PHYSICAL REVIEW B VOLUME 26, NUMBER 4 15 AUGUST 1982

Hydrogen surface segregation on Si(111) by photon-stimulated desorption at the Si *K* edge

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(Received 29 April 1982)

The photon-stimulated desorption of H^+ from cleaved Si(111) using photon energies near the Si *K* excitation threshold is reported. The time dependence of the H surface segregation from the bulk following cleavage shows two or three sequential time regimes of growth kinetics suggesting multiple sequential hydride phase formations. Removal of the H from the H-saturated surface results in the subsequent observation of only the first time regime (which we interpret as being due to formation of a monohydride phase).

I. INTRODUCTION

There has been considerable interest in the chemistry of hydrogen on the silicon surface. From photoemission[1-3] and high-resolution electron-loss[4] measurements, it has been shown that multiple hydride phases form on the silicon surface as a function of the hydrogen exposure. Evidence exists for Si(111):H, Si(111):H_2, and Si(111):H_3 phases on the Si(111) surface.[1,4] Most of the hydrogen on silicon work employs high levels of molecular hydrogen exposure to form the hydrided surface. It has been noted that atomic hydrogen is much more reactive than molecular hydrogen on the Si surface.[1,2,4,5] Recently, electron- and photon-stimulated desorption (ESD and PSD) have detected rather high levels of contaminant hydrogen on silicon surfaces, arising from the segregation of hydrogen from the bulk of the sample.[6,7] Silicon crystals prepared by many of the standard crystal-growth schemes can contain relatively high concentrations of hydrogen. Hydrogen segregating to the surface from the bulk can affect surface chemisorption and reaction measurements. ESD measurements suggest that reacting oxygen with the hydrogen contaminated silicon surface gives both hydride and hydroxide forms of hydrogen.[6]

The experiments discussed here attempt to derive chemical information for the hydrogen bonding sites on the silicon surface by examining near-edge structure in the PSD spectral dependence above the silicon *K* edge. Spectral dependence of PSD above an adsorption edge can reflect the x-ray absorption spectrum of the bonding site of the desorbed species[8] and can be used to derive structural and electronic information for the bonding site. We find that the time dependence of H^+ desorption yield after cleaving of the surface suggests that sequential multiple hydride phases are formed on the surface as a function of time, saturating after a period of one to two hours. The hydrogen comes not from an external ambient, but segregates to the surface from the bulk. It is found that subsequent *e*-beam exposure of the surface at low energy and low fluence removes the hydrogen and the surface is modified such that H coverage saturates after the first time regime. As a function of time after cleavage H^+ PSD Si *K*-edge spectra show variations suggesting that the silicon bonding site structure is changing.

II. EXPERIMENTAL

The experiments employed the Stanford Synchrotron Radiation Laboratory double crystal monochromator with InSb crystals ($1850 < h\nu < 4000$ eV, $\Delta E = 1.7$ eV at 1850 eV). The experiments used a baked UHV chamber with ion pumping and a liquid-nitrogen cooled titanium sublimation pump (base pressure $2-4 \times 10^{-10}$ Torr). The samples were cleaved Si(111) crystals from two different *n*-type silicon boules (one was 5 Ω cm and the other was 0.001 Ω cm). PSD experiments used a time-of-flight technique described elsewhere[8] with a new detector employing a deflected ion beam and an occluded line of sight to the CEMA (channel electron multiplier array) detector, to avoid detector saturation from x-ray fluorescence. X-ray fluorescence (XRF) measurements were made by recording the prompt counts from the ion detector. Total photoelectron yield (PEY) measurements were made using a biased channeltron electron multiplier.

III. RESULTS

After cleaving the Si(111) surface, it was found that the H^+ PSD signal appeared and increased with time in the absence of any hydrogen containing ambient. While we could envision pressures as high as 10^{-9} Torr of H_2 due to line-of-sight exposure of the sample to the beamline, these levels of H_2 could not lead to the degree of hydridation we observe. As has been previously observed,[6,7] the hydrogen seems to be segregating to the surface from the bulk. This migration comprises a constant, low-level supply of atomic hydrogen to the surface, an ideal condition to study hydride formation chemistry. Shown in Fig. 1 are measurements of the time dependence of the H^+ signal (at a photon energy of 1843 eV) as a function of time after cleavage for the 5 Ω cm boule. First of all, from $t=0$ to ~ 17 min, there is a *linear* increase of the H^+ signal. At $T \sim 17$ min, there is a knee in the curve followed by a more gradual increase in the H^+ signal with time. Saturation eventually occurs at $\sim 6-10$ h. Note that there seems to be a second break at ~ 70 min.

In the saturation region, to determine whether the hydrogen desorption is from minority sites or a majority surface phase, the surface was exposed to molecular hydrogen, to activated hydrogen (injected through an ionizer), and finally to a sputter beam of high-energy hydrogen ions (ranging in energy from 500 eV to 5 keV). These techniques are commonly employed to hydride the Si surface. None of these techniques resulted in any significant increase in the saturation hydrogen signal. Specifically, the H^+ signal was never more than three times the yield at the first knee in Fig. 1, curve a. If the hydrogen was bonded at defect sites, the sputtering treatment would introduce a high density of these defect sites from which enhanced desorption of hydrogen should be observed. After sputtering, however, the hydrogen signal decreased by roughly a factor of 2 and gradually returned to the previous saturation level, suggesting that the hydrogen in both cases arises from a majority chemical state, presumably a trihydride.

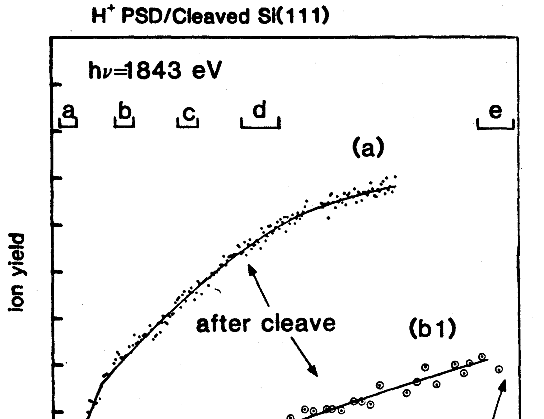

FIG. 1. H^+ PSD yield at $h\nu = 1843$ eV as a function of time after cleave: curve a, first sample; curve b1, second sample after cleave; curve b2, second sample after *e*-beam exposure at ~ 150 min of curve b1.

Shown in Fig. 1, b1 is another uptake curve taken on a cleave of a second crystal of the same boule. Again we see that for short times there is a linear uptake of hydrogen, followed by a gradual uptake above ~ 20 min. The curve a in Fig. 1 was taken only slightly past 80 min and showed two regions of H uptake and a suggestion of a second knee. The data of Fig. 1, curve b1 suggest again that there may be a third region in the time dependence above 80 min. After roughly three hours of measurement, the sample was radiated with an *e* beam of 135 eV at ~ 100 $\mu A/cm^2$ for 15 min. This irradiation caused the H^+ yield to return to the level shown in Fig. 1, curve b2 and increase with time, as shown. For $t < 17$ min, the t dependence is linear and shows the same slope seen on the initial cleaved surface, but at $t > 17$ min, instead of exhibiting the second phase, a saturation in H^+ is observed. This result suggests that the electron irradiation has done two things: (1) It has removed the hydrogen from the phase formed at saturation; and (2) thereby induced a modification of the surface such that the second hydride phase is not reformed. We note that the electron irradiation that was given to the sample after saturation is less than what is normally used in a low-energy electron diffraction (LEED) experiment. Therefore whatever hydride phase we see formed on the silicon surface at saturation is probably not observable by standard LEED techniques because the LEED beam removes the hydrogen in a short time. We also observed that the H removal rate by *e*-beam bombardment was much lower in the first observed phase than the later phases.

If, indeed, we are observing multiple phases of hydride formation as a function of time, we would expect that the silicon site to which the hydrogen is bonded should go through structural transformations as the amount of hydridation increases. One way to determine the changes in chemical state is to look at the PSD spectral dependence in the near-edge region as a function of time. Shown in Fig. 2 are a series of H^+ PSD Si *K*-edge spectra, which were taken over the time span shown in Fig. 1, curve a, plus a PEY and XRF spectrum. The PEY spectrum agrees in detail with recent data of Hussain *et al.*[9] The XRF, shown only for reference at this time, is distinctly different in near-edge structure and has a threshold 1 eV lower than the PEY or PSD. The first PSD spectrum shows a near-edge structure similar to the PEY but the peak at 1843 eV in all of our PSD spectra is smaller relative to the step above the edge than the PEY spectra. (Note that the PSD spectra are taken as the H^+ signal is rather rapidly increasing on the time scale necessary for a spectrum. The data were renormalized to the equivalent time data of Fig. 1, curve a, to arrive at an approximate spectral curve.) As the reaction proceeds there is a distinct change in spectral shape (Fig. 2, curves b, c, and d). In addition to the structure at 1843 eV another structure builds in at roughly 1845 eV, such that, in Fig. 2, curve c, a broad flat-top structure extending from roughly 1842–1845 eV is observed. The spectrum taken near saturation of the H^+ signal (Fig. 2, curve e) is seen to once again display the near-edge peak at roughly 1843 eV. These data suggest that the distribution of hydrogen bonding sites on the silicon surface goes through a transformation with time. An early stage is followed by a stage where the silicon chemistry is rather dramatically changed followed by a final saturation phase where the spectrum again resembles the earliest stage.

The time dependence of the H^+ desorption after cleavage is the most intriguing data we present. The near-edge spectral dependence, while suggestive of chemical variation, is difficult to interpret in detail. To understand the time dependence we first point out that we are exciting a Si *K* hole. The Auger cascade following such a *K*-hole creation will produce *four* or *five* valence holes.[10] Hence, we do not expect a chemical dependence to the H^+ yield, but can reasonably assume that *any* Si–H bond will be broken in such a process. Hence, we assume for this discussion that the H^+ yield simply reflects the H density on the surface. Our data suggest a *linear* filling of a first phase, followed by a slightly sublinear filling of a second, followed *possibly* by a third phase. A linear time dependence suggests chemisorption to fill the first state or site does not necessarily occur in that state or site but can occur through adsorption at some other site. Hence, the rate of filling of the first state does not diminish as it becomes saturated. The fact that the first site fills most readily suggests a labile chemistry, e.g., a monohydride formed with dangling bonds so that H-Si-Si_3 units are formed. The second phase has a less labile character (e.g., formation of H_2-Si-Si_2 by H attack of an Si–Si bond). The formation of H_3-Si-Si would be the most restrictive step, requiring breakage of another Si–Si bond. Further hydridation will then result in SiH_4 evolution into the gas phase and the process would then repeat itself. Electron irradiation of the H-saturated surface resulted in a modification or "reconstruction" such that it did not reform past the first hydridation phase. This modification may not be due so much to the presence of H as to the fact that, after the H attacks the surface and is subsequently removed (either with an *e* beam or thermally), a highly unsaturated and disordered surface remains, which can dramatically restructure to minimize energy.

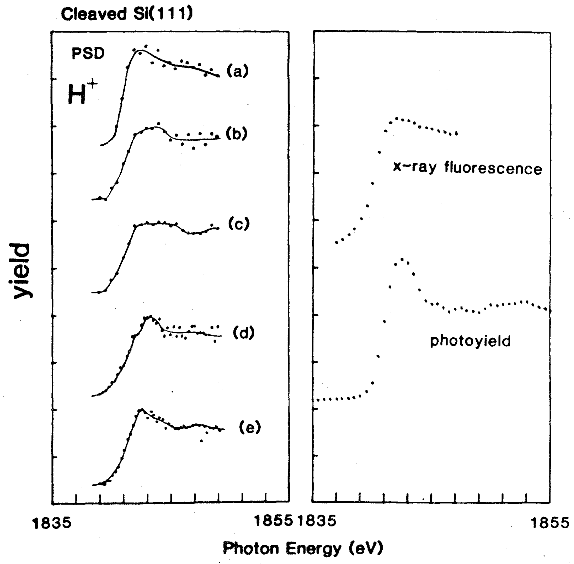

FIG. 2. H^+ PSD spectral dependence at Si *K* edge over time spans shown in Fig. 1, plus total photoyield and x-ray fluorescence on freshly cleaved samples.

In summary, these results suggest that, first of all, we are observing a majority, not a minority, hydrogen species on the Si surface. Second, the time dependence of the H^+ PSD yield, taken together with the time dependence of the spectral dependence, suggest distinct hydride phases forming with time. Finally, removal of the hydrogen leaves a highly unsaturated surface which we interpret to reconstruct due to the *removal* of the H. The reconstructed phase is stable against H attack, as has been noted for the Si(111)-(7 × 7).[1]

ACKNOWLEDGMENTS

The authors gratefully acknowledge R. J. Baughman for supplying the samples for these experiments and S. J. Haney and J. A. Borders for their excellent technical assistance. This work was performed at Sandia National Laboratories and supported by the U.S. DOE under Contract No. DE-AC04-76DP00789. Experiments were conducted at Stanford Synchrotron Radiation Laboratory, which is supported by NSF Grant No. DMR-77-27489 in cooperation with the DOE.

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