Interaction of Silicon Dangling Bonds with Insulating Surfaces

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We use first principles density functional theory calculations to study the interaction of a model dangling bond silicon tip with the surfaces of CaF_2, Al_2O_3, TiO_2, and MgO. In each case the strongest interaction is with the highest anions in the surface. We show that this is due to the onset of chemical bonding with the surface anions, which can be controlled by an electric field across the system. Combining our results and previous studies on semiconductor surfaces suggests that using dangling bond Si tips can provide immediate identification of surface species in atomically resolved noncontact atomic force microscopy and facilitate selective measurements of short-range interactions with surface sites.

The interaction of free atoms, molecules, and clusters with surfaces is at the heart of surface science. Adhesion and tribology between surfaces are determined by the interaction between surface asperities. However, studying these interactions using conventional techniques almost always involves averaging over a large number of adsorbed species and surface asperities. Scanning microscopies offer a solution as they probe the interaction of sharp tips with individual surface sites in a wide distant range. Tips are often viewed as analogues of surface asperities or clusters. Ideally, one would like to use a well-defined tip for imaging a surface with high (atomic) resolution and then to measure forces with selected, chemically identified surface sites. Achieving this proved to be particularly challenging on insulators. Although force curves have been measured selectively above different surface sites on binary insulators [1–3], the utility of these curves is questionable since the chemical identity of the tip apex and hence the surface sites has not been established. Overcoming the tip problem would therefore open an exciting opportunity for using noncontact atomic force microscopy (nc-AFM) for gaining new information regarding the interaction of individual tip features, such as dangling bonds and adsorbed molecules with regular and defect sites at insulating surfaces and interfaces. In this Letter, we employ *ab initio* simulations to demonstrate that using Si tips may offer such an opportunity. In light of the recent attempts in controlled production of silicon tips [4,5], this opportunity seems to be highly feasible.

The interaction of silicon with other surfaces strongly depends on the properties of dangling bonds at Si surfaces. Those passivated by hydrogen are very different and their interaction with surfaces can be distinguished in nc-AFM [6]. In this Letter, we present the results of calculations for the interaction of Si dangling bonds with four insulating surfaces: $CaF_2(111)$, $Al_2O_3(0001)$, $TiO_2(110)$, and

MgO(001), all widely used in technological applications and with a long history in surface science. We focus on calculating short-range interactions between the tip and surface, as they determine image contrast (e.g., chapters 5, 16, and 17 in Ref. [7]). We demonstrate that this interaction is site selective and strongest with surface anions. Furthermore, it is determined by electron transfer between an insulator and the tip and can be controlled by applied voltage. Therefore, we believe that, by using carefully prepared silicon tips with dangling bonds at the apex, one could achieve immediate interpretation in high resolution imaging, enabling force measurements at selective sites.

All calculations were performed using the SIESTA code [8], which implements density functional theory (DFT). The generalized gradient approximation has been utilized in all calculations, and core electrons are represented by norm-conserving pseudopotentials [8]. The basis set dependence of the results was checked carefully and good accuracy was achieved with double ζ with polarization basis set for all species except: Mg in MgO—double ζ; F in CaF_2—double ζ; O in TiO_2—triple ζ with polarization; Ca in CaF_2—triple ζ with double polarization. k-point sampling was checked for calculations of the surfaces alone, but the large surface slabs used in tip-surface calculations meant that the Γ point provided accurate surface structure. Details of the calculations can be found in Ref. [9].

Each surface considered in this study has been the subject of successful atomically resolved nc-AFM studies [7,10]. The $CaF_2(111)$ surface is fluorine terminated with fluorine atoms protruding by about 0.08 nm from the Ca sublattice. The surface relaxation with respect to the bulk cut is very small and hence the surface gap is only 0.2 eV smaller than the bulk gap (see Table I). MgO is also a wide gap insulator, with very small surface relaxation, but, in contrast to CaF_2, the surface gap is much smaller due to a

TABLE I. Comparison of bulk and surface band gaps and the calculated offset between the top of the surface valence band and the silicon dangling bond state for each of the materials studied.

Material	Bulk Gap (eV)		Surface Gap (eV)	Offset (eV)
	Calc.	Expt.		
CaF_2	6.8	12.3 [11]	6.6	3.0
MgO	5.4	7.8 [12]	3.0	−0.7
Al_2O_3	6.2	9.9 [13]	3.7	0.4
TiO_2	2.5	3.0 [14]	0.7	−0.5

FIG. 1 (color online). Forces with a silicon tip over anion sites for each of the surfaces studied.

strong splitting of the surface states from the conduction band edge [15]. The α-Al_2O_3 surface undergoes a large relaxation and is terminated by a layer of Al ions which are located ~0.03 nm higher than the next layer of oxygen ions. The large surface relaxation leads to a splitting of the surface states and results in a narrower surface gap. TiO_2 is a narrow gap insulator, with a very small surface gap due to large relaxation, although no surface states are present in the gap. Note that the large difference between theoretical and experimental band gaps is a systematic error of the DFT method. However, the ground-state properties of these systems are well reproduced in DFT, so this error does not affect our conclusions.

The silicon tip used in this study consists of a ten-atom silicon cluster with a single dangling bond at the apex and its base terminated by hydrogen [16]. The one-electron state of the dangling bond is split from other occupied states of the Si tip modeling the Si valence band. This tip performs well when the short-range tip-surface interaction is determined by the onset of covalent bond formation between the dangling bond at the end of the tip and surface dangling bonds [17]. During simulations, the top two layers of the tip and the bottom third of the surface were kept frozen, and all other ions were allowed to relax freely until the forces are less than 0.05 eV/Å. We considered both spin-polarized and non-spin-polarized methods, and we found that it does not make a qualitative difference to the results. The size of the slabs used to represent the surfaces in calculations was determined by checking that the area was large enough to avoid spurious tip-tip interactions and deep enough so that the physical and electronic structure was well converged [9]. The gap between the top of the tip and the bottom of the slab was always at least 2 nm to avoid spurious tip-slab interactions.

In general, we expect the interaction between a silicon tip and the surface to have two main components: (i) an onset of chemical bonding between the tip and the surface, and (ii) the weaker force due to the polarization of the tip by the ionic insulating surface. Each of these components should depend strongly on the electronic structure of the surface. Also, the polarization of the tip should depend on the surface electric field and thus effective charge of the surface ions. Figure 1 shows the
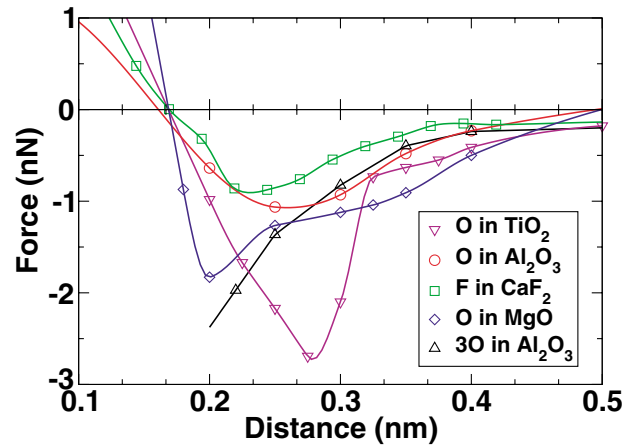
forces over anion sites in each surface with a silicon tip. For the Al_2O_3 surface, one of the curves is calculated above the center of a triangle formed by three surface oxygen ions. Note that the tip-surface distance in the figure is the nominal distance between the unrelaxed Si atom at the tip apex and the upper surface plane. The actual distances between the atom at the end of the tip and the surface atom under the tip are different from those shown in the figure due to different surface structures and induced tip and surface relaxations. Tip relaxation is mainly confined to the dangling bond Si atom and is largest above the oxygen triangle on the alumina surface at 0.22 nm from the Al surface plane. At this distance the Si atom is displaced by about 0.06 nm towards the surface. This is consistent with the large force obtained over the center of the oxygen triangle on the alumina surface. The smallest force is found for CaF_2 and the largest for TiO_2.

This interaction hierarchy is directly related to the ability of the Si tip dangling bond to make bonds with the surface ions. This effect can be characterized by the electron density transfer between the tip and the surface as a function of distance and is presented in Fig. 2(a). Note that the electrons are transferred to or from the whole tip and not just the dangling bond. However, the onset of bond formation is seen clearly in the electron density plot in the inset [Fig. 2(b)]. The electron transfer between tip and surface is calculated by summing all the Mulliken charges in the tip and surface at the relevant tip-surface separation and comparing this with a reference calculation with the tip at 2 nm from the surface [9]. This is equivalent, by definition [assuming infinite accuracy in the partial density of states (PDOS) and after normalization] to integrating over all the tip and surface states of the PDOS. We note, however, that at short tip-surface distances (<0.25 nm) the Mulliken analysis can be unreliable due to strong orbital overlap.

One would expect a qualitative correlation between the magnitude of the electron transfer for each surface and the band offset between the top of the surface valence
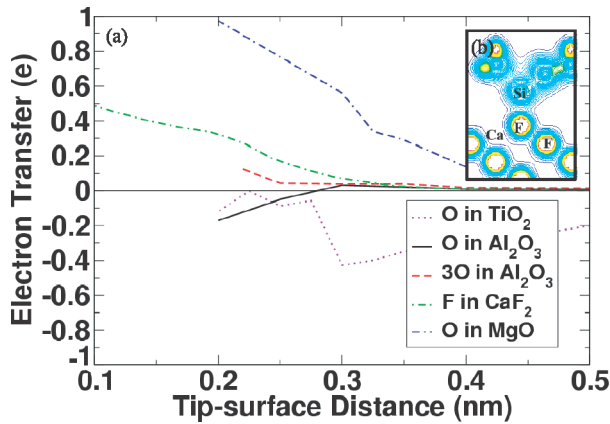
FIG. 2 (color online).   (a) Electron transfer from the surface to silicon tip (negative values mean transfer from the tip to the surface) as the tip approaches the surface over an anion site. (b) Example charge density in a plane through the labeled atoms for the tip at 0.27 nm over F in the CaF_2 surface.

band and the silicon dangling bond state. For a larger positive offset the electron transfer should be smaller. The values are given in Table I. As one can see in Fig. 2, for CaF_2, there is indeed very little electron transfer until very close approach is achieved, and when electron transfer does occur (below 0.25 nm) the tip has already entered the repulsive interaction regime. Furthermore, the singly charged fluorine ions produce only weak polarization compared to the doubly charged ions in MgO. The negative offset in MgO and TiO_2 correlates with significant electron transfer which starts at longer range—over $0.2e$ already at 0.4 nm—and increases almost linearly as the tip approaches the surface. This produces the much larger force compared to CaF_2 in the 0.3–0.4 nm range. In Al_2O_3, the electron transfer is similar to that for CaF_2. This correlates with the positive band offset and indicates that the stronger tip-surface interaction at short distances is due to the stronger electrostatic force and tip polarization above the center of the oxygen triangle where the surface electric field is the strongest.

The direction of electron transfer is a consequence of the surface electronic structure—specifically, the nature of the valence band (VB) and conduction band (CB). In CaF_2, the VB arises almost exclusively from F p states and the CB from Ca s states (seen in calculated PDOS). There are basically no unoccupied states on the anions, so effective electron transfer can be only to the tip. For the MgO and Al_2O_3 surfaces there is an admixture of Mg (Al) and O states in the VB, with the top of the valence band of purely oxygen character. For TiO_2 the direction is reversed, and bonding between the tip and anion sites in the TiO_2 surface involves effective electron transfer to the surface. This is a consequence of the large admixture of Ti and O states in the DOS (the largest of any surface), reflecting the significant covalency of the Ti-O bonds and that the CB has a significant fraction of unoccupied O p states.

Turning now to considering the forces over cation sites with a silicon tip (see Fig. 3), they are generally much smaller than the forces over the anion site, and we see correspondingly smaller electron transfer. Because of the large offset of the tip dangling bond with CB states, it is not energetically favorable to transfer electrons from the tip to cation unoccupied states in the CB. However, for MgO and TiO_2, significant VB states with cationic character exist, so this, and the interaction with neighboring oxygens, results in a larger electron transfer. The interaction of the Si dangling bond with the Al_2O_3 surface above Al sites is even stronger. This is consistent with the large dissociation energy predicted for AlSi dimers in comparison to, for example, MgSi [18].

The results of the previous section demonstrate that by controlling the nature of the tip one can immediately tell the source of contrast: the interaction of the Si dangling bond tip above anion sites is always stronger. The obtained sensitivity of the tip-surface interaction to the surface electronic structure implies that, by systematically changing the relative positions of the tip and surface electronic states, one could control the tip-surface interaction. One way of changing the energy offset between the tip dangling bond and the surface valence band is by applying a voltage across the system. This is a common practice in atomic force microscopy experiments, but may prove particularly useful when imaging thin insulating films.

To demonstrate the potential of this idea, we have studied the CaF_2 surface where electron transfer effects were smallest. As a first approximation, we have applied an electrostatic potential gradient to our supercell in the direction normal to the surface [8,9]. The system setup is the same as above, but now the tip and surface atoms are relaxed in the presence of the homogeneous electrostatic field. We note that this setup corresponds to the bias applied to a blunt macroscopic tip with an asperity at the end and an imaginary conductive substrate separated by 4 nm. With a distance of 0.270 nm between the silicon tip
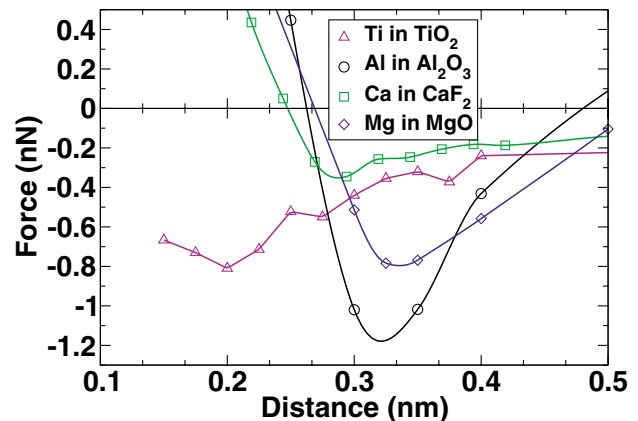

FIG. 3 (color online).   Forces with a silicon tip over cation sites for each of the surfaces studied.

apex and CaF_2 surface, we applied a field of ± 0.5 V/Å, where a positive field increases with increasing z (where z is the surface normal direction). Over the cation site, a field applied in either direction reduces the overall force, despite producing strong electron transfer in opposite directions. For the anion site, the force is strongly reduced for a positive field, but it is significantly increased for a negative field. The difference in behavior between the cation and anion sites can be understood if one recalls that over the anion site, the force is dominated by the electron transfer from the ion to the tip. A positive applied bias encourages this while a negative bias reverses it, changing the force accordingly. For the cation, at negative bias, the extra electron density reduces its effective charge and hence the polarization interaction with the tip and therefore the force. However, for positive applied bias, electrons actually transfer from the surrounding anion lattice, not the cation under the tip. Hence, there is still no formation of any strong chemical bonds, but again the ionicity of surface ions and the contribution of tip polarization to the interaction is reduced. The contrasting behavior above cations and anions suggests that, by producing experimental force vs distance curves over different atomic sites in the surface at equal and opposite bias, it should be possible to immediately tell which is an anion and which is a cation. This would involve subtracting the positive bias curve from the negative bias curve at the same site to remove the background forces (applying a bias will change the background capacitance force and mask the real change in chemical forces). The curve where the difference is largest, i.e., where changing the bias had the biggest effect, should be the anion set.

To summarize, we have shown that using dangling bond terminated Si tips offers an opportunity for chemically resolved imaging of the CaF_2, Al_2O_3, TiO_2, and MgO surfaces due to stronger interaction with the surface anions. Similar results have been obtained for the insulating $CaCO_3(10\bar{1}4)$ surface [19] and semiconductor surfaces Si(111) [16], GaAs(110), and InP(110) [7] with the contrast mechanism in images predicted to be due to the formation of covalent bonds between the tip apex and the surface. For binary semiconductors this is also always strongest over anions in the surface, suggesting that with reactive silicon tips, the source of contrast in images on semiconductors and insulators is immediately evident. The pronounced dependence of the tip-surface interaction on applied voltage suggests that this also could be used for controlling adhesion and friction between surfaces. Therefore, we suggest that dangling bond Si tips can be used for chemically resolved topographic imaging and measuring the interaction with selected, chemically identified surface sites. This represents a practical possibility, since it has been recently demonstrated that such tips can be prepared in a controlled way [4,5]. Because of the importance of Si dangling bonds at interfaces, these results can be useful for the understanding of the mechanisms of adhesion between Si and insulator surfaces in vacuum, tribological performance and understanding of wear in microelectromechanical systems, and atomic and molecular manipulation at insulating surfaces.

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