cl/Si(111) surface in Fig. 1 is estimated to be $\sim 3 \times 10^{-4}$ S.

As the UHV characterization shows the Cl/Si(111) surfaces are atomically flat with minimal contamination, the enhanced conductance is attributed to an intrinsic property of these surfaces. As chlorine is expected to withdraw electrons from the surface, chlorination is expected to induce upward band bending, leading to depletion of the majority carriers (for *n*-type Si) and hence a decrease in conductivity. However, for large band bending, the valence band edge will approach the Fermi energy, resulting in inversion (i.e., accumulation of minority carriers at the surface) and increasing the measured conductance. Kelvin probe measurements on these surfaces indicate that chlorination induces a large (1.2–1.5 eV) increase in the work function, consistent with substantial upward band bending. While adsorbate-induced inversion has been reported previously in photoemission studies of chlorine adsorbed on cleaved GaAs(110) surfaces in UHV,[1] the observation of an inversion layer on non-UHV prepared surfaces is somewhat surprising as a small concentration of electrically active extrinsic defects will prevent the inversion condition from being achieved. Thus the observation of inversion for Cl/Si(111) implies that it is possible to prepare chemically modified surfaces that maintain the low extrinsic electrically active defect densities exhibited by H/Si(111).

Certain similarities exist between the current observations and those on H-terminated diamond (*p*-type) surfaces, for which an enhanced conductance in ambient has been attributed to accumulation of holes induced by the presence of a thin adsorbed water layer.[18,19] In contrast, Fig. 1 indicates the conductance of Cl/Si(111) is degraded in air, with humidity playing a deleterious role. To further investigate the role of the ambient in the current observations, *in-situ* measurements of conductance changes induced by the chlorination reaction have been performed. Conductance as a function of UV (Hg pen lamp, Oriel) irradiation time is shown in Fig. 2. A clear increase of approximately 10% in the measured conductance after ~60 s of UV irradiation is observed. Subtracting the bulk contribution in this case yields $G_s \sim 1 \times 10^{-5}$ S, considerably lower than that of the air exposed sample in Fig. 1. Further irradiation beyond the conductance maximum results in a decrease of the conductance, presumably due to

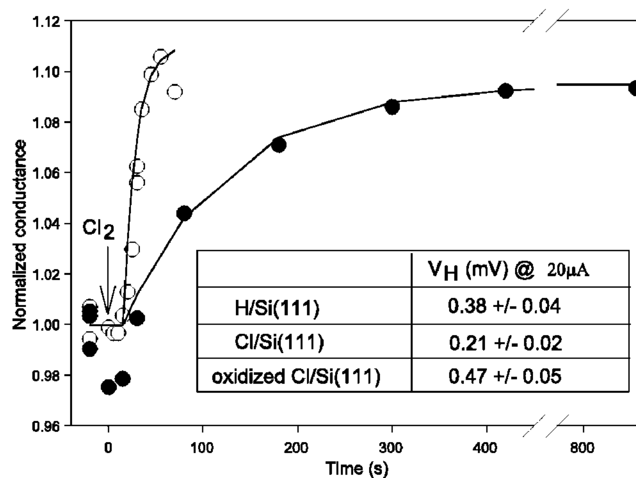

FIG. 2. Normalized conductance versus time during reaction of H/Si(111) under ~15 torr of Cl_2 in the dark (filled circles) and under UV irradiation (open circles). The solid lines are fits to an exponential rise to a maximum with time constants of 110 and 13 s, respectively. The table summarizes the Hall effect measurements for the thermally reacted sample.

defects arising from Cl-induced etching of the surface. These defects may reduce the amount of band bending and/or act as scattering centers, degrading the mobility. When these "over-irradiated" surfaces are exposed to air the conductance initially increases rapidly up to $\sim 2 \times 10^{-4}$ S, before exhibiting the usual ambient-induced degradation. These observations indicate that, in addition to the intrinsic conductance increase resulting from the chlorination reaction, physisorbed species may further enhance the conductance. This is not unexpected as once the inversion condition is reached, small additional changes in band bending can lead to substantial conductivity changes.

During the *in situ* measurements it was also noted that the conductance increases upon exposure to Cl_2 even in the absence of UV irradiation (filled circles in Fig. 2). The conductance increase is of similar magnitude (8×10^{-6} S) but takes place considerably slower than under UV excitation. The observation of spontaneous chlorination at 22 °C has not been previously reported but is not unreasonable as the reaction $Cl_2 + Si\text{-}H \rightarrow HCl + Si\text{-}Cl$ is exothermic by ~60 kcal mol^{-1}. A thermal reaction of Cl_2 with H/Si(111) has been reported at 80 °C.[20]

HREEL spectra of Cl/Si(111) surfaces prepared both with and without UV irradiation are shown in Fig. 3, along with a spectrum from the initial H-terminated surface. For H/Si(111) the two most prominent peaks at 625 and 2080 cm^{-1} are attributed to the Si-H bend and stretch modes, in agreement with previous studies.[21,22] Weaker modes at 505, 785, and 1100 cm^{-1} are assigned to Si optical phonons and Si-OH and Si-O-Si modes, respectively. Upon Cl-termination by either route an intense peak appears at 575 cm^{-1} and is attributed to the Si-Cl stretch, consistent with observations for terminally bound Cl on Si(100).[23] For the thermal reaction the small peak at 2215 cm^{-1} is due to residual Si-H and indicates that the reaction has not gone to completion after the 30 min exposure time used here.

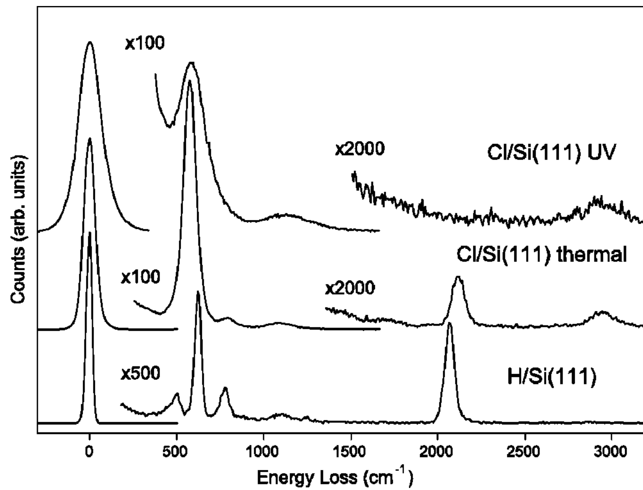

FIG. 3. HREELS spectra (E_i=6 eV) of Cl/Si(111) prepared in the dark (30 min) and under UV irradiation (5 min). A spectra of H/Si(111) with the same bulk carrier density (2×10^{13} cm^{-3}) is shown for comparison purposes. Spectra have been normalized for equal elastic peak intensities.

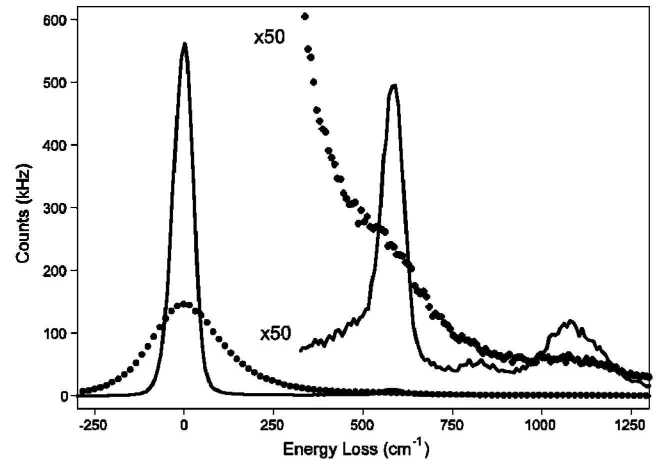

FIG. 4. HREELS spectra of Cl/Si(111) (E_i=6 eV) before (solid) and after (dotted) 5 min of e-beam irradiation (500 eV, ~1 μA).

(Longer exposures did result in completely chlorinated surfaces). Both Cl-terminated surfaces exhibit some degree of oxidation, as indicated by the 1100 cm^{-1} Si-O-Si mode, although this mode is considerably larger for the UV irradiated sample.

HREELS can also be a sensitive probe of band bending at surfaces through observation of the free carrier plasmon, the frequency of which depends on the carrier density.[24,25] As seen in Fig. 3, the elastic peak for H/Si(111) is resolution limited with a FWHM of 36 cm^{-1}. Broadening of the quasi-elastic peak is observed for both Cl/Si(111) surfaces, the FWHM increasing to 74 and 160 cm^{-1} for thermally and UV reacted surfaces, respectively. Given the bulk carrier density of the samples (~2×10^{13} cm^3), the plasmon frequency associated with bulk carriers is <5 cm^{-1} and will not contribute to the width of the quasi-elastic peak. The broadening observed for the Cl-terminated surfaces can therefore be attributed to excitation of a hole plasmon arising from the presence of the inversion layer. The fact that the inversion layer remains present under UHV conditions (even after gentle heating to 100 °C) is further evidence that this an intrinsic property of Cl/Si(111) and not solely caused by physisorbed species. The larger broadening for the surface produced via UV irradiation indicates a higher density of near surface carriers, consistent with the higher conductivity observed for these "over-irradiated," briefly air exposed surfaces. Simulations of these HREELS spectra using a two-layer model of the carrier density[25] are in good agreement with near surface carrier densities of ~4×10^{17} and 8×10^{16} cm^{-3} for the UV and thermally reacted surfaces, respectively.

The broadening of the quasi-elastic peak in the HREEL spectra confirms an increased carrier density in the near surface region, but does not distinguish the sign of the carriers. Therefore the conductance and HREELS data are entirely consistent with an excess of majority or minority carriers (accumulation or inversion). While the electron withdrawing nature of chlorine strongly suggests the latter to be more likely, Hall effect measurements were carried out in order to confirm this expectation. In the case where minority carriers are dominant in the near surface region, the "surface" contribution to the Hall voltage (V_H) will have the opposite sign of that in the bulk. As can be seen from the table in Fig. 2, V_H is observed to decrease significantly upon chlorination, consistent with the presence of an inversion layer. Since $V_H=BI/qn_s$ (where B is the magnetic field, I is the current, and n_s is the sheet carrier density), to model the observed changes in V_H the current flowing through each of the "surface" and "bulk" layers must be determined. As before, the H-terminated surface is used to determine the bulk conductance and n_{sb} (the "bulk" sheet carrier density, 1.8×10^{12} cm^{-2}). The resulting hole density in the Cl-induced inversion layer is determined to be 4×10^{11} cm^{-2}. The extracted values of the carrier density and the conductance of the inversion layer can be used to extract the mobility through the relation $\mu=1/(qn_sR_s)$. The resulting mobility is determined to be 110 cm^2 V^{-1} s^{-1}, comparable to the bulk hole mobility in Si (450 cm^2 V^{-1} s^{-1}). Hall effect measurements were also performed for chlorinated p (boron)-doped Si(111) (N_a=7 $\times10^{14}$ cm^3). In this case no measurable conductivity increase was observed (<1%), yet a small but significant increase in the Hall voltage was detected. This increase in V_H is expected since Cl termination will still give rise to upward band bending, but on a p-type substrate this implies accumulation of the majority carriers (i.e., holes).

The mobility extracted from the Hall effect measurements can then be used to determine the band bending required to account for the observed conductance changes. The surface conductance induced by band bending effects can be calculated from the expression[26] $G_s=e(\mu_{n,s}\Delta N+\mu_{p,s}\Delta P)$, where $\mu_{n,s}$ and $\mu_{p,s}$ are the electron and hole mobilities at the surface while $\Delta N=\int(n(z)-n_b)dz$ and $\Delta P=\int(p(z)-p_b)dz$ represent the excess carrier concentrations in the near surface region. From this equation it is evident that, in the absence of band bending (as for the H-terminated surface) $G_s=0$. Using

this approach we determine that the observed surface conductance of 8×10^{-6} S (for the thermally reacted surface) can be obtained with $\sim$0.68 eV of band bending, requiring a surface charge of 6.1×10^{11}. For a monolayer of chlorine this corresponds to a fractional occupancy of a Cl-induced acceptor state of 7.8×10^{-4} ($\sim$1e per 1280 Cl atoms). We note that the larger "air-enhanced" conductances of $\sim3\times10^{-4}$ S on the over-irradiated surfaces necessitates a considerably larger band bending of 0.85 eV, requiring a fractional charge of $\sim$0.02e per Cl atom. These values of band bending are consistent with the near surface carrier densities suggested by the analysis of the HREEL spectra.

If the increased conductivity is in fact due to the presence of an inversion layer, it should be possible to destroy this layer by introducing a small amount of electrically active defects. Figure 4 illustrates the effect of e-beam irradiation with 500 eV electrons on the HREEL spectrum. The quasi-elastic peak is seen to narrow dramatically upon irradiation, with the FWHM decreasing from 220 cm^{-1} down to 65 cm^{-1}. The integrated area of the quasi-elastic peak is conserved to within $\pm2\%$, indicating the reflectivity of the sample has not changed significantly. While four-probe measurements could not be carried out in the UHV chamber, the two-probe resistance of the sample was found to increase substantially upon irradiation. Both these observations are consistent with e-beam-induced defects slowly destroying the inversion layer. As the elastic peak narrows, the Si-Cl stretch mode at 575 cm^{-1} is observed to sharpen and increase in intensity. The observation of a strong Si-Cl stretch mode after irradiation indicates that only a small amount of Cl was desorbed by the electron beam. As electron-stimulated desorption of Cl from silicon is known to occur,[23] it is reasonable to suggest that the e-beam induces dangling bonds which can act as donor states (hole traps), counteracting the effect of the chlorine-induced acceptor states. If each of these defect states can trap one hole, a small number of defects ($<2\%$) could completely destroy the inversion layer. The sensitivity of the chemically induced inversion layer to e-beam irradiation suggests a route to nanoscale patterning of this layer using an SEM or STM.

In summary, measurements of electrical transport have indicated that Cl-termination of Si(111) leads to an enhancement of surface conductance relative to H-termination. This enhancement has been shown to be due to formation of a 2D hole gas resulting from the strong electron withdrawing nature of the adsorbed chlorine. The exploitation of chemical modification to tailor the conductivity of semiconductor surfaces, used in conjunction with the myriad of available strategies for micro- or nanoscale chemical patterning, suggests a new approach for the creation of low-dimensional conducting channels for both fundamental studies and practical applications.

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