

Molecular Modelling Program

PROGRAM MANAGER

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PROGRAM DESCRIPTION

The Molecular Modelling Program provides general atomistic simulation support to the experimental quantum computer fabrication programs with a particular focus on the “bottom-up” approach. We work closely with members of the Atomic-Scale Fabrication Program to develop a fundamental understanding of silicon-phosphorus-oxygen-hydrogen chemistry that underpins bottom-up fabrication. This understanding will greatly facilitate the full atomic-scale control required for qubit fabrication.

Our principal simulation methods are based on density functional theory (DFT), which provides a first-principles model of electronic and molecular structure of molecules, surfaces, and solids. Using this theory we can predict the structure and relative energetics of molecules adsorbed on surfaces structures and identify stable configurations. Via the Tersoff-Hamann approximation we can generate simulated STM images to be compared with those measured experimentally. Transition state calculations allow the estimation of reaction rates; such calculations help with the interpretation of temperature-dependent transitions observed in STM experiments. The method of kinetic Monte Carlo (KMC) is used to aggregate our accumulated knowledge of elementary chemical transitions into dynamical models that can describe phenomena at time- and length-scales relevant to fabrication.

In 2007, substantive progress was made in three areas: Firstly, in collaboration with Dr. Steven Schofield at the University of Newcastle we looked at the elementary steps of silicon surface oxidation and identified how oxygen atoms on the surface are incorporated *into* the surface to form the characteristic Si-O-Si motif of silicon dioxide. Secondly, building on our 2006 finding that hydrogen atoms on Si(001) undergo local charging, we considered in 2007 the effect of charging on hydrogen diffusion, a key reaction in the annealing stage of the bottom-up process. Finally, investments into the development of new methodologies to describe phosphorus

atom diffusion in condensed phases are beginning to pay off. We have identified a prototype diffusion pathway for a phosphorus heterodimer in the silicon surface. This provides an important estimate of the temperature below which phosphorus diffusion is suppressed.

1. Water on Silicon (001): C-defects and Initial Steps of Surface Oxidation

One of the outstanding challenges of the bottom-up fabrication process is the growth of a high-quality silicon oxide gate dielectric film with minimal thermal impact on the positioned phosphorus atoms in the silicon substrate. Towards this objective, we have initiated in 2007 a combined theory and high-resolution STM study into the elementary surface processes of silicon surface oxidation. In the Atomic Scale Fabrication Program, the initial layer of silicon oxide is grown by depositing oxygen atoms onto Si(001) surface. While STM imaging data is available from these efforts, these images have thus far been of insufficient resolution to allow any elementary processes to be identified.

Our first results came from a somewhat unexpected direction, namely dissociated water molecules on silicon: The C-defect is a common impurity of the silicon surface that is produced when residual water molecules in the vacuum chamber encounter the silicon surface and break apart. C-defects are understood to be composed of OH and H fragments attached to the surface. Our calculations [Figure 1(a-d)] focussed on the OH fragment of the C-defect and predicted that OH will release single oxygen atoms at elevated temperatures of approximately 400 to 500 K. This prediction was subsequently confirmed by our collaborator Steven Schofield who undertook to image C-defects at 450 K and observe their falling apart into a number of oxide species [Figure 1(e,f)]. This is significant because the C-defect provides us with a controlled model system allowing us generate single oxygen atoms and study the way they react with the silicon surface. A high-resolution image sequence is shown in Figure 2(a-f) in which an oxygen atom can be seen to insert into a Si-Si surface bond, creating the characteristic Si-O-Si structural motif of silicon dioxide. Our calculations [Figure 2(g)] have revealed the chemical mechanism of oxygen insertion that occurs in these images. Most importantly, we have learned from this work how surface oxygen atoms are imaged by the STM, which will help with the interpretation of images acquired in the course of gate oxide fabrication.

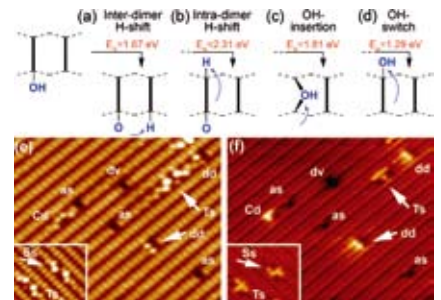


FIGURE 1

(a-d) Survey of possible reactions of a hydroxyl (OH) fragment bound to the Si(001) surface. From calculated activation energies E_a from these processes, we have identified the inter-dimer hydrogen-shift as a new route of OH-dissociation, becoming activated at approximately 450 K (Note that the OH switch, while having a much lower activation energy, does not lead to a change in structure and is thus reversible). OH-dissociation releases an oxygen atom, which will react further with the surface. (e,f) The validity of the prediction was subsequently confirmed by STM experiments conducted at 450 K, which reveal a number of oxygenated surface sites: The double-dot feature (dd), the T-shaped feature (Ts), and the S-shaped feature (Ss).

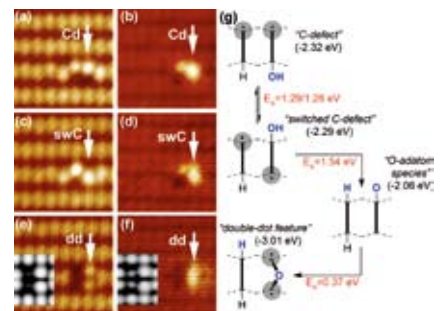


FIGURE 2

(a-f) Sequence of STM images in filled state (a,c,e) and empty state (b,d,f), showing a C-defect (labelled Cd) change into a switched C-defect (swC), which in turn dissociates into a double-dot feature (dd). (g) Schematic valence diagram of the reaction steps revealed in these images. Gray shading indicates the three-fold bonded silicon sites that typically image bright in STM images.

2. Hydrogen Diffusion on Silicon (001) is Charge State Dependent

The diffusion of hydrogen atoms on the Si(001) surface is a chemical reaction of considerable importance to the bottom-up placement of phosphorus atoms by STM H-lithography. During the annealing stage of this process at approximately 650 K, $\text{PH} + 2\text{H}$ and $\text{PH}_2 + \text{H}$ species on the silicon surface dissociate and introduce phosphorus atoms into the surface. Critically, the phosphorus incorporation reaction requires additional reactive surface Si-Si dimers that are not terminated by hydrogen atoms; i.e., we require a partial removal of the hydrogen resist. This *could* be done by further heating to 770 K, which is nominal temperature at which hydrogen desorbs from the surface to free up surface dimers; however, this is not advisable, because at these temperatures the carefully positioned phosphorus atom would also be actively migrating. Fortunately, free surface dimers are produced (transiently) at much lower temperatures by an alternative mechanism. At above 550 K, residual "missing hydrogen" or so-called 1DB defects on the hydrogenated surface begin to migrate and aggregate into "two-missing-hydrogen" or 2DB defects. These 2DB defects (essentially free Si-Si dimers) in turn begin to migrate at temperatures above 600 K and will eventually encounter a phosphine adsorption site where they facilitate the phosphorus incorporation reaction. In order to take our surface models to the next stage, we must be able to describe these diffusion processes.

Work completed in 2006 (and published in 2007) highlighted the fact that isolated dangling bond defects on silicon adopt different charge states depending on various environmental circumstances such as the doping level of the substrate or the presence of an electric field (e.g. the STM tip). A similar charging effect is known to exist for a missing hydrogen 1DB defect on the hydrogen-terminated silicon surface. This prompted us in 2007 to consider whether defect charging has an effect on the diffusion rates of hydrogen on the surface [Figure 3]. In the literature, experiments and theory on H-diffusion have not explicitly considered charging. Our calculations suggest that the activation energies of diffusion are affected profoundly by any change in charge state. For the dimer-to-dimer diffusion of hydrogen atoms on clean Si(001) for instance, an activation barrier of 1.7 eV is widely accepted based on experimental measurements. Our charge-state dependent calculations match the experimental barrier only for a positive charge state for which we obtain a barrier of 1.70 eV. In neutral and negative charge states, the activation barriers increase (to 2.28 and 1.98 eV, respectively) suggesting that under these conditions hydrogen diffusion is less likely.

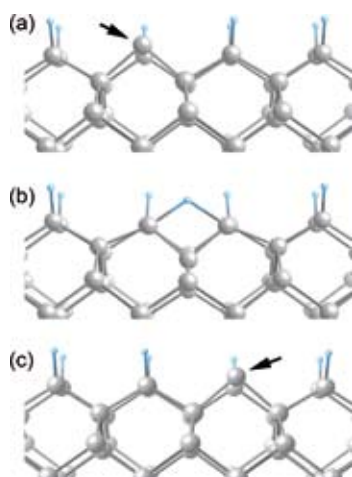


FIGURE 3

Side-views of a diffusing missing hydrogen defect (or 1DB defect) on the hydrogenated silicon (001) surface. The defect (indicated by a black arrow) is shown in panel (a) and (c) in its equilibrium configuration for a negative charge state. Panel (b) shows the transition state of diffusion. A hydrogen atom is transitioning from one dimer to another. The missing hydrogen defect diffuses in the opposite direction.

3. Phosphorus Heterodimer Diffusion on Silicon (001)

The suppression of phosphorus atom diffusion is an important objective in the bottom-up fabrication process to ensure that the carefully positioned phosphorus qubits remain in place. This imposes strict temperature limits on any annealing processes. It has been a long-standing aim of the Molecular Modelling Program to provide a theoretical model for the diffusion of phosphorus atoms in the silicon surface in order to improve our thermal (kinetic Monte Carlo) models of the fabrication process. In previous years, we have implemented and tested various methods of finding diffusion barriers in condensed environments including the Growing String reaction path optimiser and the Metadynamics simulation method. These methods are now approaching maturity and a prototype diffusion pathway for the phosphorus

heterodimer diffusion in the silicon surface has been identified. Figure 4 shows several snapshots of the calculated migration of a phosphorus atom from a surface dimer site (phosphorus in red on the left-hand side of Figure 4) to a subsurface site (red atom in right-hand side of Figure 4). Repeated surface to subsurface transitions of this kind would effect a random-walk diffusion of phosphorus along the dimer row. The calculated activation energy of this process is 2.15 eV, which suggests a thermal onset of diffusion at approximately 700 K (at a per-minute timescale). Comparison of this value with the 1.84 eV activation energy needed to incorporate phosphorus into the surface (corresponding to approximately 600 K at the same reaction rate) reveals that there is only a small thermal window (<100 K) in which phosphorus incorporation can take place without the risk of phosphorus diffusion.

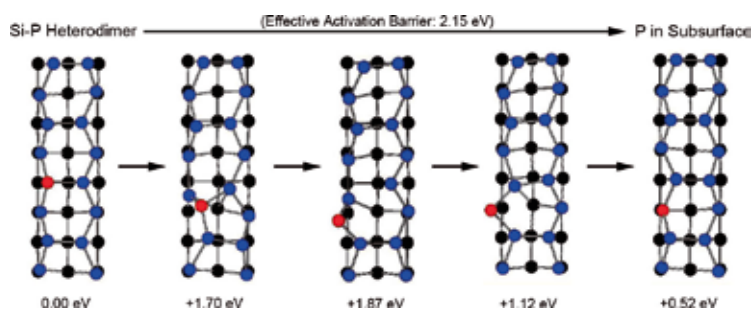


FIGURE 4

Snapshots along the thermal diffusion pathway of a phosphorus atom in the silicon surface. In the reaction shown, a phosphorus atom (red) bonded into a surface Si-P heterodimer undergoes a transition, which takes the phosphorus atom into a subsurface position. A repetition of such surface to subsurface transitions results in phosphorus diffusion along the dimer row.