Analysis of STM Images after Atom Extractions from the Si(111) 7 × 7 Unit Cell through a Cluster Model

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Using an ab initio cluster model, we have investigated the electronic information contained in scanning tunneling microscope (STM) images, which were obtained after atom extraction from the Si(111) 7 × 7 surface. Depending on the position of the created vacancy (corner versus center) and on the number of extracted atoms (single atom versus dimer), we obtain different density maps that permit us to propose a rationalization of the brightness of the spots that are observed in the corresponding experimental STM images. It can be understood by a localization of the surface state near the created atomic vacancy.

1. Introduction

Using the scanning tunneling microscope (STM),[1] Lyo and Avouris[2] have demonstrated that a single Si atom can be extracted from the Si(111) 7 × 7 surface. More recently, selective site extraction of a Si atom and the formation of polyatomic grooves have been routinely obtained on silicon surfaces.[3] Such atomic-scale modifications of the surfaces have been confirmed through the STM images. However, since the STM images reflect the electronic density of states of the surface,[4] the images of created vacancies are in many cases troublesome. For instance, even in the case of a small vacancy, it is not easy to know the exact number of the extracted atoms and the displacement of the subsurface atoms. To ascertain such information, a reliable reproduction of the experimental image, by means of theoretical calculations, is an increasing demand.

Since the work of Tersoff and Hamann,[5] calculations of the electron-density map of the system has been recognized to be important for interpreting STM images. We are therefore obliged to perform calculations within a reliable quantum mechanical framework. When few atoms are needed to define the system, some approaches were successfully applied to reproduce experimental STM images.[6,7] Such approaches are not tractable in our present study because of both the size of the unit cell and the loss of symmetry after atomic extraction. Nonetheless, in case of the Si(111) 7 × 7 surface, the reconstruction of the surface is clearly understood from the dimer−adatom−stacking-fault (DAS) model[8] and the fully relaxed atomic position was calculated under the local density approximation (LDA).[9,10] we therefore expect that ab initio single-point calculations at this reported geometry might be a first step to having some insight on the electronic properties of the defect created after atomic extraction on the Si(111) 7 × 7 surface. We have thus defined, within the Hartree−Fock approximation, an ab initio cluster model.

2. Cluster Model Presentation

There are three criteria to be considered in order to define an appropriate cluster representation for the Si(111) 7 × 7 structure. The first is a ratio between the rest and adatom sites, which governs any quantitative discussion on the charge transfer between adatom and rest sites. As shown in Figure 1, this ratio must be 2. It permits conservation of the C_{3v} point group symmetry of the Si(111) 7 × 7 perfect half unit cell. The second is the realization of T4 geometry for an adatom. This is important because of the partial bond between the adatom and the Si atom below it in the third atomic layer.[11] Finally, the chemical connectivities must be respected by adding the dimer atoms on the third layer and hydrogens to saturate the remaining dangling bonds at the boundary of the cluster. These considerations lead to the cluster model selected here for performing calculations. It consists of 60 silicon atoms and 51 hydrogen atoms and corresponds to half of the Si(111) 7 × 7 unit cell. It is reported in a schematic way in Figure 1. To mimic as well as possible the Si−Si bond, the Si−H bonds conserve the direction of Si−Si bonds defined by the DAS model.[8] We used the Gaussian 92 package and select the CEP-31G basis set quality. The SiH bond length has been optimized at the HF level with the same basis set on a SiH_4 molecule. Cluster models are widely used to calculate an optimized structure. The critical point of such a model is the role of the artificial boundary conditions. Therefore, we do not optimize the geometry of the system but use the geometry calculated from a supercell LDA model reported in ref 10, where boundary conditions are correctly described.

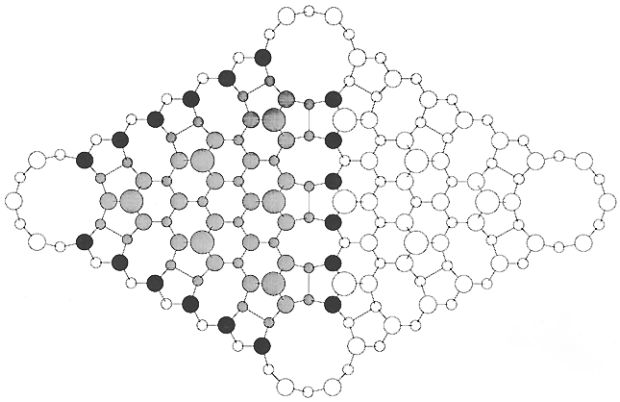

Figure 1. Cluster model. Dark atoms constitute the cluster model. Si atoms taken into account are represented in gray instead of black for the hydrogen atoms. The signification of the different circles refers to the DAS scheme.[10]

Each calculation for a selected geometry and electronic configuration in this cluster model takes 1 week of CPU time on an IBM Risc 6000 workstation and meets the limit of manageable work with our computational facilities.

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TABLE 1: Mulliken Population of the p_z Orbitals for the Different Adatoms Sites of Each Half Unit Cell

sites	calcd pop
Unfaulted Half	
corner	0.45
center	0.30
rest	1.7
Faulted Half	
corner	0.75
center	0.25
rest	1.7

3. Origin of the Surface States and Electronic Configuration

An important point of the electronic configuration of the unit cell must be discussed. After reconstruction, there remain 19 dangling bonds on the Si(111) 7 × 7 unit cell. It was demonstrated that the surface states have a strong component of these dangling bonds.[12] To ascertain our qualitative description of the surface states on Si(111) 7 × 7, we compared the energy classification of the molecular orbitals with the calculated energy band structures reported by Northrup.[12] We can fairly correlate this reported geometrical assignment of the S_1 and S_3 bands to adatom sites and of the S_2 band to the rest site[12] from the projection of the corresponding highest occupied molecular orbitals of the rest site and adatom atomic orbitals.

The most stable surface state defined by the molecular orbitals constructed from the rest site dangling bonds is fully occupied. Then, only seven electrons associated with adatoms remain on the whole unit cell. Owing to the low energy level associated with the corner hole,[13,14] we must also define a fully occupied orbital corresponding to the corner hole. We defined thus a five-electron configuration on the unit cell for the remaining surface states. This configuration embedded in our cluster model was nonetheless previously proposed on the basis of both LDA calculations[12] and experimental measurements.[15,16] From LDA calculations, whatever the center or corner position, adatoms on the faulted half have more charge than adatoms in the unfaulted half of the unit cell.[9,10] We modeled this different overall charge in each half unit cell by taking three electrons for the faulted half versus only two for the unfaulted half.

4. Charge-Transfer Phenomenon

In our chemical description, and with the LCAO approximation, these surface states have the strongest component of the p_z atomic orbitals. In Table 1, the p_z orbital population on each site is compared. The sum of these population values does not correspond to the number of electrons asssigned formally to the surface state owing to the coupling with the back-bond MOs. In the faulted half unit cell we traced a large difference between corner versus center p_z orbital population. Within our cluster model this result was expected and clearly comes from the multiplicity of the electronic configuration. The quadruplet configuration is indeed more stable than the doublet one. In the quadruplet one, the MOs defining the surface state electrons have a strong component of the corner adatom. This multiplicity is due to the finite size of the cluster and has little significance for the Si(111) 7 × 7 surface itself. Nevertheless, we obtain clear confirmation of the previously proposed charge transfer from both corner and center adatom sites to the rest site.[12,13] We calculate the density map of the cluster before atom extraction (Figure 2a) on a plane parallel to the cluster surface at a distance of 7 Å from the adatom plane position. This selected tip−sample distance is expected to be quite close to the typical one for an STM experiment. Depending on the number of MOs taken into account to calculate this density map, its shape varies. It corresponds experimentally to varying the STM image by tuning the bias voltage parameter. Nonetheless this dependence is important only close to the surface (below 4 Å). Increasing the distance from the surface decreases the contribution of the back-bond orbitals. In other words, the only significant contribution to the electronic density at a distance of 7 Å is due to the surface state. This phenomenon might be important for understanding STM images. It can explain why our experimental images are qualitatively unchanged when going from 0.5 to 2 V bias tip voltage. Increasing the bias voltage permits us to probe the energy level assigned to the back-bond orbital, but owing to the distance between tip and sample, only the *z*-oriented orbitals overlap significantly with the tip wave function. In the following all the density maps reported are calculated for the same distance (7 Å). A full dependence of the calculated maps on this parameter and single and dimer extraction on both the faulted and unfaulted half unit cell have been systematically studied and will be reported elsewhere in a more descriptive paper. We want to devote the present paper to the analysis of a set of recent experimental data obtained by our group for the unfaulted unit cell.

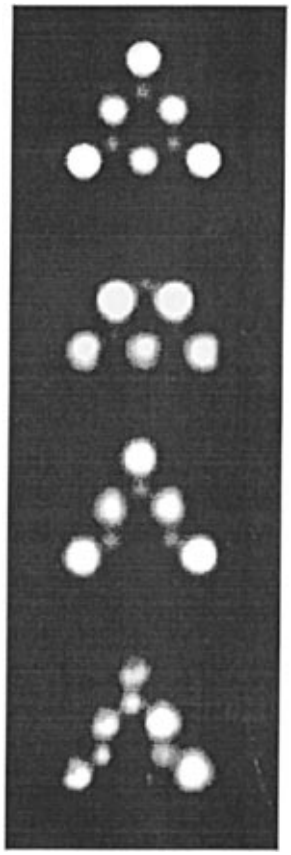

Figure 2. Electronic density map calculated in a plane parallel to the surface at a distance of 7 Å from the adatom plane. Each map is reproduced with the same contrast in gray scale (a, top) for the unfaulted half unit cell, (b, second from top) after a corner adatom extraction, (c, third from top) after a center adatom extraction, and (d, bottom) after a dimer extraction corresponding to the left atomic model in Figure 4.

5. STM Image after Corner Adatom Extraction

We extracted one corner adatom from the cluster model and performed a calculation in order to obtain the corresponding density map shown in Figure 2b. By comparison with a perfect half unit cell (Figure 2a), the lack of one bright spot located at the extracted position is clearly observed. The brighter appear-

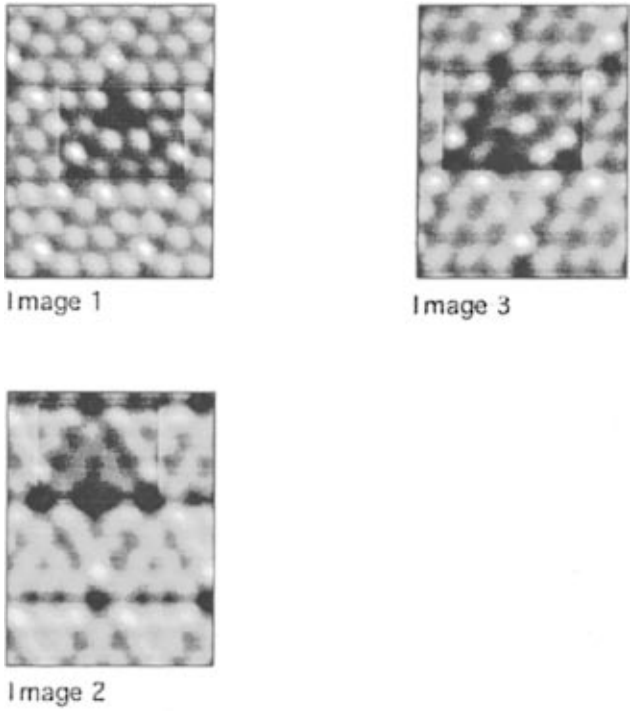

Figure 3. STM image taken at a sample bias of −2 V and 0.2 nA. As a guideline, we use a slight contrast enhancement for the unfaulted half of the Si(111) 7 × 7 unit cell where the extraction takes place. Image 1 shows extraction of a single Si atom at corner position. Image 2 shows extraction of a single Si atom at the center position. Image 3 shows extraction of dimer Si atoms at the center position.

ance in Figure 2b, of the two spots located at the two equivalent center adatoms that are close to the created vacancy is also observed in the corresponding experimental STM image 1 of Figure 3 and can be clarified by the following. After adatom extraction, in our cluster model, only one electron in the p_z-like dangling bond is connected with the top layer atoms; this electron interacts with the second-layer atom on the corner site to define the corresponding HOMO of the system. To optimize this interaction, a localization of this orbital near the vacancy occurs. From this calculation, we propose then to assign the experimental STM image 1 in Figure 3 to a single corner adatom extraction case.

6. STM Images after Center Adatom Extractions

In the case of extraction in the center site, several kinds of patterns have been obtained experimentally, namely, symmetrical images (see image 2 in Figure 3) and asymmetrical images (see image 3 in Figure 3) with respect to the σ_v plane. We recorded with the same frequency both the left asymmetrical image and the right asymmetrical image with respect to the σ_v plane. The symmetrical image is by far the most common case, the asymmetrical one corresponding to a minor possibility.

The density map obtained after extraction of one center adatom from the cluster model is reported in Figure 2c. We have a disappearance of the spot corresponding to the center site, but here, we did not obtain any special localization effect of the HOMO and the brightness of each spot remains quite similar to those obtained in Figure 2a. Once one atom is extracted, we need in principle to search a stable configuration by relaxing the geometry of the cluster in our calculations. It is not possible to perform such full geometry optimization because of the computational limitation. Nonetheless, we perform the calculation by relaxing the position of the three atoms on the second layer of the created vacancy in order to simulate the creation of a bonding between two of them. Very close to the surface, this local distortion from the DAS geometry changes slightly the density map, but this effect becomes weaker if we go far from the surface and gives a symmetrical density map at 7 Å. In summary, both the frozen geometry and the relaxed one give a result that is compatible with the experimental image 2 in Figure 3, which then might be assigned to a single center adatom extraction.

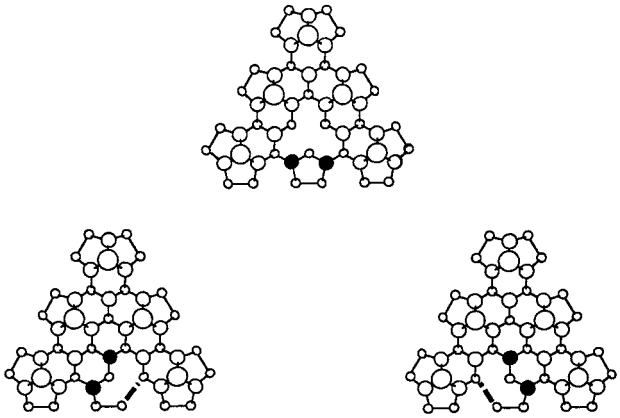

Figure 4. Possible dimer extractions at the center positions. For the asymmetrical ones, the bond creation between two second-layer atoms near the vacancy was taken into account by relaxing the geometry in the DAS model.

To explain the asymmetry exhibited in image 3 in Figure 3, a first hypothesis is to assign the different images as different minima on the potential energy surface of the remaining system after one center adatom extraction, namely, a symmetrical minimum and two equivalent asymmetrical local minima. As we saw, a local distortion from the DAS geometry did not give an asymmetrical pattern in the corresponding density map. If we want to investigate further this first hypothesis, we need to define a larger distortion in the DAS model. It requires taking into account many more atoms in the model, and this is beyond our computational facilities.

A second hypothesis is to assign the asymmetrical image to a dimer extraction. To test this hypothesis, we can select, for instance, three models reported in Figure 4 that correspond to three different possibilities for extracting a dimer from the center site. Two of them are equivalent by symmetry and can be candidates for explaining the left−right asymmetrical images obtained experimentally. The possibility of a chemical link between two of the remaining atoms located on the second layer near the vacancy (see Figure 4) is investigated. Needless to say, owing to the boundary condition of the present cluster model, such bond creation cannot be studied completely. Nonetheless, the relaxation of these two second-layer atoms from the DAS model geometry was taken into account by optimizing the energy of the cluster as a function of this interatomic distance. In the corresponding density map this improved quantitatively the appearance of the two brighter spots in Figure 2d. From a comparison between the experimental image 3 in Figure 3 and the density map corresponding to the asymmetrical dimer extraction case (Figure 2d), we propose then this dimer extraction to elucidate our reported asymmetrical STM images.

From an energy point of view, it is clearly easier to extract a single center adatom than any dimer. This can explain the large proportion of symmetrical images in the experimental data. However, some symmetrical experimental images might be related to a symmetrical dimer extraction (see Figure 4), where the calculated density map is compatible to a symmetrical image.

7. Conclusions

In this article, we report new experimental STM images obtained after atomic extraction on an Si(111) 7 × 7 surface. Within a cluster ab initio model, we could discriminate between single and dimer extractions from their corresponding density maps. We rationalized the bright spot features appearing in STM filled state images after atomic extractions on a Si(111) 7 × 7 surface. Finally, we presented evidence of the localization of surface states near the created atomic vacancies.

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