

Absence of Nonlocal Manipulation of Oxygen Atoms Inserted below the Si(111)-7×7 Surface

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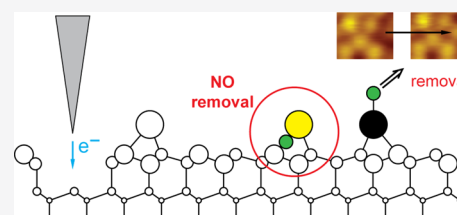


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ABSTRACT: The injection of electrons from the scanning tunneling microscope tip can be used to perform nanoscale chemistry and study hot electron transport through surfaces. While nonlocal manipulation has been demonstrated primarily for aromatic adsorbates, here we confirm that oxygen atoms bonded to the Si(111) surface can also be nonlocally manipulated, and we fit the measured manipulation data to a single channel decay model. Unlike aromatic adsorption systems, oxygen atoms also insert below the surface of silicon. Although the inserted oxygen can be manipulated when the tip is directly over the relevant silicon adatom, it is not possible to induce nonlocal manipulation of inserted oxygen atoms at the same bias. We attribute this to the electrons injected at +4 eV initially relaxing to couple to the highest available surface state at +3.4 eV before laterally transporting through the surface. With a manipulation threshold of 3.8 eV for oxygen inserted into silicon, once carriers have undergone lateral transport, they do not possess enough energy to manipulate and remove oxygen atoms inserted beneath the surface of silicon. This result confirms that nonlocal nanoscale chemistry using the scanning tunneling microscope tip is dependent not only on the energy required for atomic manipulation, but also on the energy of the available surface states to carry the electrons to the manipulation site.



INTRODUCTION

Scanning tunneling microscopy (STM) is an ideal tool for performing local nanoscale chemistry on individual atoms or molecules through the direct injection of charge.^{1–11} In “local” manipulation, the tip modifies the atom or molecule directly under the probe. Longer range “nonlocal” manipulation injects charge which modifies atoms or molecules up to tens of nanometers away.^{3,12–19} This offers not only a route to investigate chemical reactions but also a means to study hot electron transport in devices, photocurrent generation in solar cells, and plasmonics.³

While nonlocal manipulation has been demonstrated in the cases of adsorbed NO, C₆₀, and chlorine, primarily aromatic adsorbates have been studied.³ Despite the technological importance of the O–Si system and the Si–SiO₂ interface, nonlocal manipulation of oxygen molecules on the Si(111)-7×7 surface has not been studied. Silicon dioxide is the most commonly used insulator in integrated circuits, and it may undergo significant structural changes during device operation, usually attributed to the formation of oxygen vacancies.^{20–22} Although this is one of the most important phenomena determining semiconductor device reliability, the atomistic mechanisms responsible for dielectric breakdown of amorphous SiO₂ are still poorly understood.²³

Here, injected hot electrons laterally transport through the Si(111)-7×7 surface, which has been controllably oxidized. By monitoring the atomic manipulation of these O–Si bonding sites using STM, we are able to determine the effect of laterally

transported hot electrons on O–Si sites and compare the behavior to charge injected directly into the atomic site.

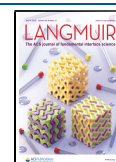
EXPERIMENTAL METHODS

Experiments were performed at room temperature using an RHK-1000 STM in ultrahigh vacuum with a base pressure below 7×10^{-11} Torr. Tungsten tips were prepared by electrochemical etching in 2 M NaOH solution followed by outgassing in vacuum through direct current annealing. Si(111) (p-type, boron-doped, 0.01–0.02 Ω·cm) was prepared by an in situ degassing and reconstruction routine to obtain the Si(111)-7×7 structure.¹⁴ A dose of 0.3 L of oxygen (Argo International, 99.6% purity, typically 0.4% total hydrocarbon (TCH) as CH₄ < 20 volumetric parts per million (vppm) and H₂O < 3 vppm) was exposed to the Si(111)-7×7 surface at room temperature. Initial imaging of the surface was performed in constant current mode under passive scanning conditions (+1 V sample bias, 0.1 nA tunneling current), where no transformation of oxygen molecules was observed. Nonlocal injection was then performed by moving the STM tip above a chosen atom and injecting 0.1 nA of current for 50 ms at bias voltages increasing from 2.5 to 10.0 V. The same surface area was then scanned again under passive scanning conditions to count the number of transformed molecules. Drift tracking was enabled to

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minimize unwanted tip displacement due to piezo creep or thermal expansion following charge injection.

RESULTS

The Si(111)-7×7 surface shown in Figure 1 is composed of top-most adatoms, two layers of rest atoms, and corner holes.²⁴

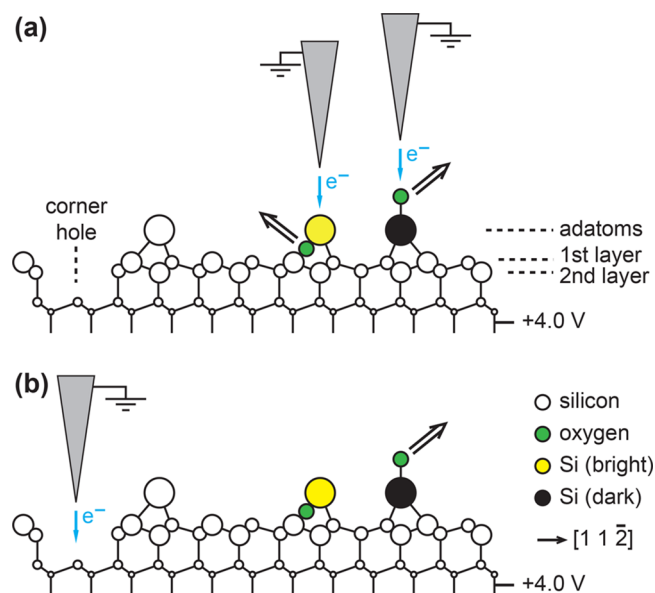


Figure 1. Schematic of the manipulation of oxygen atoms on the Si(111)-7×7 surface in cross-section. (a) In local manipulation with the probe positioned directly over the relevant silicon adatom, both surface and inserted oxygen can be manipulated and removed. (b) Electrons injected into a corner hole at the same bias can still nonlocally manipulate surface-bonded oxygen up to 10 nm away, but not inserted oxygen.

When oxygen molecules bond to the adatoms, the removal of the surface dangling bonds creates “dark sites” shown in Figure 2(a) as the darker atoms within the usual surface

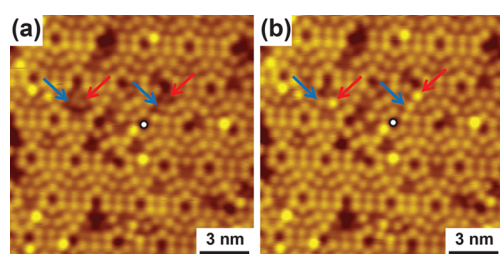


Figure 2. Nonlocal manipulation of oxygen on the Si(111)-7×7 surface at room temperature, showing 15 × 15 nm STM images at a gap (sample) voltage of +2.0 V (a) before manipulation and (b) after electron injection for 8 s at a gap (sample) voltage of +4.0 V and a tunneling current of 0.1 nA into the corner hole indicated with a black circle. Blue arrows indicate the transformations where dark sites are removed and unreacted adatoms appear; red arrows indicate the transformation from a dark site to a bright site.

reconstruction, some indicated by arrows for later discussion. If instead one or more oxygen atoms are inserted into back bonds between the adatoms and rest atom layers, the surface adatom is shifted up ~0.5 eV in energy, and at gap (surface) voltages above +1.5 V, the adatoms appear brighter in the STM image, also visible in Figure 2(a).²⁵ Increasing the

oxidation rate inserts more oxygen atoms into the back bonds maintaining bright sites and increasingly saturates more surface dangling bonds forming dark sites. Dark sites may form directly with no inserted oxygen or may form on top of the inserted oxygen, but both appear equally dark in the STM image. Eventually, the whole surface is saturated and an oxide layer is formed.²⁵

The chemistry of these bonding sites can be probed energetically by injecting charge from the STM tip, which transports through the surface causing electron–adsorbate manipulations, which decay away with distance. These manipulations can cause the adsorbates to diffuse or switch atomic positions, or transform, dissociate, or desorb from the surface, all yielding information about the bonding position, type, and energy and surface reactions.^{4,7,14,15,18,26–31} However, previous nonlocal manipulation studies have only investigated adsorbates—atoms and molecules bonded to the surface atoms of the substrate.^{2,3,13–19,26,27,32} The O–Si system is markedly different because oxygen atoms also insert beneath the surface.

No manipulations are observed to occur at +2 V, which is used as the imaging voltage to map the surface before and after manipulation. Charges are injected from the STM tip at a specific corner hole site, and the O–Si manipulations that occur up to 20 nm away from the STM tip are measured. Figure 2(a) shows an image before manipulation with the corner hole injection site indicated with a black circle and arrows indicating dark sites that exist before the manipulation. Figure 2(b) shows the same area after injection of 0.1 nA current for 8 s at a gap (sample) voltage of +4.0 V. The dark sites identified by the blue arrows have been removed, with the adatoms returning to the same brightness as the surrounding unreacted atoms. The dark sites identified by the red arrows have been transformed to bright sites.

Table 1 presents the transformation events determined here using nonlocal manipulation, with a comparison from the same

Table 1. Reaction of Dark and Bright Sites by Nonlocal (this Work) and Local Electron Injection,³³ Showing the Number of Events of each Type

transformation(D, dark; B, bright)	nonlocal (this work)		local (Mayne et al. ³³)	
	event	percentage	event	percentage
D removed	41	69.5%	9	56.2%
D transformed into B	15	25.4%	5	31.3%
D moved to next adatom	3	5.1%	2	12.5%
B transformed to D	0		10	43.5%
B removed, new D next adatom	0		7	30.4%
B remains, new D next adatom	0		6	26.1%

system studied with local manipulation by Mayne et al.³³ We used a higher initial oxygen dose, which is known to alter the proportion of bonding sites and manipulation events, but the results are in agreement by rank order of probability.²⁵

Despite dark site transformations occurring with broadly similar probabilities to the published local manipulation work, importantly, there were no transformations observed here for 165 bright sites over 12 nonlocal manipulation experiments. Our observed inability to manipulate the inserted oxygen atoms nonlocally contrasts with local manipulation studies.^{25,33} We confirmed that we could cause bright site manipulation by local injection at the same energy, despite this mechanism not

working for nonlocal manipulation of the same system under the same conditions.

In order to transport laterally through the surface, the injected carriers must couple to the surface states of silicon. Two lower-lying unoccupied surface states U1 and U2 arise from unfilled surface dangling bonds and unfilled back bonds, respectively. Scanning tunneling spectroscopy (STS) measurement of a clean faulted middle adatom has also revealed a U3 state at $+2.3 \pm 0.5$ eV above E_F .³⁴ An additional intermediary bulk state has been measured at 3.45 ± 0.15 eV above E_F using 2-photon photoemission, which is associated with increased nonlocal manipulation probability.³ STS on the clean faulted middle adatom also reveals this same higher lying state at $+3.4 \pm 0.3$ eV above E_F , which they label U4.³⁴ While resonance effects can alter these surface states, the effects occur at higher voltages, in field emission.³⁵ Furthermore, these surface states measured using STM match well with the optical techniques, suggesting that tip-induced modification of the surface states is not significant.

We have recently measured the energy threshold required for the manipulation of inserted oxygen atoms to be +3.8 V by positioning the tip directly over the relevant adatom and incrementally increasing the bias until the manipulation threshold is achieved.²⁵ Therefore, we find that electrons injected here at +4 eV above E_F must first relax to at least ~ 3.4 eV to couple to the U4 state for lateral transport, which is then below our measured threshold of 3.8 V for manipulation of inserted oxygen. Once electrons have undergone lateral transport, they no longer have sufficient energy to manipulate and remove oxygen atoms inserted beneath the silicon surface.

Focusing on the surface oxygen, by identifying the number of bonding sites present before injection $N_0(r)$ and the number of sites, which are manipulated after injection $N(r)$, we can plot the radial distribution of the total manipulation probability away from the probe at $r = 0$, as shown in Figure 3. There are two distinct regions to the distance dependence, similar to the reported aromatic molecule experiments: the manipulation probability first increases with distance away from the probe in what is termed the “ballistic-suppression” region, as carriers undergo a rapid ballistic expansion or inflation followed by an exponential decay as the hot electrons diffuse through the

surface and are scattered. From the experiments on aromatic molecules, this decay region has been shown to follow a 2D diffusion model with a single decay channel given by:

$$\frac{N(r)}{N_0(r)} = 1 - \exp\left[-\frac{n_i\beta}{2\pi D}K_0\left(\frac{r}{\lambda}\right)\right]$$

where n_i is the number of injected electrons, β is the probability that an injected electron will cause a manipulation event, D is the diffusion constant, $K_0(r/\lambda)$ is a modified Bessel function of the second kind, and λ is the diffusion length.²

Using a method similar to Ref 14, we sequentially fit the diffusive model to data, starting from the furthest point from the injection site working back toward the tip, determining the boundary between the two regions at the point the goodness of fit drops below 0.8, measured here to be 5 nm. This defines the two regions shown in Figure 3, with the fit for the right diffusion side projected back into the ballistic region to show the suppression of manipulation events here. Using this method, we also find the diffusion length $\lambda = 1.95$ nm and probability $\beta = 2.88 \times 10^{-11}$.

This two-region diffusive model was first applied to toluene on the Si(111)-7 \times 7 surface.³ It has since been applied exclusively to aromatic adsorbates, but here we find that the same behavior exists for oxygen on the Si(111)-7 \times 7 surface. We found a suppression radius of 5 nm for oxygen on silicon at +4.0 V, comparable with other species. As an example, toluene on Si(111)-7 \times 7 displays a suppression region radius from <5 nm up to almost 15 nm depending on the STM bias voltage.² Our diffusive decay length λ of 1.95 nm is less than that of toluene on Si(111)-7 \times 7, which is typically above 10 nm,² and less than chlorobenzene on Si(111)-7 \times 7, which was found to be 7.47 nm.¹⁴ All three are a comparison of the same surface, with only the adsorbate type changing the carrier dynamics. This short decay length could be explained by our probability of manipulation, which is ~ 165 times higher than toluene on Si(111)-7 \times 7.² Previous work has found no spatial dependence of manipulation when carriers are injected into the corner hole.³⁶ We find that electrons diffusing out interact more strongly at the start of the diffusion region in the Si:O system and thus the diffusion length is reduced compared with other adsorbed species on the same Si(111)-7 \times 7 surface. This further confirms that nonlocal manipulation is dependent both on the transport behavior of injected carriers through the surface of the silicon and by the adsorbed species type.

CONCLUSIONS

We find that oxygen on the surface can be desorbed by laterally transporting hot electrons, but inserted oxygen cannot be manipulated because no surface state exists above the manipulation threshold of 3.8 eV up to an injected energy of 4 eV. We confirm that nonlocal nanoscale chemistry using the scanning tunneling microscope is dependent not only on the energy required for atomic manipulation, but also on the energy of the available surface states to carry the electrons to the manipulation site. This work also adds to our understanding of the mechanism of oxygen vacancy formation when current is flowing close to the technologically relevant Si–SiO₂ interface.

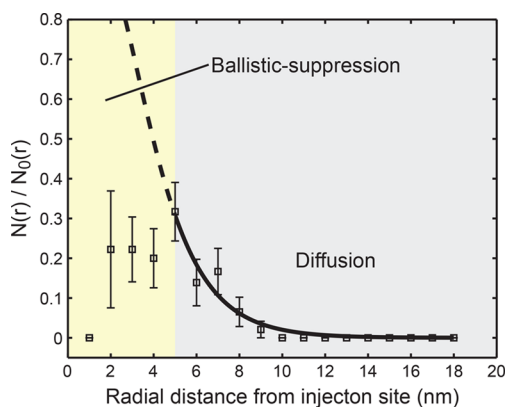


Figure 3. Rate of nonlocal manipulation of surface-bonded oxygen as a function of radial distance from the injection site following injection of 0.1 nA tunneling current for 8 s at +4.0 V gap (sample) bias. The solid line shows the fit to the diffusion region from 5 nm outward, with the dotted line showing the same fit extrapolated back into the ballistic-suppression region.

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Notes

The authors declare no competing financial interest.

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