Chemical identification of individual surface atoms by atomic force microscopy

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Scanning probe microscopy is a versatile and powerful method that uses sharp tips to image, measure, and manipulate matter at surfaces with atomic resolution.1-5. At cryogenic temperatures, scanning probe microscopy can even provide electron tunneling spectra that serve as fingerprints of the vibrational properties of adsorbed molecules6-8 and of the electronic properties of magnetic impurity atoms9, thereby allowing chemical identification. But in many instances, particularly for insulating systems, determining the exact chemical composition of surfaces or nanostructures remains a considerable challenge. In principle, dynamic force microscopy should make it possible to overcome this problem: it can image insulator, semiconductor, and metal surfaces with true atomic resolution9-10,11-13 by detecting and precisely measuring14-16 the short-range forces that arise with the onset of chemical bonding between the tip and surface atoms17-18 and that depend sensitively on the chemical identity of the atoms involved. Here we report precise measurements of such short-range chemical forces, and show that their dependence on the force microscope tip used can be overcome through a normalization procedure. This allows us to use the chemical force measurements as the basis for atomic recognition, even at room temperature. We illustrate the performance of this approach by imaging the surface of a particularly challenging alloy system and successfully identifying the three constituent atomic species silicon, tin, and lead, even though these exhibit very similar chemical properties and identical surface position preferences that render any discrimination attempt based on topographic measurements impossible.

The chemical identification of single atoms and molecules at surfaces has been pursued since the invention of both the scanning tunneling microscope and the atomic force microscope (AFM). Particularly prominent in this quest is dynamic force microscopy, which achieves true atomic imaging resolution19-20 by detecting the short-range forces associated with the onset of the chemical bond between the outermost atom of the tip apex and the surface atoms being imaged21-22 (see Fig. 1 for schematic illustration of the method and imaging examples). Moreover, dynamic force spectroscopy23-24 makes it possible to quantify these forces.

Figure 2a shows five sets of dynamic force spectra measured on a single atomic layer of Sn grown on a Si(111) substrate. Each set of force curves was obtained over an Sn atom and an Si atom having the same local surface configuration as the corresponding atoms highlighted in the topographic image shown in Fig. 1d, always using identical acquisition and analysis protocols (see Methods). However, the sets were collected over multiple measurement sessions, using tips that had different apex terminations. These tips apices presumably differ in both structure and composition (Sn or Si), as sometimes slight tip–surface contacts were intentionally produced before the acquisition of each set of force curves. The sets seem to share only one feature: curves measured over the Si atoms are characterized by a stronger attractive interaction force. Given the high degree of stability, lateral positioning accuracy, and reproducibility provided by our acquisition protocol25-26, we attribute the variability seen in the data in Fig. 2a to a strong tip dependence of both the registered

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Atomic force microscopy

Atomic force microscopy [1] is one of the most versatile and widely used scanning probe techniques, as it provides access to the characterization of processes taking place at insulator, semiconductor or metal surfaces in environments ranging from vacuum to liquid or air conditions. An atomic force microscope (AFM) basically consists in a sharp tip placed at the end of a flexible, microscopic cantilever that bends under the presence of an interaction force between the AFM tip and the probed sample surface when scanning the cantilever over a surface area. AFM is currently used in material characterization and testing at the micro- and nano-scale by imaging surface structures and studying their mechanical properties such as friction, adhesion or hardness. It has also found important applications in biology, since it enables, for instance, to study the mechanical properties of proteins, or directly image and interact with biologic material in a liquid environment.

In this work, we have operated the AFM in dynamic mode, in a technique known as dynamic force microscopy (DFM) [2]. Under this scheme, the tip at the end of the cantilever is oscillated at a given amplitude and frequency, and these two magnitudes do change under the presence of a tip-surface interaction force [3]. In our case, we keep the oscillation amplitude constant and record the variations on the oscillation frequency with changes in the tip-surface interaction force. In the most refined experimental set ups, this technique allows one to detect and quantify the short-range chemical interaction force between two atoms [4, 5]. If the oscillating tip is driven close enough to the surface, so that the apex of the AFM tip gets closer than 5 angstroms during the turning point of the oscillation, the onset of the chemical bonding between the outermost atom of the AFM tip and the individual atoms of the surface takes place. This is, indeed, the mechanism behind the capability of DFM to truly image the atoms at insulator, semiconductor, and metal surfaces.

Measurement of chemical bonding forces toward chemical identification

The chemical identification of single atoms and molecules at surfaces has been pursued from the invention of both the scanning tunnelling microscope (STM) and the AFM, since it could multiply the already outstanding capabilities of these techniques. The intrinsic detection nature of the STM and the AFM has hindered, until now, most of these efforts, and single atom chemical identification still remains a challenge. On this quest for single-atom chemical identification, DFM may have an advantage since the imaging mechanism is based on detecting the short-range forces associated with the onset of the chemical bonding between the outermost atom of the AFM tip and the atoms at the surface.

Forces associated with the chemical bonding between two atoms are related to the nature of the atomic species involved. Thus, the short-range chemical forces we are measuring over the different surface atoms when exploring a heterogeneous surface with DFM should contain information about these surface atoms’ chemical nature. However, to extract this information is not trivial at all since, as we demonstrate in this paper, these short-range chemical forces present a strong variability upon the tip used to probe the surface, that is, for different AFM tip terminations we obtain unlike short-range chemical forces. This variability is illustrated in Fig. 1, where the short-range chemical bonding force between the outermost atom of the AFM tip and two different atomic species at a surface, namely tin (Sn) and silicon (Si), is shown. The typical behaviour of these short-range chemical forces when approaching the tip towards the surface is a curve with an initial reduction of the force values from zero down to a minimum, from which the forces start increasing towards positive values; here, negative forces mean an attractive interaction between the atoms. As it can be seen in Fig. 1, the set of force curves in Fig. 1a is completely different from the set shown in Fig. 1b, even when they were very precise measured over a Sn atom and a Si atom with exactly the same acquisition an analysis protocol [6, 7]. The only difference between the two sets of curves depicted in Fig. 1a and 1b, respectively, is that they were measured using two different AFM tip terminations.

Finding the “atom’s fingerprint”

We have found a magnitude that remains nearly constant independently of the AFM tip termination we used. This magnitude is the relative interaction ratio of the minimum values of the short-range chemical forces measured over two different atomic species probed with the same tip (relative interaction ratio for short in the following). This can be also seen in Fig. 1.
If we take the minimum force value for the curves measured over the Si atoms as 100%, the minimum force value for the curves measured over the Sn atoms will be in both cases close to the 77%. We have corroborated this finding also for other atomic species like lead (Pb) and indium (In). We have measured the short-range chemical forces over Pb and Si (mixing the two atoms over the same surface) using different tips, and then we have quantified the relative interaction ratio for these two species, resulting in a value of 59%. The same procedure, mixing In and Si on a surface, yielded a ratio of 72% for In and Si. In both cases (Pb-Si and In-Si), we found that the values of relative interaction ratio were almost independent of the AFM tip. This property makes it possible to use the relative interaction ratio as a fingerprint for the chemical identification of atoms at surfaces.

**Chemical identification of individual surface atoms**

The identification method we report in this paper consists in measuring the short-range chemical interaction force over each of the atoms in a surface area using the same AFM tip, and then to compare the ratio of the minimum force values between pairs of atomic species with the previously tabulated relative interaction ratio for the expected atoms to be contained at the surface. To demonstrate this method, we have used a surface alloy mixing Si, Sn and Pb in equal proportions, and identified each of the atoms in the imaged surface area (Fig. 2). When looking at the topography of this alloy (Fig. 2a) only one of the three species seems to present a different contrast while the other two cannot be differentiated. After systematically measuring the tip-surface, short-range chemical boning force over each of the atoms, we can see that the minimum force values registered over these atoms can be clearly classified into three groups, as it is shown in the histograms in Fig. 2b. When taking the previously tabulated values of the relative interaction ratio into account (77% for Sn and Si, and 59% for Pb and Si), these groups can be assigned to forces obtained over Sn, Pb, and Si atoms, and therefore each surface atom can be associated with the corresponding chemical element (Fig. 2c).

**Outlook**

As mentioned above, this capability of identifying atoms at surfaces could multiply the already outstanding possibilities that DFM offers. This method might be of relevance in surface chemistry, material science, nanoscience and nanotechnology, and even in semiconductor technology; in particular, when combining this identification method with the ability of DFM for the manipulation of individual atoms at surfaces [8, 9].

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**References**


