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2009 Nanotechnology 20 445301

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Adsorption of small NaCl clusters on surfaces of silicon nanostructures

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Received 10 June 2009, in final form 8 September 2009

Published 5 October 2009

Online at stacks.iop.org/Nano/20/445301

Abstract

We have studied possible adsorption geometries of neutral NaCl clusters on the disordered surface of a large silicon model tip used in non-contact atomic force microscopy. The minima hopping method was used to determine low energy model tip configurations as well as ground state geometries of isolated NaCl clusters. The combined system was treated with density functional theory. Alkali halides have proven to be strong structure seekers and tend to form highly stable ground state configurations whenever possible. The favored adsorption geometry for four Na and four Cl atoms was found to be an adsorption of four NaCl dimers due to the formation of Cl–Si bonds. However, for larger NaCl clusters, the increasing energy required to dissociate the cluster into NaCl dimers suggests that adsorption of whole clusters in their isolated ground state configuration is preferred.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The development of efficient *ab initio* methods and increasing computational power have made theoretical investigations of surface processes on the atomic scale feasible. In particular, adsorption mechanisms of molecules on ideal surfaces have been studied extensively during the past years. Gajdos *et al* [1], for example, used density functional methods with different exchange–correlation functionals to predict adsorption properties of CO molecules on various close packed metal surfaces, and Cai *et al* [2] studied tungsten clusters with up to four atoms on an ideal MgO(001) surface. In both cases, the possible stable adsorption sites and molecular structure of the adsorbates are well assessable due to the crystalline properties of the substrate. However, up to now there have not been many reports on adsorption processes of molecules on nanostructures which are too small to form well defined surface structures. Although investigations of non-ideal surfaces are more complicated, they are inevitable for the detailed understanding of adsorption processes under

realistic conditions. As an example especially relevant in non-contact atomic force microscopy (NC-AFM) [3] experiments, we have chosen to study the adsorption of molecules on NC-AFM silicon model tips.

Silicon tips are widely used in NC-AFM experiments [4]. Initially they are covered by a thin oxide layer, but before scanning during cantilever preparation, they are sputtered by Ar⁺ or heated or both procedures are used simultaneously in order to remove the oxide layer [4–6]. The rate of reoxidation of the tips can be dramatically reduced in ultrahigh vacuum (UHV) environments used for high contrast NC-AFM imaging. Silicon tips have been used in several experiments to study alkali halide surfaces [7–10] or alkali halide thin films on metals [11, 12] or molecules on alkali halide surfaces [13, 14]. The tips of NC-AFM are often intentionally or spontaneously crashed into the sample during experiments [15]. Theoretical studies suggest that atoms from the sample are transferred onto the tip apex of NC-AFMs when in contact with the surface [16]. Silicon model tips used in NC-AFM simulations [17] should provide a realistic surface environment to study adsorption mechanisms of molecules. Up to now, few theoretical studies on contaminated NC-AFM model tips have been reported and

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only small silicon model tips with up to 33 Si atoms have been used [18, 19].

Both charged and neutral isolated alkali halide clusters have been studied extensively in the past (e.g. early theoretical results by Martin [20]) and proven to have a strong tendency of forming simple, cuboid structures whenever possible. As a result of their well-known structural properties, alkali halide clusters are an ideal choice as adsorbates on the complicated silicon tip surfaces in a first approach. In this work we present the results on adsorption properties of small NaCl clusters on large NC-AFM silicon model tips as well as adsorption properties of small and large NaCl clusters on a large perfect reconstructed silicon surface, Si(100) $c4 \times 2$.

2. Methods

The clean Si₁₂₈H₉₆ silicon model tip used in our investigations is the lowest energy configuration among 35 000 local minima configurations found during a search aimed at finding low energy structures using the minima hopping method (MHM) [21]. The apex of the tip protrudes in the [100] direction and consists of 50 unconstrained atoms, supported by two layers of fixed Si atoms. To maintain bulk properties, the 96 dangling bonds of the lowest layer are terminated by fixed hydrogen atoms. An extended Lenosky tight-binding scheme [22], which additionally includes a modeling of the Si–H and H–H interaction, was used to evaluate the energy and forces. During the molecular dynamics part of the MHM, the temperature did not exceed 900 °C; thus, reported environmental conditions in experiments were preserved [23]. In contrast to more simplistic silicon model tips, the tips of this type were used to reveal new energy dissipation mechanisms arising from an AFM silicon tip [17].

The MHM was also used to find global minimum configurations of isolated NaCl clusters. The energy and forces were evaluated with the pairwise Born–Mayer–Huggins–Fumi–Tosi (BMHFT) rigid ion potential [24]. Various neutral isolated clusters were investigated consisting of up to 128 atoms.

Since there are no classical potentials available to accurately model the interaction between Si, Na and Cl atoms, an *ab initio* method has to be used for this purpose. All electronic structure calculations of the tip with the NaCl clusters were performed with BigDFT, a density functional theory (DFT) code using a wavelet basis set [25]. The local density approximation (LDA) was used for the exchange–correlation functional in combination with the Hartwigsen–Goedecker–Hutter pseudopotentials [26]. A combination of the steepest descent and the conjugate gradient method was used for the geometry optimization both within the MHM runs and the BigDFT calculations.

3. Results and discussion

The silicon model tip used as the input configuration for the MHM simulation featured a sharp pyramidal apex with a single twofold coordinated atom at its end 10.86 Å above the first Si layer (see figure 1). During the simulation the pyramidal shape

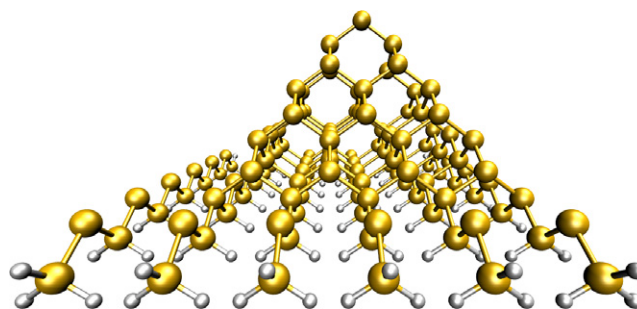


Figure 1. Initial Si₁₂₈H₉₆ silicon model tip structure before applying the MHM.

was reduced to a slight elevation of only 4.82 Å above the base Si layer. Assuming that the model tip is a segment of a sphere, the upper boundary of the tip radius can be estimated as 40 Å, a value comparable with real industrially manufactured state-of-the-art silicon tips used in experiments.

Several different geometries of the four Na and four Cl atoms adsorbed on the silicon model tip were used as input guesses for geometry relaxations to the nearest local minima on the potential energy surface (PES) within DFT calculations. Two main effects were found to contribute significantly to the lowering of the total potential energy. First, the global ground state configuration of the (NaCl)₄ cluster is a cube, so preserving this structure during adsorption will ensure a low potential energy. Second, a lowering of the energy can be obtained by the formation of bonds between Cl and low coordinated Si atoms. The upper limit of the energy released during this process was estimated by using a small Si₄H₉ model tip protruding in the [111] direction with a single Si atom on the apex providing a dangling bond for the Cl–Si interaction [27]. When taking into account the dissociation energy of 1.59 eV per dimer needed to separate the (NaCl)₄ cube into four NaCl dimers, the energy released during the formation of a single Cl–Si bond is 0.72 eV. Figure 2 shows the model tip both with and without an adsorbed NaCl dimer. A considerable amount of electronic charge is located around the Cl atom due to its high electronegativity. The above results suggest that the energetically most favored adsorption geometry of four Na and four Cl atoms is a cube with all Cl atoms located next to low coordinated Si atoms. However, the surface properties of our model tip do not allow such structures without dramatically deforming the cubic shape of the (NaCl)₄ cluster leading to an increase in potential energy. In agreement with this energetic preference the dimer adsorption is the most favored configuration.

We have found three possibilities for adsorption geometries of the four Na and four Cl atoms which in general lead to low energies. Each of them will be presented below. One low lying energy structure of each adsorption type is shown in figure 3; all configurational energies are listed in table 1.

NaCl dimers. One possible type of adsorption is placing four NaCl dimers oriented in a way that the Cl atoms are located near low coordinated Si atoms. To reduce the repulsive forces of the ionic interaction, a minimal distance of two times the NaCl bond length was kept between the Cl atoms and the

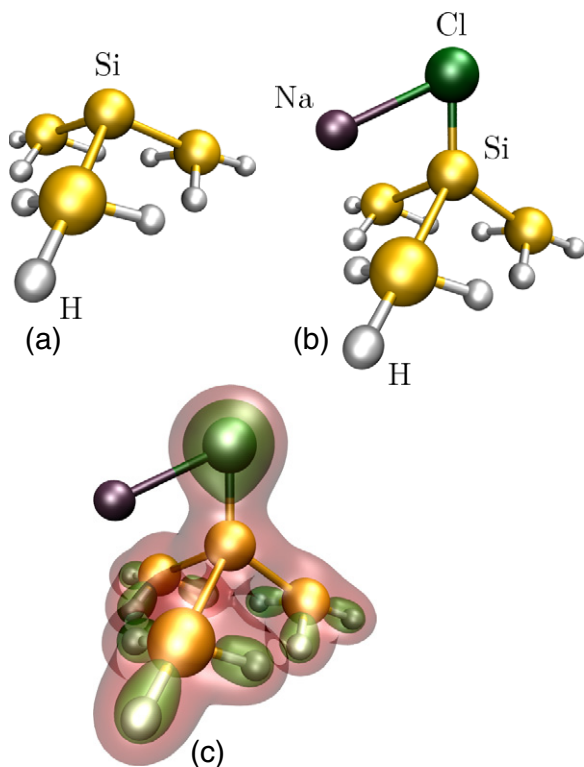


Figure 2. (a) Clean model Si_4H_9 tip. (b) Adsorbed NaCl dimer on Si_4H_9 . (c) Same as (b) with additional illustration of the isosurface on the normalized charge density. Red (light gray) corresponds to the value 0.1%, green (dark gray) to 0.28%.

Na atoms respectively. Although several adsorption sites can be found, most Si atoms on the model tip apex are fourfold coordinated; therefore, all dimers have to be placed around the apex. As expected, the lowest energy configuration was found with this adsorption type.

Cube in hole. Another possibility is to place a $(\text{NaCl})_4$ cube in a hole with one Na atom pointing toward the bulk and three Cl atoms near low coordinated Si atoms. In this way, a Cl atom is positioned at the apex leading to a negatively terminated tip. According to the results of NC-AFM simulations reported by Barth *et al* [28] in 2001, the atomic resolution imaging of $\text{CaF}_2(111)$ surfaces can be explained only with positively terminated tips. However, there exists mainly one site on our model tip which allows this kind of adsorption. The repulsive forces between the Na atom in the hole and the surrounding Si atoms as well as the resulting distortion of the relaxed $(\text{NaCl})_4$ cube shape prevent achieving an optimally low potential energy.

Cube on dimer. The cube can also be adsorbed face down such that only two Cl atoms are near low coordinated Si atoms. Our silicon model tip reveals five pairs of neighboring low coordinated Si atoms. Placing the cube with one of its faces toward such a Si dimer so that the connecting line between two Cl atoms is aligned with the Si–Si bond has proved to be a good choice for lowering the potential energy. The distance between two Cl atoms on the same face of an isolated and relaxed $(\text{NaCl})_4$ cube is 3.7 Å, which is significantly larger

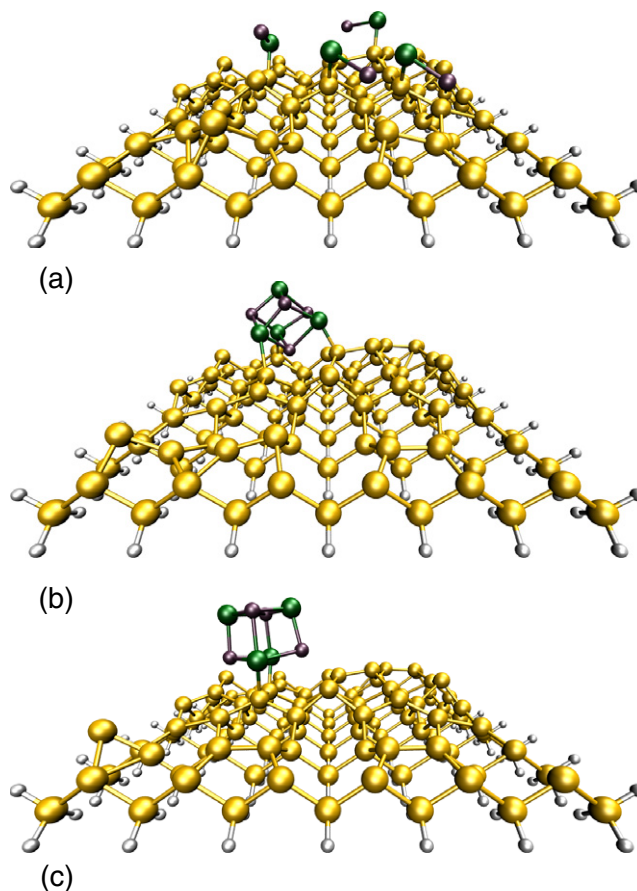


Figure 3. The Na and Cl atoms are adsorbed on the rough surface structure of the silicon model tip. The lowest energy configurations for the three different adsorption types: (a) NaCl dimer adsorption, (b) $(\text{NaCl})_4$ cube in a hole and (c) $(\text{NaCl})_4$ cube on a low coordinated Si dimer. The color coding is: green (dark gray large sphere) Cl, purple (dark gray small sphere) Na, yellow (light gray large sphere) Si and white (light gray small sphere) H.

Table 1. The energies of the lowest configurations in ascending order in eV. All values represent the difference in energy of the adsorbed structure and the isolated $(\text{NaCl})_4$ cube with the isolated model tip after relaxation.

Cube in hole	Cube on dimer	NaCl dimer
–1.48	–1.61	–1.84
–1.48	–1.53	–1.32
–1.45	–1.44	–0.88
–1.30	–1.43	
–1.00	–1.26	

than the average Si–Si bond length on our model tip of about 2.3 Å. Despite this mismatch and the fact that only two Cl–Si bonds are formed the overall second lowest adsorption energy was found with this type of adsorption.

However, the dimer adsorption is not the most preferred adsorption geometry when larger NaCl clusters are adsorbed. Alkali halide clusters are considered strong structure seekers in comparison to other atomic clusters. We have performed extensive MHM runs with the BMHFT potential on various large, neutral NaCl clusters with between 54 and 128 atoms. In

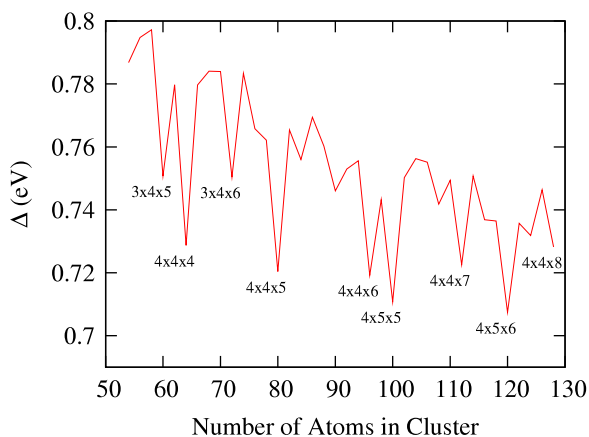


Figure 4. The difference in binding energy per atom between cluster and bulk structure according to $\Delta = \frac{E_{\text{tot}} - N E_{\text{coh}}}{N^{2/3}}$ as a function of the cluster size N . Particularly stable configurations are labeled with the number of atoms in each dimension $l \times m \times n$.

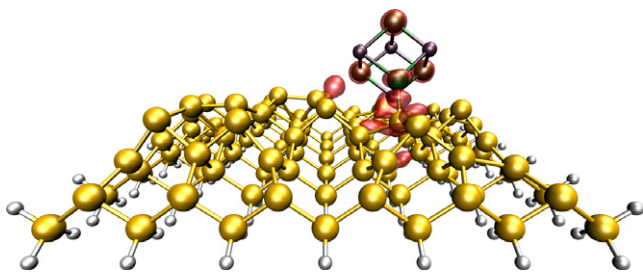


Figure 5. A $(\text{NaCl})_4$ cube adsorbed in a hole of the silicon model tip. The green (dark gray large sphere) and purple (dark gray small sphere) spheres denote Cl and Na atoms respectively, the Si atoms are represented by yellow (light gray large sphere) and the H atoms by white (light gray small sphere) spheres. The difference in the normalized charge density before and after the adsorption is illustrated by the red isosurface for a value of 0.2%.

agreement with *ab initio* results by Ochsenfeld *et al* [29], we found that clusters which consist of fragments of the solid state fcc lattice are particularly low in energy (see figure 4). We also found that the global minimum configuration is always found rapidly when the formation of a cuboid with close packed fcc lattice structure is possible (e.g. about 50 minima have to be visited for $(\text{NaCl})_{32}$). Similarly, Rose *et al* [30] observed within molecular dynamics simulations that cuboid structures were formed rapidly when cooling liquid $(\text{KCl})_{32}$ even at an unrealistically fast rate. In addition to being low in energy, the ground state cuboid structures have a considerable energy gap toward the first excited configuration, which is on average 0.72 eV higher.

The above results suggest that the formation of cuboid structures of NaCl clusters occurs rapidly when Na and Cl atoms are transferred to the NC-AFM tips during contact. The increasing dimerization energies with respect to the cluster size indicate a preference for the adsorption of whole clusters. For a $(\text{NaCl})_{32}$ cube, the dimerization energy calculated with DFT is already 2.08 eV. In the limit of bulk NaCl, the dissociation into dimers requires 3.25 eV per molecule, which is considerably larger than the 2.31 eV released during a single dimer adsorption on the silicon surface.

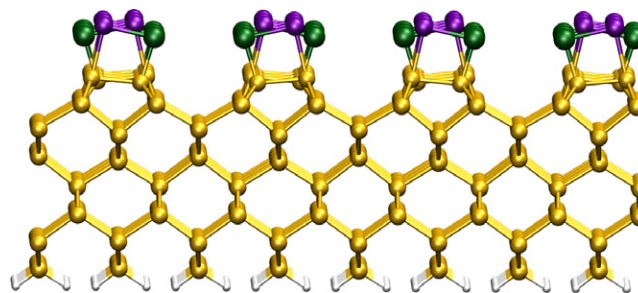


Figure 6. 32 NaCl dimers on a Si(100) $c4 \times 2$ reconstruction. The silicon surface reconstruction disappeared and the pattern of NaCl dimers mimics the original silicon surface reconstruction.

Table 2. The energies (eV) of adsorbed NaCl cubic structures and NaCl dimers on a perfect silicon surface, Si(100) $c4 \times 2$ reconstruction. The values are the difference in energy of the adsorbed structure and the corresponding isolated cubic structure with the clean reconstructed silicon surface after relaxation.

System size	Cube on surface	NaCl dimers
Small (few)	-1.33	-2.68
Large (many)	-4.0	4.85

For several adsorption geometries we have observed a deformation of the model tip during the geometry relaxation. In some cases the deformed model tip does not relax back into the initial tip structure when the NaCl clusters are removed and reveals lower potential energies than the original model tip. For all adsorption geometries, the energetically lower model tip structures were always used to calculate the adsorption energies. The largest energy difference between the original and deformed isolated model tip is 0.61 eV.

In order to compare the adsorption of NaCl clusters on a rough silicon surface with the adsorption of NaCl clusters on perfect silicon surfaces, we calculated the adsorption energies of small $(2 \times 2 \times 2)$ and large $(4 \times 4 \times 4)$ NaCl cubes on a perfect silicon surface, Si(100) $c4 \times 2$ reconstruction. The NaCl dimers on the perfect silicon surface are also studied and the number of dimers is such that the number of Na and Cl atoms are the same as the corresponding cubic system. Results are listed in table 2. Similar to the adsorption on the rough silicon surface the dimer adsorption structure has a lower energy than the small cube on the surface. Since the number of Na and Cl atoms for the small system is the same as used for the model tip the energies can be compared directly with those in table 1. Clearly the dimer adsorption on the perfect surface is the most favorable structure for the small NaCl clusters. The results of the large cube on the surface and many dimers on the surface confirm our prediction that the adsorption without dissociation is preferred over the dimer adsorption for larger clusters. The adsorption energy for dimers on the surface given in table 2 is positive because of our definition of adsorption energy, that is $E_{\text{adsorbed}} - (E_{\text{isolated cube}} + E_{\text{clean silicon}})$, can be positive if the energy of the adsorbing process is not large enough to compensate the dissociation energy of the cube. However, in this case another effect is also partially responsible, that is the disappearance of the silicon surface reconstruction leading

to a regular pattern for NaCl dimers on the surface. This is illustrated in figure 6.

To illustrate the effect of the adsorption on the electronic structure, the charge density of the model tip was calculated. The charge densities of the isolated model tip and the NaCl were subtracted from the charge density of the combined system and the resulting isosurface is shown in figure 5. The formation of the Cl–Si bond can be observed very clearly by the accumulation of charge between the Cl and Si atoms after adsorption. Due to their high electronegativity, additional electronic charge is drawn from the whole tip toward the Cl atoms.

4. Summary

We have studied the adsorption geometries and electronic structures of NaCl clusters adsorbed on silicon model tips used in NC-AFM simulations with DFT. Compared to the adsorption of molecules on ideal surfaces, a much larger number of possible adsorption geometries and adsorption sites exist on the model tip. We have studied and compared a set of the most promising configurations when four Na and four Cl atoms are adsorbed on the silicon model tip. Both the ground state geometry of the (NaCl)₄ cluster and the formation of Cl–Si bonds lead to a lowering of the potential energy. As a result, an adsorbed (NaCl)₄ cube in a hole of the surface leads to a negatively terminated tip. However, the most favored adsorption type was found to be four NaCl dimers on top of low coordinated Si atoms. This is in agreement with the positive balance of energy when the dissociation of the (NaCl)₄ cube into dimers and the formation of Cl–Si bonds is taken into account. However, this behavior changes when larger NaCl clusters are adsorbed. The increasing dimerization energy with respect to the cluster size and the formation of stable cuboid geometries of isolated NaCl clusters suggest that the adsorption without dissociation is preferred over the dimer adsorption for larger clusters. Contrary to the disordered adsorption of dimers, an adsorption of large NaCl clusters on tips would result in an improved contrast formation in atomic resolution NC-AFM imaging.

Acknowledgments

We thank Ernst Meyer for interesting and helpful discussions. This work has been supported by the Swiss National Science Foundation and the Swiss National Center of Competence in Research (NCCR) on Nanoscale Science. The calculations were done at the Swiss National Supercomputing center (CSCS) in Manno.

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