

LETTERS

Effect of Illumination on the Preferred Oxygen Initial Adsorption Sites at a Si(111)7×7 Surface

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A *p*-Si(111)7×7 surface was exposed to oxygen both while being illuminated with super-band-gap energy photons and while in the dark. The initial sticking probability into an adsorption mode that appears as a protrusion in scanning tunneling microscope images doubled due to illumination with 500 mW/cm² 532 nm light. No changes were observed in the ~3:1 preference of the “faulted” over the “unfaulted” halves of the 7×7 unit cell. However, exposure to O₂ under illumination removed the ~5:1 preference of the “corner adatom” over the “center adatom” sites, which was observed after exposure in the dark.

Introduction

The complex Si(111)7×7 reconstructed surface unit cell offers a large variety of adsorption sites, and various small molecules show preference to one site over another.¹ In this paper, we try to elucidate the effect of charge carrier distribution on the choice of an initial adsorption site; we examined whether it is possible to alter a site preference through illumination-induced generation of free carriers.

The clean Si(111)7×7 unit cell (according to the DAS model;² see Figure 1) consists of 12 “adatoms” in the topmost layer, with localized half-filled dangling bond states that appear distinctly in scanning tunneling microscope (STM) images,³ and six “rest atoms” between them in the second layer. However, the adatoms are not equivalent: Six of them are located next to the “corner holes” at the corners of the 7×7 unit cell, and hence are named “corner adatoms”, while the remaining six are named “center adatoms”. One-half of the 7×7 unit cell (three “center” and three “corner” adatoms) is “faulted” with respect to the bulk atom arrangement, while the other half is referred to as “unfaulted”. When imaging this surface with STM at positive sample bias, all adatoms appear equivalent. However,

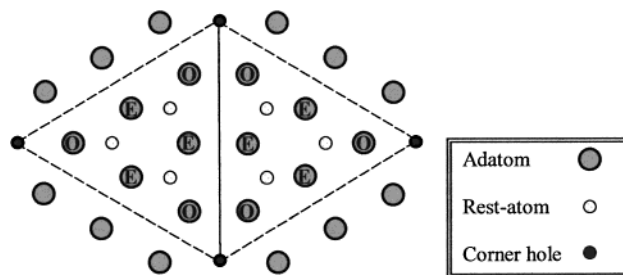


Figure 1. A schematic drawing of the adatoms (O = corner, E = center), the rest atoms and the corner hole atoms in the Si(111)7×7 unit cell (inside the dashed line). The solid line divides the unit cell to the faulted and unfaulted halves.

when a negative sample bias is applied, the adatoms at the faulted half appear slightly higher, suggesting a somewhat higher density of filled states near the Fermi level energy. Surface photovoltage imaging with a STM⁴ showed that the faulted half 7×7 unit cell screens the STM-tip-induced electric field more efficiently than the unfaulted half, suggesting once more a higher electron density near the Fermi energy. Further, it was shown that the occupation of corner adatom dangling bond states is higher than that of center adatoms^{5,6} due to a weaker charge transfer from the former sites to the rest atoms.^{1,7}

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At very low coverages, adsorbed oxygen appears as “bright” protrusions on adatom sites, in constant current topography (CCT) STM images. The nature of this initial adsorption mode is still controversial (i.e., either molecular,^{8–10} or dissociative^{11–14}). It turns out that oxygen exhibits a preference for the “corner” over the “center” adatom sites and a preference to the “faulted” over the “unfaulted” halves of the unit cell.^{9,15,16} A second oxygen adsorption mode, which appears “dark” (as a missing Si adatom) in CCT STM images, also starts to appear at low coverage and becomes dominant as the exposure to O₂ is increased.^{15,17} It was shown that the STM tip could induce conversion between the bright features to the dark features¹⁷ or vice versa.¹⁴

Oxygen is an acceptor and was shown to be negatively charged in its low-coverage adsorbed form on the Si(111)7×7 surface.¹⁸ However, are the faulted half of the 7×7 unit cell and the corner adatom preferred as initial adsorption sites for oxygen merely due to the higher availability of electrons there? Avouris et al.¹⁹ explained the 2:1 preference of the center over the corner Si adatom sites for the initial adsorption of water by the fact that the center adatom has two neighboring rest atoms while the corner adatom has only one. In the latter example, the charge distribution at these different sites does not seem to affect the site preference.

In this paper, we examine the effect of flooding the surface with electrons, which are photoexcited in the sample while an exposure to oxygen takes place, on both the initial sticking probability and the preferred initial adsorption sites. Hwang et al.²⁰ observed that above 300 °C, where diffusion becomes detectable, the center adatom turned into the preferable adsorption site for the bright adsorbed oxygen. This observation suggests that the bright sites, as viewed at room temperature, are the sites where the first step of adsorption took place and are not necessarily the most thermodynamically stable. Therefore, a change in the ratio between the number of the different reacted sites is likely to reflect a change in the initial sticking probability at different locations in the unit cell.

Experiment

The experiments were conducted in an ultrahigh vacuum chamber (base pressure of $<2 \times 10^{-10}$ Torr). The chamber and a home-built STM are described elsewhere.^{21,22} Si(111) wafers (Virginia Semiconductors) were boron-doped (*p*-type, 0.1 Ω·cm), cut into 5 mm × 20 mm samples, and degreased with acetone and ethanol. The Si samples were degassed over 8 h at 600 °C and flashed to 1100–1200 °C through resistive heating, to remove the native oxide. CCT STM images, showing large areas with very little defects of 7×7 reconstructed surface, were obtained prior to each experiment. Oxygen (99.998%) was fed into the chamber through a leak valve. The samples were dosed by filling the chamber to a pressure that did not exceed 5×10^{-9} Torr. During dosing, the tip was pulled $\sim 1 \mu\text{m}$ away from the sample and the sample bias was zeroed to omit electric fields. The samples could be illuminated during the exposure to oxygen with 532 nm light from a continuous frequency-doubled diode-pumped Nd:YVO₄ laser 65° from the surface normal at *p*-polarization, giving rise to 500 mW/cm² at the surface. The estimated temperature rise at the illuminated region does not exceed 3 K.

All experiments were run on samples that were cut from the same Si wafer.

Results and Discussion

In the absence of illumination, the Fermi level is pinned approximately in mid-gap at Si(111)7×7 surfaces. The resulting

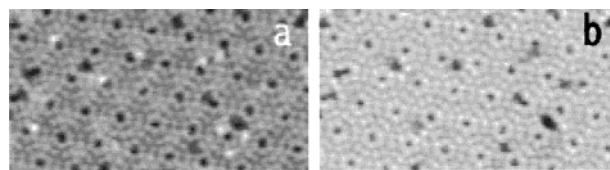


Figure 2. STM CCT images of a *p*-Si(111)7×7 surface which was exposed to 0.1 langmuir O₂ under illumination with 500 mW/cm² of 532 nm light, taken simultaneously at (a) $V_s = +2.2$ V and (b) $V_s = +1.8$ V ($I_{\text{tun}} = 0.3$ nA).

energy difference between the conduction band minimum (CBM) and the Fermi level (E_F), as well as the difference between E_F and the valence band maximum (VBM), is $\Phi_b \approx 0.55$ eV.

Upon super-band gap photon illumination of the Si(111)7×7 surface, electrons, and holes are photoexcited in the bulk. Immediately, when the light is switched on, photogenerated minority charge carriers rush down the potential hill to the surface and reduce the surface equilibrium charge. The degree of band bending is lowered, and hence, the Schotky barrier for the majority carriers to reach the surface is reduced. Since the carrier recombination rate at the Si(111)7×7 surface is high, the band bending stabilizes at a steady-state value where equal fluxes of photoelectrons (j_e^{ph}) and photoholes (j_h^{ph}) reach the surface. The surface photovoltage (SPV), which is a voltage that is built between the illuminated surface and the dark back of the sample, equals the change in the degree of band bending.

In a previous SPV-imaging study on samples from the same batch,²¹ we showed that illumination of a clean *p*-type Si(111)7×7 surface with 532 nm light at 500 mW/cm², gave rise to $V_{\text{SPV}} = -0.12$ V, which was homogeneously distributed everywhere at the surface. This means that under illumination, the photoelectron and photohole fluxes can be evaluated by calculating the change in the majority carrier (holes) thermal emission above the reduced barrier:²³

$$j_e^{\text{ph}} = j_h^{\text{ph}} = A^* T^2 e^{-\Phi_b/k_b T} (e^{-qV_{\text{SPV}}/k_b T} - 1)$$

where A^* is the effective Richardson constant, which is $\sim 1.9 \times 10^{20}$ carriers·cm⁻²·s⁻¹·K⁻² for holes in silicon,²⁴ and k_b is the Boltzmann constant. For a substrate temperature of $T = 300$ K, we obtain $j_h^{\text{ph}} = j_e^{\text{ph}} = 1 \times 10^{18}$ carriers·cm⁻²·s⁻¹, compared to the oxygen flux of 3.6×10^{11} molecules·cm⁻²·s⁻¹ that impinges on the surface at 1×10^{-9} Torr.

Exposure of the *p*-Si(111)7×7 surface to 0.2 langmuir of oxygen (100 s at 2×10^{-9} Torr) in the dark yielded bright features in the STM CCT images at an average coverage of 0.008 ± 0.001 ML (1 ML = 7.37×10^{14} cm⁻²). Similar dosage under the above-mentioned illumination conditions (532 nm, 500 mW/cm²) gave rise to about twice the coverage of bright sites. Hence, to study the oxygen adsorption site distribution under illumination and compare it to adsorption in the dark, we reduced the exposure during illumination to 0.1 langmuir (100 s at 1×10^{-9} Torr). The dark oxygen feature coverage also grew from about a third of the bright sites coverage, for 0.2 langmuir O₂ exposure in the dark, to equal coverages, for 0.1 langmuir exposure under illumination. Nevertheless, since we do not know how many of the extra dark sites are due to water adsorption from the background,⁹ we wish to concentrate our attention on the bright sites.

Figure 2 shows a typical STM CCT image of *p*-Si(111)7×7 surface that was exposed to 0.1 langmuir O₂ under illumination, where every line is repeated at a sample bias of $V_s = +2.2$ V (a) and $V_s = +1.8$ V (b). The initial oxygen adsorption mode

TABLE 1: Ratio between Different Initial O₂ Adsorption Sites ("Bright" Protrusions in STM Images with Sample Bias above 2 V) on a Si(111)7×7 Surface, with and without Illumination with 500 mW of 532 nm Light^a

	0.2 L O ₂ in the dark			0.1 L O ₂ under illumination		
	Corner	Center		Corner	Center	
Faulted	12	2	2.8	3	2	2.5
Unfaulted	4	1	1	1	1	1
	5.3	1	Total	1.3	1	Total

^a The numbers on the gray background indicate the ratio between the four individual adsorption sites (in respect to the unfaulted/center site), while the numbers on the white background show the ratio of the faulted to the unfaulted half of the unit cell, and the ratio of the corner to the center adatom site.

TABLE 2: Ratio between Different "Dark" O₂ Adsorption Sites on a Si(111)7×7 Surface, after 0.1 langmuir Exposure under Illumination with 500 mW of 532 nm Light^a

	0.1 L O ₂ under illumination	
	Corner	Center
Faulted	2	4
Unfaulted	1	1
	1	1.6
	Total	

^a The numbers on the gray background indicate the ratio between the four individual adsorption sites, while the numbers on the white background show the ratio of the faulted to the unfaulted half of the unit cell, and the ratio of the corner to the center adatom site.

appears as a regular Si adatom at $V_S = +1.8$ V and as a bright protrusion at $V_S = +2.2$ V. This allows us to verify that we do not count protrusions that are not due to oxygen species. It is important to note that similar illumination of a Si(111)7×7 surface that was exposed to oxygen in the dark, did not give rise to changes in the adsorption sites nor to a conversion of bright sites to dark sites and vice versa.

The ratios between the different adsorption sites for the bright features for exposure in the dark (0.2 langmuir O₂) and under the above illumination (0.1 langmuir) are presented in Table 1, where 500 bright sites were counted. For exposure in the dark, the observed ratio between bright sites at faulted and at unfaulted halves of the 7×7 unit cell was found to be ~3:1, in comparison to previous reports of ~8:1,¹⁶ ~4:1,¹⁵ and ~2.5:1⁹ on samples with different doping. Exposure under 500 mW of 532 nm illumination did not seem to change this ratio distinctly. On the other hand, the ratio between the corner and center adatom sites was strongly affected by the illumination: A corner-to-center ratio of ~5:1 in the dark (in comparison with ~4:1,¹⁶ ~2:1,¹⁵ and ~1.4:1⁹) was changed to ~1:1 when the O₂ adsorption was performed under illumination.

The dark oxygen features, which were distributed evenly between the different types of Si adatoms for exposure in the dark, became more abundant on the center adatom in the faulted half of the unit cell (see Table 2).

The surface recombination velocity at Si(111)7×7 surfaces is very high due to the continuum of surface states bands that overlap the bulk band gap. Competition between recombination and inelastic scattering in a short-lived physisorbed oxygen molecule²⁵ might make the photogenerated carriers inefficient in inducing change in the initial adsorption process. Nevertheless, the flux of photocarriers in our experiments was sufficient to bring about an increase in the initial sticking probability into the bright and dark oxygen adsorption modes. Obviously, if the surface recombination velocity at Si(111)7×7 surfaces had been lower, or if the light intensity had been dramatically larger, the effect could have been more pronounced, and maybe also be seen in the ratio between the initial adsorption probabilities at the faulted versus the unfaulted halves of the unit cell.

The structure of the first and second surface atomic layers in the faulted half of the 7×7 unit cell does not differ significantly from the unfaulted half. Hence, one would expect that *only* electronic factors affect their relative reactivity. However, we observed only an illumination-induced reduction in the preference of the "bright" features to the corner over the center adatom sites. We cannot determine whether the latter observation stems from a photocarrier flux that washes out the difference in the electron availability between these two sites, direct absorption in the surface states which alters their relative occupancy, or a light effect on the location and dissociation dynamics of the O₂ precursor, without additional wavelength- and doping-dependent experiments as well as a detailed theoretical study of this system.

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