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Investigating the effects of silicon tip contamination in noncontact scanning force microscopy (SFM)

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Abstract

We have studied the possible modifications to a noncontact scanning force microscopy (SFM) silicon tip due to adsorption of species from the gas phase and due to contact with a NaCl surface. A model of the tip was developed based on a 33 atom silicon cluster, and then the different adsorbates were added and changes to tip electrostatic properties investigated. The interaction of a silicon tip with a NaCl surface was modelled quantum mechanically, allowing us to calculate the charge state of the adsorbed chlorine ion in the process of separation of the two surfaces. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Silicon tip contamination; Noncontact SFM; NaCl surface

1. Introduction

Recent advances in scanning force microscopy (SFM) based on dynamic-force methods, such as the noncontact mode of SFM operation [1], bring us closer to ‘true’ atomic resolution on insulators [2,3]. In this technique, the cantilever oscillates with large amplitude and information regarding the surface is generated from analysis of frequency or amplitude changes of these oscillations due to the tip–surface interaction [1,4,5]. These developments are vital for a wide range of SFM applications including studies of point surface defects, and construction and modification of nano-structures at surfaces. However, existing uncertainty of the tip atomistic structure hampers our understanding of SFM images and the possibility of controlled surface modification. The problem is complicated by the fact that even in the noncontact mode of SFM operation, where the tip is supposedly not touching the surface, the tip and surface modifications are impossible to avoid completely [3,6]. They may be caused by avalanche adhesion which takes place for many metallic and ionic tips and surfaces at tip–surface distances less than about 4.5 Å [7–11].

In this paper, we focus on some of the issues related to the silicon tip structure in typical UHV SFM experiments, and tip modification due to contact formation and breaking on ionic surfaces. Most of the commercial cantilevers are microfabricated from silicon and are covered by a native oxide layer. The surface is then cleaned by sputtering with Ar^+ ions. However, the chemical structure and geometry of the end of the tip is practically impossible to control. The factors which dominate the tip structure

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could be summarised as follows: the silicon nano-tip should bear the characteristic features of the most stable Si(111) (7 × 7) surface; it may have some residual oxide layer or oxygen adsorbed on it; it can be contaminated by hydrogen or water residual in the vacuum chamber; it can also be contaminated by the surface material. The charge state of adsorbed species depends on the tip and surface electronic structure. The questions we would like to address are the following: (i) what are the charge states of ions extracted by a silicon tip from ionic surfaces? and (ii) how does adsorption of different species on a silicon tip change its properties?

2. Methods

To model the contact formation between a silicon tip and the (001) NaCl surface, we used an embedded cluster model and the ab initio Hartree–Fock method implemented in the Gaussian94 code [12]. The quantum mechanically treated tip interacted with a quantum cluster modelling the surface which included the central chlorine ion and five surrounding cations, and was embedded in a finite array of $8 \times 8 \times 4$ classical ions which were treated in the shell model [13]. These ions interact between themselves via pair potentials [10] and produce an electrostatic embedding potential for the electrons and cores in the surface quantum cluster and in the tip. The shell model allows us to take into account the polarisation of the classical ions; the positions of the quantum and classical ions were optimised to minimise the system total energy at each tip position. This method is similar to that discussed in Ref. [11]. All quantum ions were described using the Hay and Wadt pseudopotentials and standard double zeta basis sets [12].

To model the silicon surface and tips modified by adsorbed species, we used the periodic DFT method based on the Car–Parrinello technique [14], in which the total energy of the system is minimised with respect to the plane wave coefficients of the occupied orbitals. We used the VASP code [15,16] where 'soft' Vanderbilt pseudopotentials [17,18] are implemented. The method employs the generalized Gradient Approximation (GGA) functional of Perdew and Wang [19,20] known as GGA-II. The calculations were performed for a periodic arrangement of clusters separated by large vacuum gaps and using a periodic slab model for surface calculations.

3. Results

As a basic silicon tip model we used a Si_{33} cluster [21] which possesses the structural features characteristic to the DAS Si(111) (7 × 7) reconstruction model [22]: the dimer pairs and adatoms. To check whether this really is a representative model for the Si(111) surface, we have calculated the geometric and electronic structure, and the electrostatic potential for the (5 × 5) surface reconstruction. This is the smallest cell which retains all the features of the (7 × 7) reconstruction [23]. The electron density and the electrostatic potentials near similar features on the Si surface and the Si_{33} cluster proved to be very similar. In particular, a charge density integration around the surface and cluster adatoms gave an almost identical charge distribution. The three coordinated adatom possesses a dangling bond and is the most chemically active surface site [24]. Two other tip models also were considered. (i) To have a more practical tip model for future ab initio calculations of the tip–surface interaction, we assumed that the adatoms, which are also the most outstanding surface atoms, are most likely to serve as the probe species. Our calculations of electrostatic potentials show that a surface adatom can be well represented by a smaller Si_{10} cluster [25], although without H-termination of the base it does have a slightly stronger charge distribution into the vacuum. (ii) To model a more inert tip, we used a Si_{29} cluster which does not have the four adatoms of the Si_{33} cluster. In this short paper, we only present the results of calculations for the Si_{29} cluster nano-tip interacting with the NaCl surface. Calculations for other tips give similar results.

We brought the quantum mechanically treated Si_{29} cluster to different distances above the chlorine ion on the NaCl surface and calculated the adiabatic potential for the displacements of the ion towards the tip. When the tip–surface distance is less than about 3.5 Å, the only stable position of the chlorine ion is between the tip and the surface, at about 1.0 Å above the original surface site, demonstrating the familiar instability effect [11]. If the tip–surface distance increases, the single-well adiabatic potential transforms into the double well, where one stable position corresponds to the chlorine ion in its surface site and another to its adsorption on the tip. As the tip and surface separate further, two things may happen [11]: (i) a single chlorine is trapped by the tip; and (ii) adsorption of chlorine on the tip may initiate formation of a string or neck of ions. We did not pursue the second scenario in this paper, but rather focused on another issue: the charge state of the adsorbed chlorine if it remains on the tip. The alternatives are: (i) it can be ionic chlorine and an anion vacancy will remain at the surface, which corresponds to tip and surface charging; or (ii) it can be atomic chlorine and the electron will remain in the vacancy forming an *F*-centre.

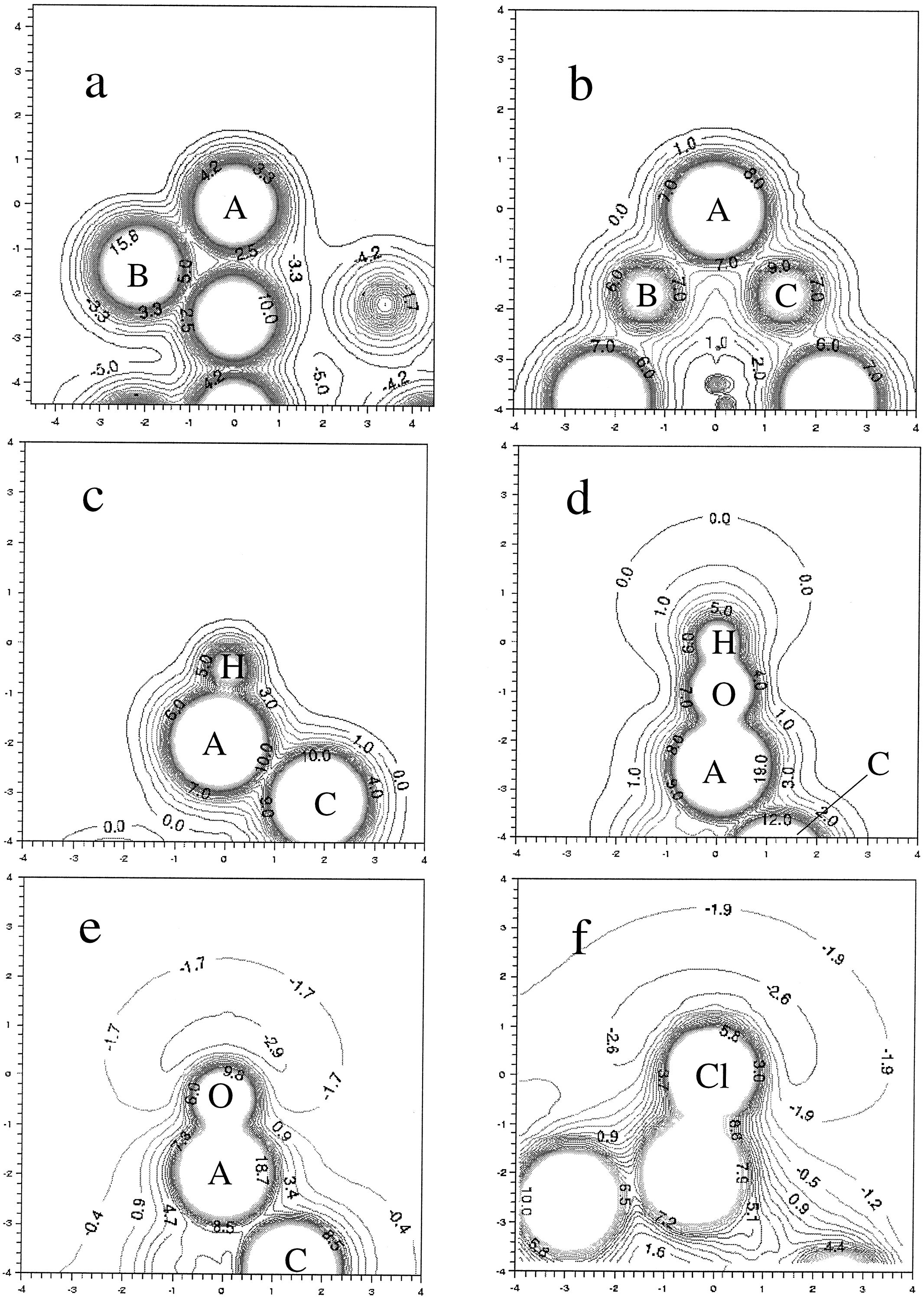
To check which one of these configurations takes place, we have calculated the Si_{29} cluster with adsorbed chlorine at different distances above the NaCl surface with the anion vacancy. To provide the correct electron affinity of the anion vacancy, the basis set was extended by several Gaussians centred in the vacancy. The exponents of these Gaussians were optimised to reproduce the ionisation energy and the optical absorption energy of the surface *F*-centre. These calculations demonstrated that adsorption of the chlorine ion on the tip is more energetically profitable than that of an atom. The effective charge of the adsorbed ion is about $-0.4e$ and the remaining extra charge is delocalised by the peripheral cluster atoms. The calculated adsorption energy of the chlorine ion on the Si_{29} cluster is 4.1 eV.

The most important component of the tip–surface interaction with ionic surfaces at long distances in NC-SFM is the electrostatics [26]. Therefore the gradient of the electrostatic potential is the most meaningful criterion for comparison of different tips. In this discussion, we assume that low coordinated tip sites are most likely to serve as surface probes. The electrostatic potentials near the adatom on the Si(111) surface and that produced by the Si_{10} cluster are shown in Fig. 1a,b. As one can see, despite the surface polarisation by the low-coordinated atoms, the electrostatic potential in both cases is decaying very quickly. We should note at this point that only the gradients of the electrostatic potentials are meaningful, since the potential is calculated in a periodic model and it is defined only up to a constant which is different for different systems and periodic cells.

We also considered Si tips contaminated by several species which can be present in UHV chamber. In particular, water is known to dissociate to the hydrogen atom and the OH radical on Si surfaces [27]. Therefore we considered the silicon tip with these species adsorbed on the adatom site. To model the residual oxide and the silicon tip contamination by oxygen due to contact with an oxide surface, an oxygen atom was adsorbed on the tip adatom. Test calculations for the Si_{33} and Si_{10} clusters with adsorbed species gave very similar results. Therefore in Fig. 1c–e, we present the electrostatic potentials calculated only for the Si_{10} cluster.

One can see that the adsorption of the hydrogen atom does not significantly affect the tip potential. However, the adsorption of a polar OH group produces a much more extended potential which extends to about 2 Å from the terminating H atom (Fig. 1d). An even stronger electrostatic potential is produced by the tip with the oxygen atom adsorbed on the adatom site (see Fig. 1e). This is caused by the negative oxygen charge due to electron density flow from the nearest silicon atoms to the oxygen. Comparison with the Hartree–Fock calculations of the electrostatic potential produced by the chlorine ion

Fig. 1. Sections of the electrostatic potential calculated for several silicon structures using the Hartree–Fock and the periodic DFT methods. The scale on the axes is in Ångstroms and the units of the contours are eV. A, B and C represent equivalent atoms in the Si surface and Si_{10} cluster, atom A is the adatom. (a) The adatom site on the reconstructed Si(111) (5×5) surface; (b) the adatom modelled by the Si_{10} cluster; (c) the hydrogen atom adsorbed on the Si adatom in the Si_{10} cluster; (d) the OH radical adsorbed on the Si adatom in the Si_{10} cluster; (e) the oxygen atom adsorbed on the Si adatom in the Si_{10} cluster; (f) the Cl^- ion adsorbed on the Si_{29} cluster. Note that in (b) the section is made in the symmetry plane, whereas in (c–e) the section is through atoms A and C, and the adsorbed species.


a
A
B
15.8
4.2
3.3
2.5
5.0
10.0
-3.3
-4.2
-1.7
-5.0
b
A
B
C
1.0
7.0
8.0
0.0
6.0
9.0
2.0
c
H
A
C
5.0
6.0
3.0
10.0
7.0
9.0
1.0
4.0
0.0
d
H
O
A
C
0.0
1.0
5.0
6.0
4.0
7.0
8.0
19.0
3.0
12.0
2.0
e
O
A
C
-1.7
-2.9
9.8
6.0
0.9
7.3
18.7
3.4
4.7
8.5
-0.4
f
Cl
-1.9
-2.6
5.8
3.0
3.7
0.9
6.6
7.9
5.1
6.5
7.2
1.6
10.0
-0.5
-1.2
4.4
-4
-3
-2
-1
0
1
2
3
4

adsorbed on the Si_{29} cluster (Fig. 1f) demonstrates similar properties.

4. Summary

We have studied the modification of a silicon tip due to adsorption of different species from the gas phase and due to contact with the NaCl surface. The embedded cluster Hartree–Fock calculations demonstrate the instability of chlorine ions when a silicon tip modelled by an inert Si_{29} cluster is closer than about 3.5 Å to the NaCl surface. When the tip and surface separate, the chlorine adsorbs on the tip in ionic form leaving an anion vacancy at the surface. The calculations of the electrostatic potential produced by modified tips demonstrate that the presence of polar groups or chemisorbed species, such as oxygen atom or chlorine ion, makes the electrostatic forces acting on the surface ions from the tip much stronger than for the Si and Si–H tips. Since, as demonstrated in Ref. [26], the electrostatic interaction is mostly responsible for the contrast formation in noncontact SFM on ionic surfaces, this is vital for really nonintrusive tip–surface interaction. Gradients of electrostatic forces in some cases can be measured at tip surface separations as large as 5.0–6.0 Å.

Finally, we would like to note that these are the first quantum mechanical calculations which treat the question of the charge of the adsorbed species in the process of separation of two surfaces. The ion and electron transfer due to contact formation and breaking, similar to that demonstrated in this paper, is responsible for contact electrification and tribocharging [28]. Using these processes one could construct nano-structures from vacancies in different charge states, or extract unwanted surface impurities by a tip.

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