Atom inlays performed at room temperature using atomic force microscopy

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The ability to manipulate single atoms and molecules laterally for creating artificial structures on surfaces¹ is driving us closer to the ultimate limit of two-dimensional nanoengineering^{2.3}. However, experiments involving this level of manipulation have been performed only at cryogenic temperatures. Scanning tunnelling microscopy has proved, so far, to be a unique tool with all the necessary capabilities for laterally pushing, pulling or sliding⁴ single atoms and molecules, and arranging them on a surface at will. Here we demonstrate, for the first time, that it is possible to perform well-controlled lateral manipulations of single atoms using nearcontact atomic force microscopy⁵⁻⁷ even at room temperature. We report the creation of 'atom inlays', that is, artificial atomic patterns formed from a few embedded atoms in the plane of a surface. At room temperature, such atomic structures remain stable on the surface for relatively long periods of time.

Near-contact atomic force microscopy (NC-AFM) is a scanning probe technique based on the measurement of the force between atoms instead of a tunnelling current. This technique has demonstrated its ability to atomically resolve semiconducting⁸⁻¹⁰, metallic¹¹ and purely insulating surfaces¹² to quantitatively determine the interaction forces involved¹³, as well as to perform controlled vertical manipulations of single atoms¹⁴. In spite of these remarkable results, it seems a really challenging task to achieve the gentle force control needed to extend the capabilities of NC-AFM to the lateral manipulation of single atoms, considering the general method for obtaining atomic resolution: a tip placed at the end of a microscopic cantilever is oscillated at the cantilever's first mechanical resonant frequency with a typical amplitude of several nanometres, driving the tip apex at a distance of only few angströms above the surface^{8,15}.

We have used a home-built ultrahigh vacuum (UHV) dynamic atomic force microscope (AFM) working at room temperature. The AFM was operated in the frequency-modulation detection scheme¹⁶ using large cantilever oscillation amplitudes, that is, 'classic' NC-AFM⁷. Low resistivity (0.01–0.025 Ω cm) n-doped commercial silicon cantilevers (NanoWorld, Neuchâtel, Switzerland) were oscillated keeping the oscillation amplitude constant. The dynamics of the cantilever were detected and regulated by using phaselocked-loop-based commercial electronics (easyPLL plus detector



Figure 1 Induced directional diffusion of the Sn adatoms in the Ge(111)c(2×8) surface. a, NC-AFM topographic image showing the typical morphology of the substitutional Sn adatoms in the Ge(111)-c(2×8) surface. Tin adatoms appear brighter than Ge adatoms due to a stronger short-range attractive interaction force with the semiconductor-tip apex. This feature allows discrimination between both atom species, when taking the small amount of Sn atoms deposited on the surface into account. b, Increasing the attractive interaction force by slightly reducing the tip-surface distance produces a reduction in the energy barrier associated with the concerted interchange diffusion of the Sn adatoms with the first neighbouring Ge adatoms. The induced adatom interchange is identified as striped features in the adatoms' shape. The existence of unperturbed adatoms, labelled with dots for clarity, indicates the presence of different local energy barriers for different surrounding adatom configurations, likely to happen in an anisotropic surface such as Ge(111)-c(2×8)^{21,24,25}. Image size is 6.8 × 6.8 nm². NC-AFM acquisition parameters were 269 Å of cantilever oscillation amplitude with a 34.5 N m⁻¹ of measured cantilever spring constant and a free oscillation first-mechanical resonant frequency value of 168.999 kHz, setting frequency shift values of -2.2 Hz in a, and -2.5 Hz in b, respectively.

and controller, Nanosurf, Liestal, Switzerland). Data acquisition, microscope operation, and single-atom lateral manipulation processes were performed through a very versatile commercial scanning probe controller based on digital signal processor technology (Dulcinea, Nanotec electrónica, Madrid, Spain). Before the experiments, the а



Figure 2 Sequence of topographic images illustrating the method for the controlled lateral manipulation of substitutional Sn adatoms in the Ge(111)-c(2×8) surface. a, After imaging the surface at tip-surface interaction forces that do not activate the interchange between Sn and Ge adatoms, the scan size was reduced and the tip fast-scan direction was aligned with the line connecting the centres of the adatoms selected for manipulation, as indicated by the square and the arrow, respectively. b, The surface was imaged until the line connecting the centres of the adatoms (marked with a grey arrow) was reached, and the slow scan was stopped at this position. Successive topographic scans over this line gradually reducing the tip-surface distance lead to the adatom interchange. This process is monitored by a swap in the height signals associated with each adatom type (see the white arrow). These line-scans were performed by lifting the oscillating tip up typically 1 Å above the surface on the way back c, The surface area was imaged again without perturbing the adatoms. Image size is 4.6 × 4.6 nm² for a, and c, and 1.9 × 1.9 nm² for b. NC-AFM acquisition parameters were 176 Å cantilever oscillation amplitude with a cantilever of 34.8 N m⁻¹ spring constant and 169.430 kHz free oscillation first-mechanical resonant frequency, setting constant frequency shift values of -8.3 Hz for a and c, and a maximum applied frequency shift for inducing the adatom interchange of -11.3 Hz in b, respectively.

cantilever Si tip apex and the Ge(111) surface were prepared in UHV conditions. Clean reconstructed Ge(111)-c(2×8) surfaces were produced from n-type samples with resistivity less than 0.4Ω cm by successive cycles of Ar sputtering while heating the sample. Details of the tip and sample preparation can be found in the Supplementary Information accompanying this contribution. In the experiments presented in this work, both the cantilever and the sample were always electrically grounded.

Substitutional Sn adatoms in the plane of the $Ge(111)-c(2\times 8)$ surface have been chosen for the lateral manipulation of single atoms at room temperature. The bare $Ge(111)-c(2\times 8)$ semiconductor surface^{17,18} presents a relatively weak bonding of the Ge adatoms to the substrate¹⁹ comparing with, for example, Si(111)-(7×7) (ref. 20). The $Sn/Ge(111)-c(2\times 8)$ surface behaves quite similarly to the already studied isovalent Pb/Ge(111)-c(2×8) system^{21,22}. After the deposition of a few hundredths of a monolayer of Pb on the $Ge(111)-c(2\times 8)$ surface and a gentle annealing to temperatures less than 400 K, Pb atoms sparsely occupy adatom sites of the $c(2\times 8)$ reconstruction in a T₄ bonding configuration^{22,23}. These substitutional Pb adatoms can independently diffuse near room temperature within the plane of the $Ge(111)-c(2\times 8)$ surface with a measured activation energy of 0.54 eV (ref. 21). The proposed mechanism associated with this diffusion process is a concerted interchange of the positions occupied by the Pb and the Ge adatoms²¹. Substitutional Sn adatoms in the Ge(111)-c(2×8) surface can be produced by following the same experimental procedure as in the Pb/Ge(111)-c(2×8) case. When exploring this surface using NC-AFM in topographic mode, the Sn adatoms appear slightly brighter than the Ge adatoms (Fig. 1a). This fact indicates a stronger attractive interaction force with the AFM tip when probing the Sn adatoms. The origin of this interaction force is the onset of a covalent bond formation between the outermost atom of the tip and the atoms at the surface, as it is expected for the NC-AFM imaging mechanism on a semiconductor surface^{13,15}.

The Sn adatoms, however, seem to present a higher diffusion energy barrier than the Pb adatoms. The tracking of the same surface area for several hours scanning at a weak enough tip-surface attractive interaction force (see the Supplementary Information) provides an upper limit for the Sn diffusion rate of 5.7×10^{-7} jumps per second per atom at room temperature, which is several orders of magnitude lower than the measured value for the Pb/Ge(111)-c(2×8) system²¹. The precise experimental determination of the diffusion energy barriers requires measurement of the adatom diffusion rate at several different temperatures—in this case above room temperature—in order to complete the corresponding Arrhenius plot²¹; however, an estimation of 1.1 eV for the expected minimum energy barrier value can be obtained from the upper limit for the Sn diffusion rate at room temperature. This value is approximately twice the measured energy barrier reported for the Pb/Ge(111)-c(2×8) system, and it suggests the formation of stronger bonds with the underlying Ge atoms in the case of the Sn adatoms.

In spite of the low interchange rate between Sn and Ge adatoms at room temperature, it is possible to induce directional diffusion of the Sn adatoms to first neighbouring adatom positions by scanning at a stronger attractive interaction force (Fig. 1b). These induced diffusion processes are produced by the concerted interchange between the Sn adatoms and the Ge adatoms in the plane of the $Ge(111)-c(2\times 8)$ surface. The timescale at which this interchange occurs is much shorter than the maximum image acquisition speed allowed for our system. This fact prevents us from distinguishing- at room temperaturepossible complex intermediate metastable position of both adatoms^{23,24} during the interchange (Fig. 1b). These experimental results indicate that increasing the tip-surface attractive interaction force over a threshold value produces a reduction in the energy barrier for the concerted interchange between Sn and Ge adatoms. Assuming that the timescale associated with the adatom interchange has an upper limit defined by the time in which the tip is over the adatoms involved, a minimum reduction of a 30% in the energy barrier value is expected considering an image acquisition fast scan frequency of 1 Hz.

The induced interchange between Sn and Ge adatoms can be controlled by an appropriate selection of the tip-scan direction, and

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Figure 3 Final topographic NC-AFM image of the process of rearranging single atoms for the construction, at room temperature, of 'an atom inlay'. Image size is 7.7×7.7 nm². The image was acquired with a cantilever oscillation amplitude of 157 Å, using a Si cantilever of 29.5 N m⁻¹ measured spring constant, setting a frequency shift value of -4.6 Hz with respect to a free oscillation first-mechanical resonant frequency of 160.450 kHz.

by tuning the tip-surface attractive interaction force. The method we have followed for manipulating a substitutional Sn adatom on the Ge(111)-c(2×8) surface consists of a few basic steps. The first requirement is to align the fast tip-scan direction with the vector that connects the centres of the selected Sn adatom and the first neighbouring Ge adatom chosen as a final destination (Fig. 2a). The fast scan is set for starting from the Sn adatom towards the Ge adatom (Fig. 2a), and the tip is lifted up typically 1 Å above the surface on the way back. The slow tip-scan is stopped when the line connecting the centres of the two adatoms is reached. Gradual reductions of the tip-surface distance in successive topographic line-scans over this line lead to gradual increments of the attractive interaction force acting between the outermost atoms of the tip apex and the atoms at the surface. At a certain closest approach distance, the interaction force overcomes the threshold value needed for activating the interchange between Sn and Ge adatoms during the line-scan, making the Sn adatom follow the tip (Fig. 2b). The fact that the manipulation has taken place can be identified by checking the height signals associated with each adatom type in subsequent line-scans; the height signals change in location after the adatom interchange (Fig. 2b). Finally, reducing the tip-surface interaction force to values at which the adatoms remain unperturbed at their adsorption positions, the surface is imaged again (Fig. 2c). This process can be inverted by simply reversing the fast scan direction and repeating the above mentioned procedure; the Sn adatom will interchange again with the Ge adatom recovering its initial position.

This new lateral manipulation method is well controlled, and it has been used for creating artificial nanostructures formed from a few in-plane embedded atoms at the surface (Fig. 3). A movie displaying a selection of sequential images acquired during the process of laterally rearranging substitutional Sn adatoms at room temperature for composing the letters of the symbol associated with the Sn element (Fig. 3) is shown in the Supplementary Information. The creation of these nanostructures has required more than 120 single-atom lateral manipulation events performed within almost nine hours of continuous microscope operation. Taking into





Figure 4 Topographic NC-AFM images showing the lateral manipulation of a substitutional Sn adatom farther than its first neighbouring adatom positions. a, Initial atomic configuration. b, Immediately after the lateral manipulation of the Sn adatom (labelled with an arrow) performed following the method described in the text. The Sn adatom has experienced a total displacement of two first neighbour adatom positions in the [1T0] crystallographic direction of the Ge(111)-c(2×8) surface. Image size is 4.0×4.0 nm². NC-AFM images were acquired at a frequency shift value of -4.7 Hz from a free oscillation first-mechanical cantilever resonant frequency of 160.450 kHz, using a cantilever oscillation amplitude of 157 Å. The measured cantilever spring constant was 29.5 N m⁻¹.

account the experimentally estimated minimum mean lifetime of an unperturbed substitutional Sn adatom placed in a well reconstructed area of the Ge(111)-c(2×8) surface $(1.75 \times 10^6 \text{ s})$, in principle, artificial nanostructures formed in this way could remain stable on the surface at room temperature for relatively long periods of time, decreasing the probability of having a longer mean lifetime when increasing the amount of adatoms composing the nanostructure. For the nanostructures reported here, a minimum mean lifetime of 25 hours is estimated.

Lateral manipulations involving more than one adatom position displacement have been achieved along the $[1\overline{10}]$ direction (that is, parallel to the Ge adatom rows of the Ge(111)-c(2×8) surface), as well as in (2×2) patches that on occasions decorate this surface. These manipulations can be performed following the abovementioned procedure, but setting longer line-scans. To accomplish lateral manipulations only to first neighbours in directions out of the [110] crystallographic direction is a consequence of the already stated inherent anisotropy that the Ge(111)-c(2×8) surface presents for the diffusion of adatoms within the surface plane^{21,24,25}.

The induced interchange between adatoms is strongly determined by the tip-scan direction. When the fast tip-scan is properly aligned with the line connecting the centres of the two adatoms, almost no interchange events with other neighbouring Ge adatoms out of this line have been detected. This observation indicates that the reduction in the energy barrier for the interchange process by the potential well generated due to the presence of the semiconductor tip is very localized. Additionally, the tip-surface interaction force threshold value needed for inducing the interchange seems to depend on the tip apex atomic configuration. For the same cantilever and the same oscillation amplitude, the frequency shift set-point value required for the accomplishment of an interchange between adatoms could change between two structurally equivalent manipulation events if a slight tip change has occurred between both processes. The very localized reduction of the diffusion energy barrier, and the change in the interaction force threshold value when changing the outermost atomic configuration of the tip, are in good agreement with theoretical predictions²⁶ about the conditions required for laterally manipulating a single atom on a semiconductor surface using a Si tip in both constant-height and constant-force scans.

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The experiments described here show, for the first time, the capability of the NC-AFM technique for laterally manipulating single atoms at surfaces using the short-range interaction force between a semiconductor tip and a surface. Under the appropriate conditions, lateral manipulation using NC-AFM allows the creation of artificial structures formed atom by atom even at room temperature. The work presented here paves the way for creating artificial nanostructures at surfaces that may be used as templates for the implementation of nanoscale devices.

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Supplementary information

Video Custance-1: Low diffusion rate of substitutional Sn adatoms in the Ge(111)-c(2x8) surface at room temperature.

This movie is composed of twelve topographic near contact atomic force microscopy (NC-AFM) images acquired over the same surface area scanning at a weak tip-surface interaction force and at room temperature. During the relatively long period of time (more than five hours) of continuous surface observation, no single concerted interchange event between Sn and Ge adatoms in the Ge(111)-c(2x8) surface has been observed. Thus, this movie indicates the low diffusion rate of substitutional Sn adatoms in the Ge(111)-c(2x8) surface at room temperature. Imaged area dimensions are 15.9x15.9 nm². The images were acquired at a constant frequency shift value of -3.0 Hz using a cantilever oscillation amplitude of 218 Å with a Si cantilever of 172.468 kHz free oscillation first mechanical frequency and a measured spring constant of 34.2 N/m. The timing between the images of the movie is almost equally spaced embracing a total observation time of 19440 sec. Thermal drift was compensated during the data acquisition using the WSxM free software (http://www.nanotec.es/) associated with the scanning probe microscope controller.

Video Custance-2: Artificial creation process of an "atom inlay" at room temperature using near-contact atomic force microscopy.

This movie shows the creation, at room temperature, of the first artificial "atom inlay" on a semiconductor surface using NC-AFM. Tin adatoms embedded in the plane of a well-reconstructed Ge(111)-c(2x8) surface are rearranged following the lateral manipulation method described in the text for creating the letters "Sn" of the symbol associated with the Tin element. The movie is composed of a selection of NC-AFM topographic images acquired in between more than 120 single atom lateral manipulation events performed within near 9 hours of continuous microscope operation. Details about the experimental acquisition parameters are available in the text.

Cantilever tip apex and surface preparation procedure:

The cantilever Si tip apex was carefully cleaned up by argon-ion bombardment for 45 min. with a beam energy of 0.6 keV and a measured ion current of 0.2 μ A. The ion beam was focused directly on the cantilever tip position with normal incidence. Clean reconstructed Ge(111)-c(2x8) surfaces were prepared by successive cycles of argon-ion sputtering while heating the sample at 770 K. Typical ion bombardment parameters were 1 keV of ion beam energy, with an ion current measured at the sample of approximately 4 μ A, and 45° of incidence angle. After the ion bombardment, when recovering a vacuum pressure of 1x10⁻¹⁰ Torr, a further sample annealing at 1020 K during 3 min. followed by a slow cool down to room temperature completed the surface preparation.