

Departure from a stable SiH₃ phase on Si(111)

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A combined ultraviolet-photoemission- (UPS) and Auger-electron-spectroscopy investigation on the interaction of atomic hydrogen with the Si(111) surface shows that for high H exposures [$> 10^3$ L ($L = 10^{-6}$ Torr sec)] coadsorbed oxygen impurities build up at substrate temperatures below 200 °C. The oxygen contamination gives rise to a UPS spectrum which is virtually identical with the spectra so far attributed to a stable (up to 700 °C) SiH₃ phase under similar experimental conditions.

I. INTRODUCTION

The interaction of atomic hydrogen with silicon single-crystal surfaces has been the subject of numerous publications. Based on ultraviolet-photoemission-spectroscopy (UPS) and low-energy-electron-diffraction (LEED) investigations, it was concluded that a monohydride phase forms at first on the (100)-(2 × 1) surface and that upon further H dosing at room temperature a dihydride phase (SiH₂) develops which relaxes the (2 × 1) reconstruction.^{1,2} Also on the (110)-(5 × 1) surface a SiH phase forms under relaxation of the (5 × 1) reconstruction and additional H adsorption is considered to occur at nontetrahedral sites.^{3,4} A monohydride phase was also deduced for the Si(111)-(7 × 7) surface.^{2,5} Apart from the nontetrahedral binding configuration invoked for the Si(110) surface, the chemisorption of hydrogen so far considered proceeds via the saturation of available dangling bonds. In case of the (100) plane this process necessitates already the breaking of the dimer bonds of the (2 × 1) reconstruction for the SiH₂ formation and places the Si surface atoms essentially back into bulklike positions.

Pandey *et al.*⁶ observed dramatic changes of the UPS spectrum after high doses of atomic hydrogen to the quenched Si(111)-(1 × 1) surface. Supported by theoretical work they attributed this to the formation of a stable SiH₃ phase. The creation of this phase necessarily implies the breaking of Si-Si bonds to provide for the -SiH₃ bonding configuration. Our recent study⁸ on Si vibrations on the Si(111)-(7 × 7) surface led us also to consider the breaking of Si-Si bonds to account for the occurrence of SiH₂ units especially for substrate temperatures below 250 °C. We did not find direct evidence for SiH₃ complexes. Above about 250 °C only SiH units are stable on Si(111) (Refs. 8 and 9) as well as on Si(100).^{1,9} However, the SiH₃ phase, as deduced from the photoemission spectra, was found to be stable up to 700 °C (Ref. 6) which is much higher than the tem-

perature (350 °C) required to remove hydrogen from SiH units. The present study reveals that oxygen impurities accumulating at the Si(111) surface during the high hydrogen exposure desorb at around the same temperature and that their contribution to the UPS spectrum fully accounts for the drastic changes so far ascribed to a SiH₃ phase. In fact, UPS spectra obtained for oxygen adsorption alone and those obtained for high hydrogen doses at substrate temperatures below 200 °C are virtually the same and match the spectrum attributed to the SiH₃ phase by Pandey *et al.*⁶ The finding that this spectrum could only be obtained by starting from the quenched Si(111)-(1 × 1) surface structure⁶ can be reconciled by invoking different sticking probabilities for the oxygen-carrying species impinging from the gas phase onto the well-annealed (111)-(7 × 7) or the quenched (111)-(1 × 1) surfaces.

Based on the present results we would like to point out that coadsorbed oxygen might have also been the reason for the UPS features attributed to SiH₃ by Pandey *et al.*⁶ and recently in a similar work by Fujiwara.¹⁰

II. EXPERIMENTAL

The measurements were performed in a ultrahigh vacuum (UHV) system with a base pressure of 2×10^{-10} Torr equipped with a double-pass cylindrical mirror analyzer for UPS and Auger electron spectroscopy (AES), a differentially pumped He discharge lamp, and a four-grid LEED system. The UPS (He I) spectra were recorded with a pass energy of 25 eV and a resolution of 0.1 eV. The analyzer axis lying in the plane of incidence of the uv light (grazing incidence) formed an angle of about 50° with the sample normal. The kinetic-energy distribution curves (EDC) are given relative to the Fermi level determined by the rather steep onset of the EDC obtained from a clean Mo surface.

Atomic hydrogen was produced by dissociation of

H₂ (purity 99.999%) at a hot W ribbon placed about 5 cm in front of the sample and held at a temperature of about 2000 °C during H₂ dosing. As the arrival rate for atomic hydrogen was not known we specify the H₂ partial pressure times the exposure time. The samples were cut from Si wafers of (111) orientation and cleaned in UHV by heating to 900 °C and Ar⁺ sputtering. The samples were considered "clean" before H adsorption if the ratio of AES peak heights for impurities (predominantly C and O) and for Si (*L_{2,3}VV*, 91 eV) was smaller than 2×10^{-3} . Well-annealed surfaces exhibiting a sharp (7 × 7) superstructure, quenched samples with a (1 × 1) structure, as well as sputtered surfaces giving rise to only a featureless background in LEED, were prepared and subsequently exposed to atomic hydrogen at various substrate temperatures ranging from -10 up to 300 °C. After hydrogen exposure the Si surfaces were again characterized by AES which proved very important especially after H₂ exposures larger than 1000 L (1 L = 10^{-6} Torr sec) and substrate temperatures below 200 °C. Cursory desorption experiments were also conducted for determining the temperature at which hydrogen desorption occurs.

III. RESULTS

Figure 1 shows typical UPS results for the clean Si(111)-(7 × 7) surface and for increasing H exposures at substrate temperatures below 200 °C. The clean surface exhibits rather broad maxima around -3 and -7.5 eV and a shoulder at -2 eV in agreement with earlier studies.^{6,11} After H exposures up

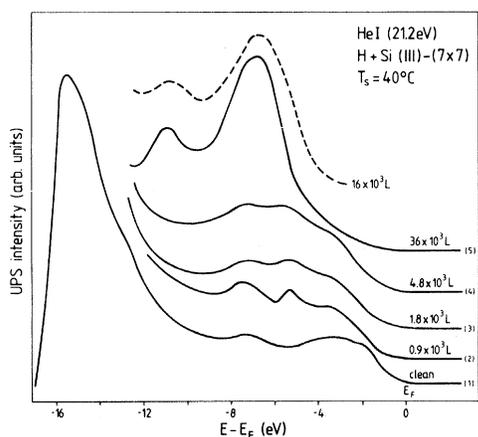


FIG. 1. UPS spectra for the clean Si(111)-(7 × 7) surface and for increasing H exposures at a substrate temperature of 40 °C. Exposures are given in langmuirs (10^{-6} Torr sec). The actual H₂ pressures in Torr were 3×10^{-6} [curve (2)], 1×10^{-5} [curves (3) and (4)] and 2×10^{-4} [curve (5)]. The dashed curve shows for comparison the spectrum obtained by Pandey *et al.* (Ref. 6) which was obtained after 90 min at 3×10^{-6} Torr.

to about 10^3 L (several minutes at 5×10^{-6} Torr) two H-induced peaks at -5.3 and -7.4 eV develop and saturate which are attributed to a SiH phase.⁵ Upon further doses of hydrogen the valley between the hydrogen peaks smears out and at even higher exposures two new peaks develop at around -6.7 and -10.6 eV. The new structure appearing for H exposures between 5×10^3 and 30×10^3 L is compared with the spectrum obtained by Pandey *et al.*⁶ (dashed curve) which was obtained at 16×10^3 L. Peak positions and relative peak heights are very similar. Concomitant AES measurements indicated that the development of the latter UPS spectrum is accompanied by the buildup of increasing amounts of oxygen as well as carbon impurities.

UPS spectra for chemisorbed oxygen on Si(111) (Refs. 11 and 12) also exhibit similar structures and peak positions. We therefore exposed the Si(111) surface to various oxygen exposures at room temperature and observed UPS and AES spectra. Figure 2 shows a UPS spectrum (upper curve) recorded after an oxygen exposure of 240 L and, for comparison, a spectrum obtained after an H exposure of 30×10^3 L at 30 °C. The peak positions in both cases coincide and the overall shapes are very similar. Sections of the corresponding Auger spectra showing the Si(*L_{2,3}VV*) transition at 91 eV and the O(*KLL*) transition at 506 eV are drawn on the right-hand side of Fig. 2. The indicated oxygen coverages were derived from the peak-to-peak height ratios of the oxygen and silicon transitions. Assuming monolayer coverage at saturation of the oxygen peak above 600 L (Ref. 13) the respective Auger-peak height ratio was considered to correspond to 1 ML (monolayer).

Figure 3 relates the height of the oxygen-induced

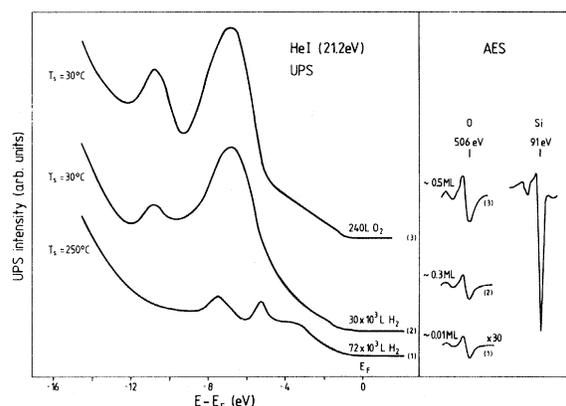


FIG. 2. UPS spectra obtained for Si(111)-(7 × 7) after H exposure of 6 min at 2×10^{-4} Torr and 250 °C [curve (1)], 2.5 min at 2×10^{-4} Torr and 30 °C [curve (2)], and after oxygen exposure of 2 min at 2×10^{-6} Torr and 30 °C [curve (3)]. On the right-hand side are shown the corresponding Auger lines for the O(*KLL*) transition at 506 eV and the Si(*L_{2,3}VV*) transition at 91 eV.

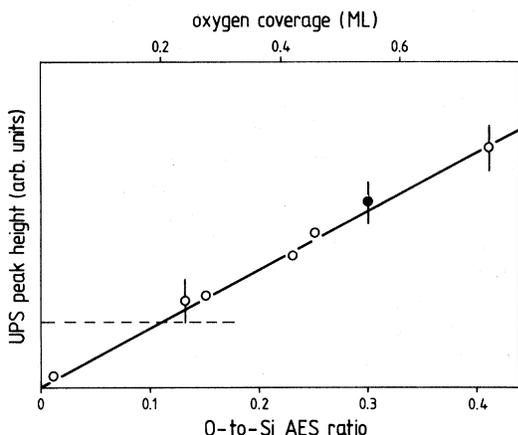


FIG. 3. UPS peak height (-6.7 eV) after oxygen exposure on Si(111) vs oxygen coverage characterized by the O(*KLL*) to Si(*LVV*) AES peak ratio. The upper scale denotes the coverage in monolayers according to the calibration described in the text. The filled circle refers to the respective value obtained after heavy H exposure at 40°C .

UPS peak at -6.7 eV to the measured Auger-peak height ratio for various oxygen exposures. The UPS peak height was taken as the difference of the emission yields at -6.7 eV measured for the oxygen-covered and the clean surface, respectively. The dashed line in Fig. 3 gives an upper limit for the emission yields obtained for the hydrogen-induced UPS peaks at -5.3 and -7.4 eV as obtained for H exposures up to 10^3 L at 40°C or for much higher exposures at elevated temperatures as described below. This comparison shows that oxygen impurities above 0.03-ML coverage seriously effect the hydrogen-induced UPS features. Furthermore, the UPS peak height at -6.7 eV observed for 30×10^3 -L H exposure [Fig. 2, curve (2)] is fully accounted for by the measured oxygen impurity concentration as indicated by the filled circle in Fig. 3. In this case the peak height was taken with respect to the emission yield for low-H exposure.

In contrast to the UPS results for H exposures at around room temperature, even very high hydrogen doses at elevated temperatures do not cause the appearance of the two peaks at -6.7 and -10.6 eV, respectively. As an example, we show in Fig. 2 the lower spectrum which was obtained after H exposure of 72×10^3 L at 250°C . The two hydrogen-induced peaks at -5.3 and -7.4 eV are well separated by a minimum at -6 eV despite the fact that the applied exposure is 80 times higher than for the similar spectrum in Fig. 1. However, the accumulated oxygen concentration in this case amounts only to about 0.01 ML and is therefore expected to give only a negligible contribution to the spectrum.

The much smaller buildup of oxygen impurities at elevated temperatures is not caused by a concomitant

reducing action of atomic hydrogen. This was clearly demonstrated by first exposing the sample to a high H dose at room temperature in which case a spectrum similar to curve (5) in Fig. 1 was obtained together with a corresponding oxygen Auger signal. After raising the temperature to 250°C and further heavy H exposure, no change in the UPS spectra occurred nor did the oxygen Auger signal decrease. We therefore conclude that the sticking probability for the oxygen carrying species decreased markedly with increasing substrate temperature. At the same time we can exclude oxygen diffusion into the bulk for this temperature range.

IV. DISCUSSION

The result of this study shows unambiguously that the UPS peaks at -6.7 and -10.6 eV below the Fermi level developing at high H exposure and near room temperature are caused by oxygen impurities. It is not surprising that exposures in excess of 10^3 L may lead to surface contamination due to either long exposures times and/or the liberation of contaminants via the interaction of the exposure gas with the walls of the vacuum system. Likely contaminants to carry oxygen to the sample surface are CO and H_2O . Besides the recorded carbon Auger signal we did not detect UPS features characteristic for molecular CO. Even pure CO exposures (several langmuirs) did not lead to either a carbon or an oxygen AES signal (without hot W filament). After raising the sample temperature to above 700°C in order to remove oxygen picked up during high H exposures (carbon still remains on the surface during this treatment) the UPS spectrum of the clean Si(111) surface was recovered. From this result we conclude that these small C impurities do not give rise to an appreciable emission yield in the UPS spectrum. Water, however, chemisorbs readily on Si(100) and to a much lesser extent on Si(111) (Ref. 14) by forming SiOH and SiH units. Additional atomic H exposure leads to Si-O-Si units via the association of hydroxyl-hydrogen and atomic H.⁹ For this reason atomic H will not reduce SiO once this species has formed on the surface. Water is therefore a likely candidate for oxygen contamination and its sticking probability is structure and temperature dependent.¹⁴

The UPS spectrum observed by Pandey *et al.*⁶ after dosing the Si(111)-(1 \times 1) surface with 16×10^3 -L hydrogen at around 150°C is very similar to our "oxygen"-induced spectra. Their spectrum was ascribed to a SiH₃ phase. A theoretical calculation based on a tight-binding model⁷ led to a virtually identical spectrum and thus supported the assignment. We suggest reconsideration of the SiH₃ assignment in the work of Pandey *et al.*⁶ as well as in the recent study of Fujiwara¹⁰ and rather attribute the respective structures in their UPS spectra also to oxy-

gen contamination.

Oxygen is known to desorb from Si surfaces at around 700 °C (Refs. 12 and 13) probably as SiO. At the same temperature Pandey *et al.*⁶ observed the UPS spectrum ascribed to SiH₃ to recover to the spectrum of the clean surface. On the other hand, it is very unlikely that SiH₃ units on silicon are stable up to 700 °C. Studies on hydrogenated amorphous silicon¹⁵ show that SiH units exhibit much higher thermal stability than SiH₂ or SiH₃ units. Our recent work on H vibrations on Si(111) (Ref. 8) as well as the conclusions drawn for the SiH₂ phase on Si(100) (Ref. 1) prove that SiH₂ units are less stable (up to 150–200 °C) than SiH units.

So far we only put forward arguments against the assignment of a stable SiH₃ phase to the respective UPS spectrum. We do not argue against the formation of SiH₃ units as intermediates for the production of SiH₄. Recent investigations^{16,17} show that atomic hydrogen breaks Si–Si bonds⁸ and leads to the production of silane.^{16,17}

Finally, we would like to comment on the observation of Pandey *et al.*⁶ that only the quenched Si(111)-(1 × 1) structure was capable of producing the discussed UPS spectrum. The different sticking probabilities of contaminants like H₂O for the quenched Si(111)-(1 × 1) or the well-ordered Si(111)-(7 × 7) structure might well be the reason for the observed difference. Different preparation conditions of Si(111) surfaces led to different H exposures for obtaining the UPS structures assigned to the SiH₃ phase in the recent work of Fujiwara.¹⁰ Future studies on this system should necessarily employ Auger measurements after the H exposure. It should also be checked whether H₂ (or eventually SiH₄) desorbs at a temperature as high as 700 °C.

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