## Complex Patterning by Vertical Interchange Atom Manipulation Using Atomic Force Microscopy

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plitude stability of the PSWS experiment. Such studies could help to promote a fundamental understanding of spin-polarized transport in various itinerant ferromagnets, in that spin waves provide both a well-defined inhomogeneous magnetization configuration for performing spin transfer and an accurate probe with which to measure it.


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Materials and Methods

SOM Text

Figs. S1 and S2

References


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# Complex Patterning by Vertical Interchange Atom Manipulation Using Atomic Force Microscopy


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**The ability to incorporate individual atoms in a surface following predetermined arrangements may bring future atom-based technological enterprises closer to reality. Here, we report the assembling of complex atomic patterns at room temperature by the vertical interchange of atoms between the tip apex of an atomic force microscope and a semiconductor surface. At variance with previous methods, these manipulations were produced by exploring the repulsive part of the short-range chemical interaction between the closest tip-surface atoms. By using first-principles calculations, we clarified the basic mechanisms behind the vertical interchange of atoms, characterizing the key atomistic processes involved and estimating the magnitude of the energy barriers between the relevant atomic configurations that leads to these manipulations.**


Scanning tunneling microscopy (STM) has proven to be the method of excellence for creating nanostructures on surfaces, manipulating atoms and molecules one at a time (*1*–*3*). A new panorama has recently been opened by the capability of atomic force microscopy (AFM) to create similar nanostructures atom by atom (*4*) and to quantify the forces involved in these lateral manipulations (*5*, *6*).

When exploring a surface with these scanning probe methods, the apex of the probe can be contaminated with atomic species present at the surface (*7*) by picking up atoms in accidental or intended mechanical contacts with the surface. Advantage could be taken of this situation, and an atomic version of the dip-pen nanolithography (*8*) may be implemented: Atoms wetting the tip apex could be individually deposited to write patterns at heterogeneous surfaces. We provide evidence that such an atomic pen can be implemented by using AFM.

We performed the AFM experiments (*9*) in dynamic mode under the frequency modulation detection scheme (*10*), keeping the cantilever oscillation amplitude constant. Commercial silicon cantilevers, which have very sharp tips at their free ends, were used to image the Sn/Si(111) − $(\sqrt{3} \times \sqrt{3})R30°$ surface (*11*) by detecting the short-range chemical interaction force between the closest tip and surface atoms (*9*).

The inset of Fig. 1A shows topographic images of a single atomic layer of tin (Sn) atoms, which appear as bright protrusions, grown over a silicon (111) single-crystal substrate. Among the atomic defects this surface exhibits (*11*), the most representative ones are substitutional silicon (Si) atoms (*12*) at the perfect Sn atomic layer, and these appear as protrusions with diminished contrast. We have observed that these Si defects can be vertically manipulated during force spectroscopy (*13*, *14*) experiments. After imaging the surface and positioning the AFM tip with a lateral precision better than ±0.1 Å (*15*) over the topmost part of the marked Si atom, we moved the sample toward the oscillating AFM probe. At a given tip-surface distance, an instability in the frequency shift occurs, as highlighted by the arrow in the graph. In an image taken after the sample was retracted, the Si atom was no longer visible, and a Sn atom was found to occupy the corresponding lattice position instead (Fig. 1A, bottom right inset). One hypothesis to explain this event is that the Si atom at the surface has been replaced by a Sn atom originally located at the tip apex, as sketched out by the illustration in Fig. 1A. The same procedure can be consecutively applied to the freshly deposited Sn atom (marked with a circle in Fig. 1B, left inset), resulting in the replacement of this surface atom by a Si atom coming from the tip and in a partial loss of atomic contrast (Fig. 1B, bottom right inset). Because all the images shown in Fig. 1 were acquired under the same experimental parameters,


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The following is a comment on the published paper shown on the preceding page.

# "Atomic Pen" Performed with Force Microscopy

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## Introduction

Scanning probe microscopy (SPM) is a technique for imaging the surface topography and other properties using tapered probe tip. As an excellent application, the method for creating nanostructures on surfaces by manipulating atoms and molecules has been performed using scanning tunneling microscopy (STM) that is one of the SPM families[1]. Recently, using another SPM, atomic force microscopy (AFM), we had performed lateral atom manipulations at room temperature[2-4].

"Atomic Pen" that we disclosed in SCIENCE journal[5] was slightly different from the previous results using SPMs. We have found the phenomenon of "Atomic Pen" when imaging a surface. During the image scan, the AFM tip pick up surface atoms accidentally and vice versa. By controlling the tip-sample displacement with better than pico-meter ($1/10^{12}$ [m]), we were able to control to interchange (pick-up and deposit) atoms (Fig.1).

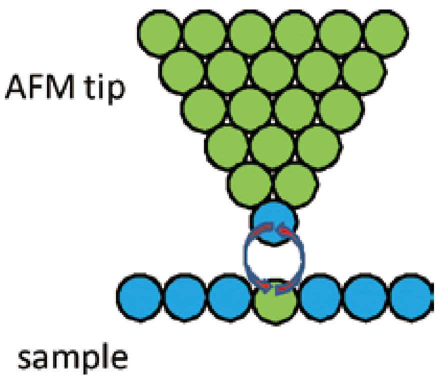


**Fig.1** Model of Atomic Pen in which atom of tip apex and sample surface are inverted vertical at a distance close to the surface.

## Experimental and Theoretical Methods

The experiments were performed in ultrahigh vacuum using an atomic force microscope (AFM) operated at room temperature. We use the frequency modulation detection method, in which the cantilever oscillation amplitude is kept constant. In this operation mode of AFM, the observable is the frequency shift $\Delta f$ of the cantilever resonance due to forces acting on the tip. In order to obtain surface topography, scanning the surface keeping the frequency shift constant was performed. At the same time, we acquired root-mean-square value of the cantilever oscillation amplitude during the scan for detecting non-conservative (dissipative) tip-surface interactions. We used samples produced by evaporation of Sn over a clean Si(111)-(7x7) surface. For force sensor, commercial silicon cantilever was used. Before the experiment, tip apex that had coated silicon-oxide layer was removed using $Ar^+$ sputtering. In order to perform precise tip-sample positioning, we used "atom-traking and feedforward" technique that can keep the relative tip-surface lateral position with a precision better than ±0.1Å. For understanding the experimental results better, we collaborate with theoreticians from Spain who perform the simulations based on density functional theory first-principles calculations implemented with a local orbital basis using the FIREBALL code[7].

To model the experimental tip apex, we considered a rigid tip on which only the two atoms in the dimer defining the apex were allowed to relax upon interaction with the surface.

## How to use the AFM tip as Atomic Pen?

Figure 2 (a) shows an AFM topographic image of a single atomic layer of tin (Sn) atoms, which appear as bright protru-

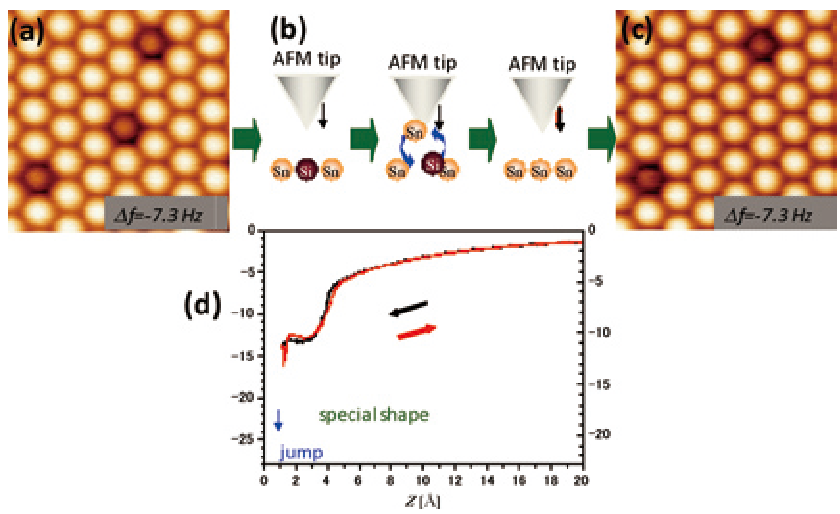


**Fig.2** (a) and (c) AFM topographic image of the Sn/Si(111) surface after and before Atomic Pen, respectively. (b) Procedures Atomic Pen to interchange atoms. (d) frequency shift ($\Delta f$) vs displacement curves during Atomic Pen.

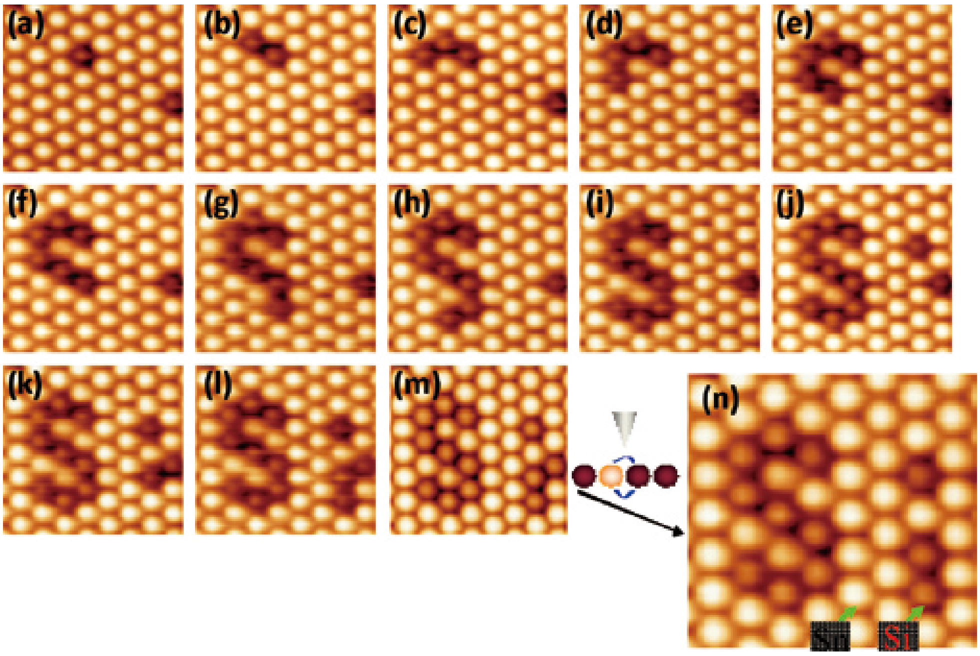


**Fig.3** Atomic patterning with Atomic Pen on Sn/Si(111) surface.

sions. Dim spots in the AFM topographic are atomic defects of silicon (Si) atoms. We have observed that these Si defects can be vertically manipulated by changing the tip-sample displacement. After imaging the surface as in Fig.2(a) and positioning the AFM tip with a lateral precision better than ±0.1 Å over the topmost part of the marked Si atom, we decreased tip-sample displacement with measuring the frequency shift and the cantilever amplitude at the same time (Fig.2 (b)). As indicated by the the arrow in Fig. 2 (d), an instability (jump) in the frequency shift occurs at a given tip-surface distance. In an image taken after the AFM tip was retracted, a Sn atom was found at the corresponding lattice position instead of Si atom as in Fig. 2 (c). This means that Si atom at the surface has been replaced by a Sn atom originally located at the tip apex. The same procedure can be consecutively applied to deposition of Si atom of the tip apex (In this case, image contrast changed.). With the first principle calculation, we have found that this contrast change should correspond to a modification of the tip apex. Atom Pen in which strongly bound atoms between the tip and the surface are interchanged vertically differs from methods previously reported using STM, in which an atom weakly bonded on a metallic surface can be reversibly transferred between the tip and the surface. It is also different from other methods of atom manipulations recently achieved with AFM[2-4] that is used to move atoms laterally.

## Atomic Patterning at room temperature.

Figure 3 shows an example of the creation of complex atomic patterns by successively depositing individual Si atoms coming from the tip. These patterns were constructed by the successive substitution of Sn atoms at the surface one atom at a time with Si atoms coming from the tip. In Figs. 3(a) to (m), series of AFM topographic images showing the creation of atomic patterns displaying the symbol of silicon. These patterns were constructed by the successive deposition of tip Si atoms to substitute  Sn atoms at the surface. Same procedures (Atomic Pen) as in Fig. 2 were performed between image acquisitions to make the atomic pattern. From Figs.2 (m) to (n) to remove the silicon defect atom originally existing at the surface, we did lateral atom interchange manipulation[2].

## Conclusion

The possibility of combining AFM-based vertical (Atomic Pen) and lateral atom manipulations with the capability of AFM for single-atom chemical identification[8] may bring closer the advent of future atomic-level applications, even at room temperature. This manipulation technique may pave the way toward realizing atomic level devices such as selective semiconductor doping, solid-state quantum computing, or atomic-based spintronics.

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