

Brief Reports

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Chemical dependence of the multiple-tip effect in scanning tunneling microscopy

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Simultaneous imaging by multiple atomic tips in scanning tunneling microscopy has the effect of superimposing displaced images, which for a two-atom tip may appear as a doubling of atoms. In this paper we present spectroscopic images where the doubling is voltage dependent. We interpret this effect by proposing a tunneling tip with two protruding chemically different atoms. The relative contribution of each atom to the total current is proportional to the atoms' local density of states that can participate in tunneling. If the two protruding tip atoms are chemically different, then the contribution of each tip, and thus the doubling of the image, can be voltage dependent.

The scanning tunneling microscope (STM) has found great use in the study of the topography and the electronic structure of surfaces, because the tunneling current between the pointed STM tip and the flat sample surface depends predominantly on the properties of the sample. The STM images reflect the sample geometry because usually current flows through the same portion of the STM tip as it scans on a scale of volts over the corrugated sample. The structureless density of states near the Fermi energy of transition metals used as the tip material allows the energy dependence of only the local density of sample states to influence the STM images. However, since the structure of the tip is not controlled at an atomic level, anomalous tips may occasionally appear. These nonideal tips can modify the STM topographs in unusual ways, such as a distortion or a doubling of atoms, and one must be careful in not attributing the anomalies to properties of the sample.

Consideration of nonideal STM tips first arose in the study of graphite. Both the geometric and the electronic structures of graphite are well known, and one expects to see a centered hexagonal lattice. However, a variety of STM images were obtained for the graphite surface. Many of these images did not reflect the threefold symmetry of the graphite surface and therefore it was proposed that the image must depend also on the tip. A semiquantitative explanation for the variety of images can be obtained by assuming the tunneling takes place through two or more perhaps widely separated atoms at the end of the tip.¹ The superposition of the tunneling current through each tip atom distorts the shape of the sample atoms. STM topographs of regions near a grain boundary show directly that multiple atomic tips exist

and that they can be separated by over 100 Å.²

Multiple atomic tips have also been observed while scanning over silicon surfaces.³ In the 7×7 reconstruction of the Si(111) surface, the adatom spacing is larger than the graphite-atom spacing, so multiple atomic tips cause a doubling of atoms in the STM topographs. Apparent pairing of defects shows that the tip atoms can be as close as 3 Å, while images of step boundaries show that they can be over 20 Å apart.

In this paper we report on how imaging with two chemically different tip atoms plays a role in the voltage dependence of these anomalous images. We begin with summarizing the effect of different atoms in STM images of semiconducting surfaces.

The STM monitors the local density of states near the Fermi level at the position of the tip.⁴ The electronic structure of a semiconductor is well approximated by assuming the electrons are localized in hybridized orbitals associated with each atom. The energy of the electrons occupying these bonds depends on the identity of the atoms with which the bond is associated in addition to the coupling between the atoms. The variation in the energy of these bonds between different atoms is on the order of volts, an energy difference that can be probed by the STM at room temperature.

When the tip is biased at a positive voltage, electrons flow from the sample to the tip and therefore the local density of filled sample states is probed. On the other hand, when the tip is biased at a negative voltage, electrons flow to the sample and the local density of unoccupied sample states is probed. This means that orbitals with an energy below the Fermi energy will be imaged at positive tip voltage, while orbitals with an energy above

the Fermi energy will be imaged at negative tip voltages.

STM atomic resolution images of semiconducting surfaces are dominated not only by the topography, but also by the electronic structure of the surface. The electronic structure has been seen to affect the image in two ways. Orbitals localized on single atoms contribute significantly to the tunneling current when the energy of the orbital lies in the range of states available to tunneling. Different atoms will enter this window as it is changed by selecting the bias voltage. Examples of this effect include the STM observation of GaAs(110),⁵ O/GaAs(110),⁶ Al/Si(111),⁷ In/Si(111),^{8–10} and Ga/Si(111).¹¹ Hybridized atomic orbitals combine to make bonding and antibonding orbitals between two atoms, with the bonding orbital having a different shape than the antibonding orbital. One may dominate over the other by adjusting the window of states available for tunneling. Examples of this effect include images of Si(111)2×1 (Ref. 12) and Si(100)2×1.^{13,14}

Spectroscopic variations in the image can also arise from the electronic structure of the tip. The tunneling tip is made of tungsten metal, whose integrated density of occupied and unoccupied states are very similar. Therefore the double-tip effect will not depend on the polarity of bias voltage if the double tip is formed of two W atoms. However, if a foreign atom, for example, Si, forms a double tip alongside a tungsten atom, the double-tip effect may depend on the polarity of the tunneling voltage. Figure 1 shows such a polarity-dependent double-tip effect. Figure 1(a) is a STM image of Si(111)7×7 taken with a bias voltage of -2 V on the tip, while Fig. 1(b) is taken with a bias voltage of $+2$ V. These dual-polarity images are taken simultaneously by alternating the bias voltage on each scanning line.

On the bottom half of the image of occupied states [Fig. 1(b)] we see a doubling of Si adatoms, which is very similar to double-tip images we have reported previously.³ The doubling of atoms disappears on the upper half of the image, indicating one of the two tip atoms moved away during the acquisition of the image. This effect does not appear on the image of unoccupied states [Fig. 1(a)]. The asymmetry of the lower halves of the images is impossible for rigid identical tip atoms, so we must make the assumption that not only is tunneling occurring simultaneously from a double tip, but these two tips are chemically different species.

In Fig. 2, we display another double-tip image of Si(111)7×7 with low In coverage (approximately 0.05 monolayers). We see several bright elongated dots in Fig. 2(a) (unoccupied states), which represent In atoms replacing Si adatoms. The elongated dot is a superposition of two closely spaced images. In Fig. 2(b) (occupied states) we see slight depressions at the position of In replacement. With an ideal single tip, we see circular bright dots in unoccupied states and slight depressions in occupied states similar to Fig. 2(b).⁹ In Fig. 2, the occupied state image is not doubled but the unoccupied state image is. This is just the opposite behavior to that seen in Fig. 1.

In order to understand this behavior in more detail, we consider a specific model for the tip atoms contributing to the tunneling current. The calculations of Lang¹⁵ illustrate that the apparent height of single atoms of different species adsorbed onto a flat jellium surface depends strongly on the atomic electronic configuration. To take a specific example, the apparent height of a Na atom is larger than that of a S atom due to its higher density of states at the Fermi level (E_F). Although Lang's calculation applies to the case of low bias, the apparent

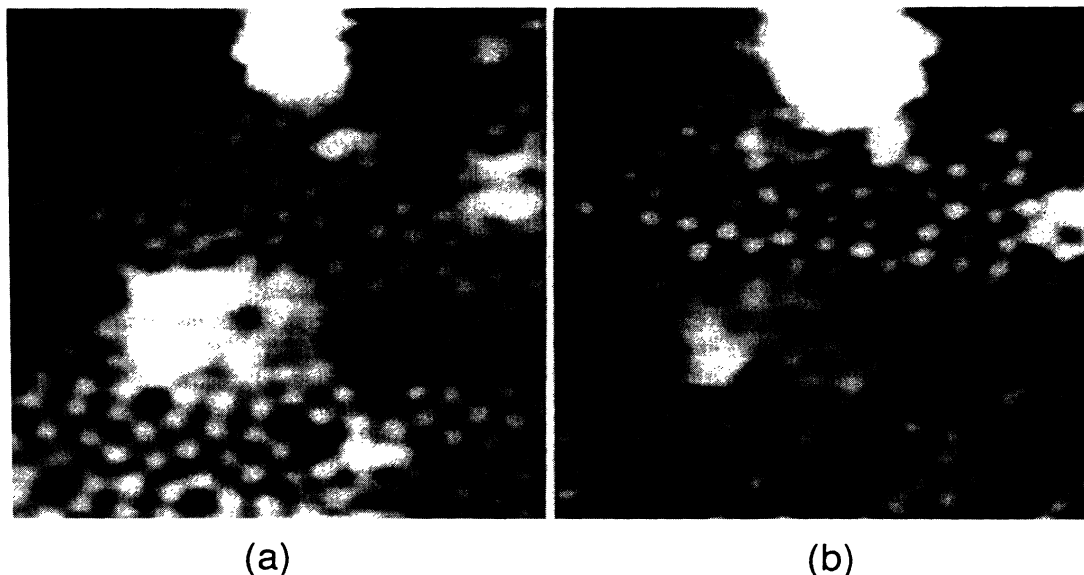


FIG. 1. A dual-polarity image of the Si(111)7×7 surface obtained with (a) -2 V and (b) $+2$ V bias on the tip. The doubling of adatoms appears only in the lower half of the occupied states (b). The scale is 120×120 Å.

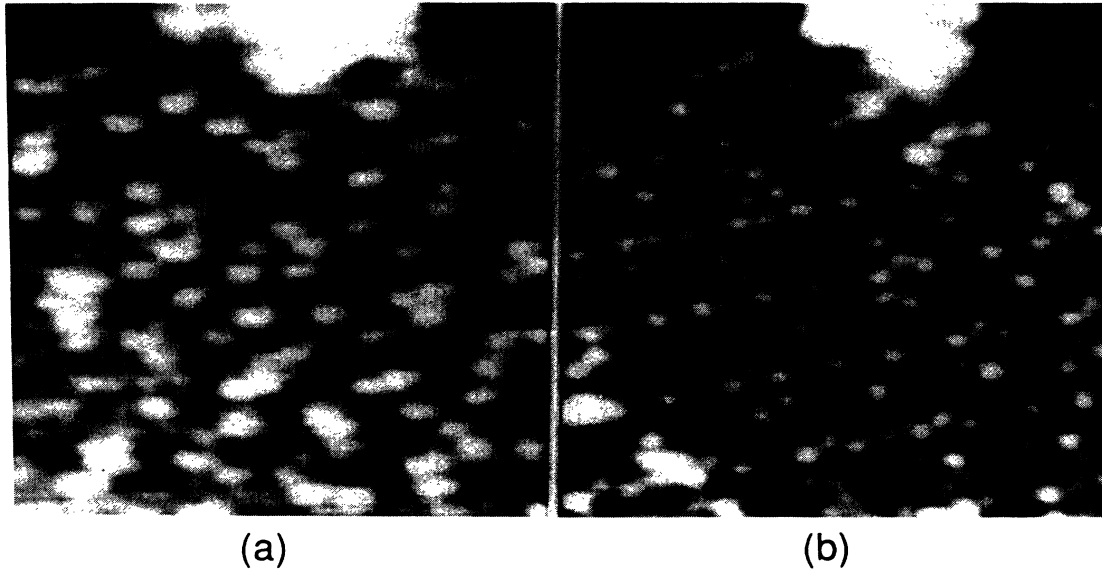


FIG. 2. Dual-polarity image of the Si(111)7 \times 7 surface with low indium coverage. The atoms in (a) appear doubled.

heights of the species will still be different at finite bias where one must allow the densities of states in the appropriate energy window to contribute to tunneling. In this specific case, the Na atom creates a peaked density of states centered above E_F , whereas the S atom has states centered below E_F . Thus, depending on whether one samples states lying above or below E_F , the relative heights of the two species can change and even reverse at opposite bias polarities.

If we view the structure of the tip in the same light, we see that if atoms of different species can contribute simultaneously to tunneling, then the relative contribution from the different tip atoms can change with bias voltage. Consider a tip with two atoms, labeled *A* and *B* (Fig. 3). Suppose we take *A* to be a normal tip atom, i.e., an atom that might have a substantial density of states both above and below E_F , and *B* to be an atom with a much higher

density of states above E_F than below E_F . In this case, the apparent shape of the tip is different depending on the polarity of the bias voltage. A contour of a constant local density of filled states (dashed lines) and empty states (solid lines) within the energy range accessible to tunneling is shown schematically in Fig. 3. If atom *A* is physically slightly closer to the sample than atom *B* [Fig. 3(a)], then at positive tip bias both atoms can contribute to tunneling, whereas at negative tip bias only *A* is close enough to the sample. This might account for the type of behavior shown in Fig. 1. If, on the other hand, *B* is slightly closer to the sample than *A* [Fig. 3(b)], the tip can be doubled at negative but not positive tip bias: this corresponds to the case of Fig. 2.

We can naturally assume atom *A* to be a tungsten atom, which has uniform density of states near E_F . We do not have direct evidence about the identity of atom *B*. However, it is plausible that it is a silicon atom. Since the Si *p* orbital has a higher energy term value than a tungsten *d* orbital, the *p* orbital of chemisorbed Si will be mostly unfilled. This yields a higher density of unoccupied states on Si, which satisfies our assumption of the last paragraph.

In conclusion, we have presented several STM images which contain polarity-dependent double-tip artifacts. The double tip is supposed to consist of a W atom and a foreign atom, perhaps Si. The difference between occupied-state and unoccupied-state images can come not only from the actual surface characteristics but also from a double tip consisting of chemically different atoms.

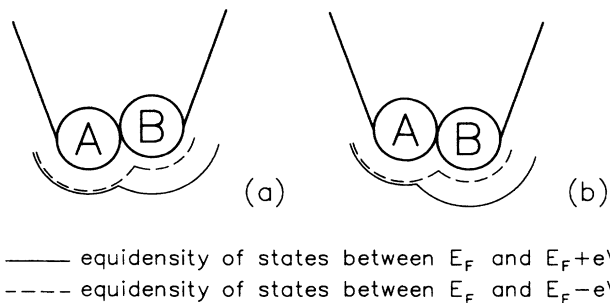


FIG. 3. A model of double tip that can show the polarity-dependent double-tip effect as shown in Figs. 1 and 2.

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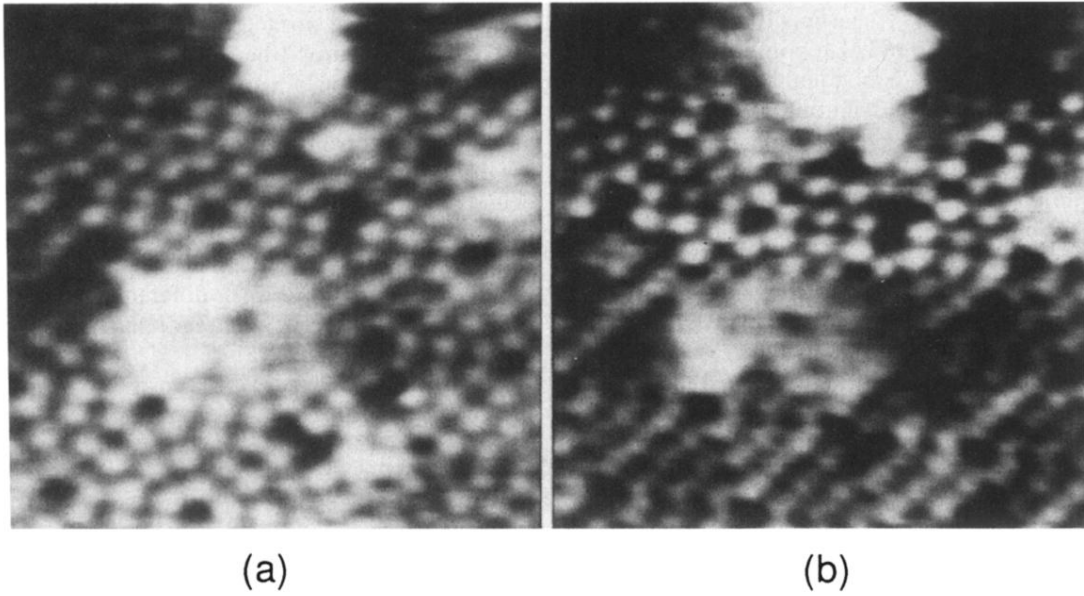


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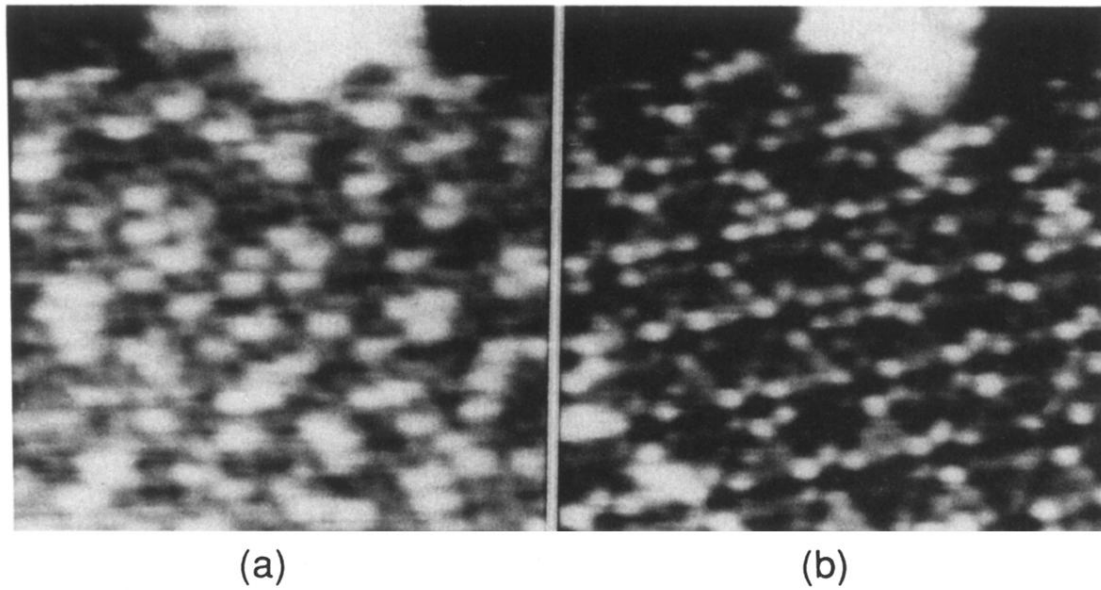


FIG. 2. Dual-polarity image of the Si(111) 7×7 surface with low indium coverage. The atoms in (a) appear doubled.