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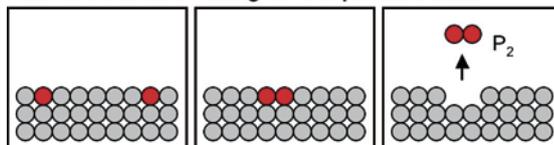
PROGRAM DESCRIPTION

The Molecular Modelling Program provides 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 the silicon-phosphorus-hydrogen chemistry that underpins bottom-up fabrication. This understanding facilitates 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 the electronic and atomic structure of molecules, surfaces, and solids. Using this theory we can predict the atom positions and relative energetics of molecules adsorbed on surfaces 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 the elementary chemical transitions into dynamical models that can describe phenomena at time- and length-scales relevant to fabrication.

In 2009, substantive progress was made in three areas: Firstly, as continuation of our studies into phosphorus diffusion, we looked into the mechanism of phosphorus desorption from the silicon surface which takes place at temperatures between 800 and 1200 K. Secondly, we made significant improvements to our first-principles model of phosphorus δ -doped silicon, arriving at a model that is more accurate and more economical in the computational aspects, while at the same time providing a better representation of the inherent disorder of

Path 1: In-Surface Pairing of Phosphorus Atoms



Path 2: Phosphorus Ejection and Addimer Formation on the Surface

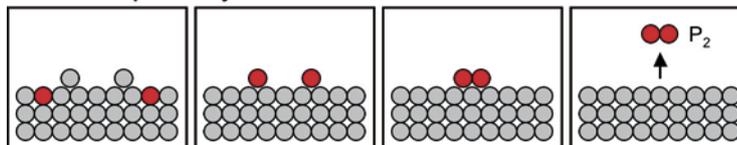


FIGURE 1

Schematic outline of two conceivable pathways of phosphorus dimer desorption from the silicon surface at high temperature. Our calculations have determined the second path to be the preferred mechanism. This path is facilitated by the presence of silicon adatoms on the surface.

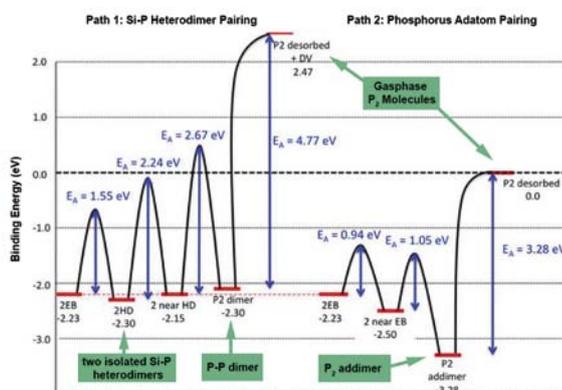


FIGURE 2

Overview potential energy diagram of phosphorus dimer (P_2) desorption from the silicon surface.

phosphorus atoms in the dopant plane. Thirdly, in a further demonstration of our ability to resolve atomic scale processes on the silicon surface, we identified the mechanism behind a sequence of STM induced reactions in an acetophenone molecule bonded to the silicon surface.

1. Phosphorus Dimer Desorption from Silicon (001) Surface at High Temperature

Our studies into the high-temperature processes of the phosphorus doped surface focussed in 2009 on the process of thermal phosphorus dimer (P_2) desorption. As observed in temperature programmed desorption (TPD) experiments, P_2 molecules are ejected from the surface at temperatures between 800 and 1300 K depending on the initial phosphorus coverage. The context most compatible with our calculations is the limit of low coverage for which the experimentally reported desorption temperature is between 1020 and 1090 K. This corresponds to an estimated activation energy of between 2.6 and 3.2 eV which provides a point of reference for our modelling work. After the incorporation-anneal temperature regime (~650 K), phosphorus atoms exist in the silicon

surface in the form of Si-P heterodimer. With our calculations we seek to distinguish between two conceivable reaction pathways for how these Si-P dimers combine into P_2 molecules (see Figure 1). In the first path, two Si-P heterodimers diffuse and pair up within the surface to form a P-P homodimer. Once formed, the P-P dimer breaks off from the surface into the gas phase as a P_2 molecule, leaving behind a dimer vacancy defect. In the second path, the two Si-P heterodimers release a phosphorus atoms onto the surface as phosphorus adatom in a process that is facilitated by the presence of silicon adatoms on the surface. In effect, the silicon and phosphorus atoms trade places in this reaction. Once formed, the phosphorus adatom can rapidly diffuse on the surface to pair up into P-P ad-dimers that subsequently desorb as P_2 molecules. Our calculated energetics of these two processes (see Figure 2) show that only the second path is consistent with the experimental data. The calculated activation energy (E_a) of desorption of 3.28 eV gives an estimated temperature of desorption of about 1000 K, which compares favourably with the experimental findings. The activation energy for the first path is much larger, and can therefore be ruled out.

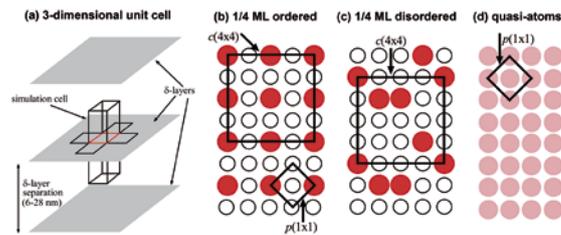


FIGURE 3

Schematic illustrations for the various unit cells used in our calculations on phosphorus δ -doped silicon. (a) The 3-dimensional unit cell. (b) A 1/4 monolayer ordered distribution of phosphorus atoms (red) in the δ -plane with a $c(2 \times 2)$ unit cell. (c) A simulated disordered distribution of phosphorus atoms by use of a large $c(4 \times 4)$ unit cell. (d) Our representation of disorder using quasi-atoms.

2. The Electronic Structure of Phosphorus Delta Doped Silicon

In the bottom-up fabrication of Si:P devices, phosphorus δ -doping is variously used to realize the conducting leads and gates of a device. In order to support ongoing experimental efforts into the electronic properties of these structures, we have developed a full density functional theory (DFT) model of δ -doped silicon. An article describing our initial model was published early in 2009. While our initial aims for 2009 were to apply this model to other nanostructures (double δ -layers and wires), it became necessary to first resolve another, more technical issue: the representation of disorder in the dopant plane. In this aspect our original model sharply collided with reality. The placement of phosphorus atoms in a fabricated device is highly disordered, whereas our model, by virtue of the small in-plane unit cells used, represents a highly ordered scenario [see Figure 3(a,b)]. This has a significant effect on the calculated electronic structure due to symmetry. Somewhat counterintuitively, a disordered system has a higher degree of symmetry than an ordered system. In a disordered system, all in-plane lattice sites are symmetry-equivalent, having the same probability of being silicon or phosphorus. In contrast, symmetry is lowered in an ordered system because lattice sites are distinguished into either silicon or phosphorus. By using a quadruple-sized in-plane unit cell and distributing

phosphorus atoms over several sites [see Figure 3(c)], we were able to emulate a degree of disorder in our original model; however, this came at considerable computational cost and was not sustainable as long-term solution.

In order to address this problem we developed in 2009 an alternative approach in which dopant disorder is represented using quasi-atoms. These quasi-atoms are a fractional composite of a silicon and a phosphorus atom. Thus instead of using one phosphorus and three silicon atoms to represent a 1/4 monolayer (ML) phosphorus of δ -layer, we now use four quasi-atoms that are a 25/75 percent mixture of phosphorus and silicon. When these atoms are used, all in-plane lattice sites become equivalent and thereby the symmetry of the electronic structure is recovered. The effects of order vs. disorders and the use of quasi atoms are illustrated by the band structure plots shown in Figure 4. Focussing on the few bands that extend into the gap (white background), observe that for the disordered systems [Figure 4(b,c,d)] the bands have a simpler, more parabolic structure. In the ordered system [Figure 4(a)], two of the bands are coupled due to the loss in symmetry, resulting in a more complex band shape.

There is one additional advantage in using these quasi-atoms: it allows us to separate the size of the unit cell from the phosphorus content in the δ -layer. In our original model, 1/4 ML δ -layer required at least four atoms in the in-plane unit cell, and a 1/8 and 1/16 ML

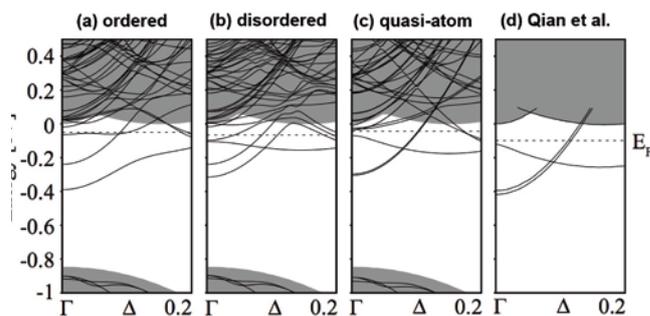


FIGURE 4

Calculated bandstructure of 1/4 ML δ -doped silicon using a 40 layer model highlighting the effects of order vs. disorder and the use of quasi-atoms: (a) 1/4 ML explicitly ordered dopants [cf. Figure 3(b)], (b) explicitly disordered dopant atoms using a quadruple-sized in-plane unit cell [$c(4 \times 4)$; see Figure 3(c)], (c) disorder represented using quasi-atoms, and (d) the selected bands taken from conduction-band-only model of Qian *et al.* [Phys. Rev. B 71 (2005) 045309].

δ -layer required correspondingly larger cells. Now, we can represent all coverages using the smallest possible in-plane unit cell (2 atoms for a (001) oriented δ -doped system) by simply adjusting the admixture of phosphorus into the quasi-atom used. This fact alone resulted in a massive saving in computational cost that we can transfer to improve other aspects of the model, such as the number of atoms in the plane-perpendicular direction or the sampling points in the irreducible Brillouin zone.

3. Molecular Functionalization of the Silicon (001) Surface

In a further project we have been exploring the reaction mechanism of adsorption and dissociation of some organic molecules on the Si(001) surface. A significant result in 2009 was our resolution of the adsorption mechanism of the acetophenone molecule ($\text{H}_3\text{C-CO-C}_6\text{H}_5$) on the Si(001) surface. This mechanism provide a full interpretation of scanning tunnelling microscopy (STM) image data recorded by our collaborators at the University of Newcastle. Most interesting in the experimental data is a set of reactions that is induced by the STM tunnelling current. An example is shown in Figure 5, wherein the acetophenone adsorbate appears a bright two-lobed protrusion. The induced reaction results in a 90 degree rotation of the two lobed feature in the image. Our calculations have been able to identified the species involved in this transition. As illustrated in the valence schematics in Figure 5, the molecule is attached flat onto the surface via four covalent bonds; one Si-O bond and three Si-C bonds. The induced reaction results in a transient breaking of the three Si-C bonds, which allows the molecule to pivot about the remaining Si-O bond into the rotated orientation as shown. This work further highlights our ability to resolve the often complex chemical processes observed in STM experiments.

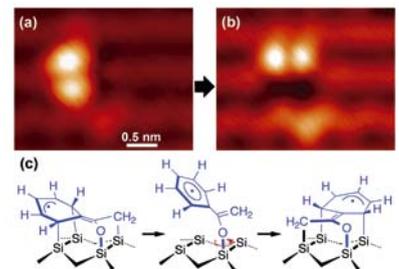


FIGURE 5

STM images showing a current induced transition in an acetophenone molecule adsorbed on the Si(001) surface. Shown below is the valence structure interpretation of the observed process based on our DFT calculations. The prominent two-lobe bright protrusion in these features is due to the allyl group in these species, indicated by a half-circle and a dot in the valence structure diagram.