Atom-By-Atom Extraction Using the Scanning Tunneling Microscope Tip-Cluster Interaction

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We investigate the atomistic details of a single atom-extraction process realized by using the scanning tunneling microscope tip-cluster interaction on a Ag(111) surface at 6 K. Single atoms are extracted from a silver cluster one atom at a time using small tunneling biases less than 35 mV. Combined total energy calculations and molecular dynamics simulations show a lowering of the atom-extraction barrier upon approaching the tip to the cluster. Thus, a mere tuning of the proximity between the tip and the cluster governs the extraction process. The atomic precision and reproducibility of this procedure are demonstrated by repeatedly extracting single atoms from a silver cluster on an atom-by-atom basis.

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The interaction between a scanning probe tip and an adsorbate continues to unveil diverse phenomena in surface physics. In recent years, the single atom-molecule manipulation has been a major advance in scanning tunneling microscope (STM) applications [1–18]. The main appeal of STM manipulation is the ability to access, control, and modify the interactions between the tip and the adsorbate, a few angstroms apart [2–6,9]. A STM manipulation procedure known as lateral manipulation (LM) [2,9] utilizes the tip-atom interactions to precisely position atoms on surfaces, enabling construction of nanostructures on an atom-by-atom basis [1,3,4,6,7]. The STM tip-height or current signals during LM provide atomistic dynamics, revealing the intrinsic details of the tip-atom interactions [2,6,17,18]. To date, atom manipulation using a STM or an AFM tip [19] has been restricted to flat surfaces. In this Letter, we report extraction and manipulation of individual atoms on three-dimensional nanoclusters. The atomistic details of the mechanism are explained by means of statistical analyses and theoretical modeling, which reveals that just by locating the STM tip in proximity of the nanocluster greatly reduces the extraction barrier of the topmost cluster atom.

The experiment was performed using a homebuilt ultrahigh-vacuum low-temperature STM operated at 6 K [20]. The Ag(111) sample was cleaned by repeated sputter-anneal cycles. An electrochemically etched polycrystalline tungsten wire was used as the STM tip. The tip was prepared by dipping into the substrate [3], which reshapes the tip apex and makes it atomically sharp. Moreover, the tip gets coated with the substrate material, and, thus, the chemical identity of the tip apex is known [3].

For the experiment, a large terrace on the Ag(111) surface is first selected. A silver cluster is then deposited on the surface by making a controlled tip-sample contact (Fig. 1). The irregularities in the cluster, seen as protrusions in three-dimensional images, are chosen to be the ideal target zones to extract the atoms with ease [Fig. 1(a)]. For the atom extraction, the tip is initially positioned near a protrusion of the cluster, and the tip height is then reduced. An increased tip-cluster interaction is thus achieved. The tip is laterally moved from one side of the cluster towards the terrace for a short distance in constant current mode [Fig. 1(a)]. The subsequent STM image after the manipulation confirms the successful atom extraction [Fig. 1(b)].

The dynamics of this atom extraction can be inferred from the STM manipulation signals, which show a peak at the topmost cluster location caused by sudden changes of vertical tip position [Fig. 1(c)]. Hundreds of repeated experiments confirm that such peaks can be associated with a successful atom extraction. There are two types of peaks: The first type shows an upward curve followed by a sharp drop and is commonly observed at the initial atom extraction [Figs. 1(c) and 1(d)]. Here the tip initially climbs up the contour of the protruding part, producing a curvelike increase in tip height. When the topmost cluster atom is moved away from its position, the tip height drops suddenly because of the constant current mode. Since the extracted atom is a constituent of the cluster, removing it from the original position involves severing the bonds with neighboring atoms. The atom occasionally readsorbs at a next favorable site at the downward slope of the cluster. Several subsequent atom removals occur along the lateral tip movement, producing more peaks in the manipulation signal. If the atom is loosely bound at the next site, it can easily move back under the tip, causing an abrupt increase in tip height followed by the downward slope of the tip along the atomic contour [second type of peak, Fig. 1(d)]. At the flat terrace, the tip height suddenly increases due to the positioning of the atom under the tip followed by a smooth manipulation curve (sliding mode [2,17,18,20]). Here the atom is trapped under the tip while still remaining on the surface, and the tip and the atom move together smoothly across the surface [2,17,18,20]. This behavior is consistently observed throughout the atom extraction [21]. In order to demonstrate the reliability of the procedure, we

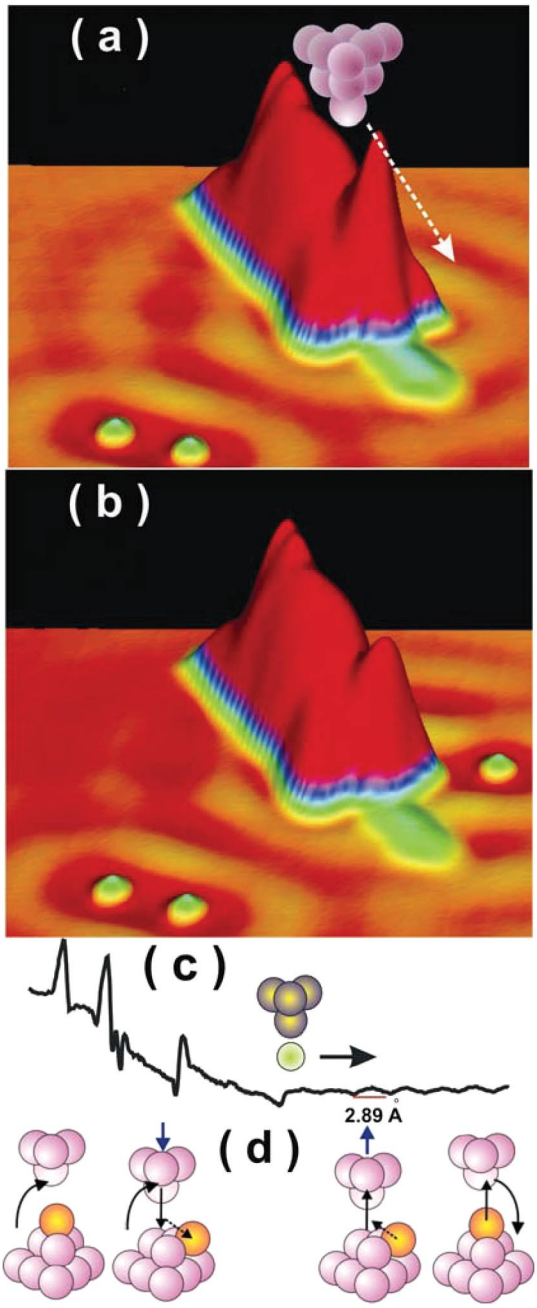

FIG. 1 (color). Atom extraction. (a) A 3D STM image of a silver nanocluster deposited by tip-surface contact. The tip is brought close to the protruded part of the cluster and then moved laterally towards a destination on the surface. (b) The STM image acquired after this shows a height reduction of the cluster protrusion and the extracted atom on the surface destination. (c) The manipulation signal of this event reveals the atomistic details of the atom extraction. (d) The drawings demonstrating the two types of tip-height peaks.

present a series of snapshot images from an STM movie (Fig. 2) (see Ref. [21]) showing repeated atom-by-atom extraction from a silver cluster.

The environment that the extracted atom faces during this atom-extraction process is different from the atom

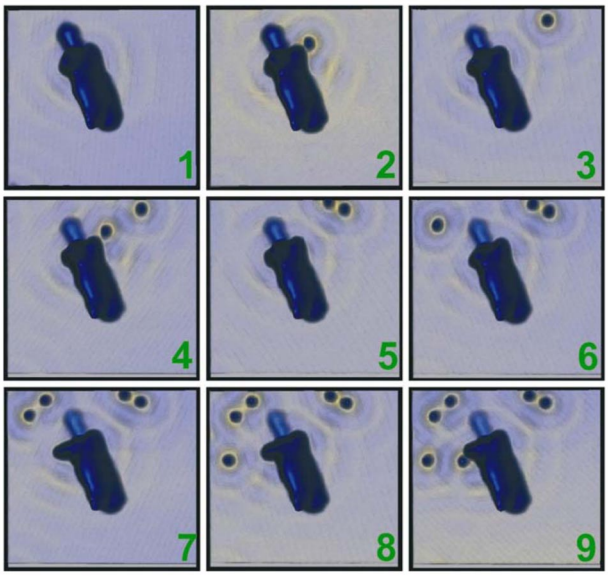

FIG. 2 (color online). Atom-by-atom extraction sequence. A sequence of STM images from an STM movie [21] shows atom-by-atom extraction from a silver cluster. This series proves the reliability of our atom-extraction process.

manipulation on a flat surface. In particular, it involves removing the topmost cluster atom and then moving it along a rough terrain on a three-dimensional cluster surface. To investigate the underlying process in detail, we first determine the threshold tunneling resistance (R_{th}) necessary for the atom extraction. The atom-extraction probability is defined as the ratio between the atom's travel distance (L_{atom}) and the lateral tip movement distance (L_{tip}). The $L_{\mathrm{atom}}/L_{\mathrm{tip}}$ values are determined by varying the tunneling current at different biases. A plot of $L_{\mathrm{atom}}/L_{\mathrm{tip}}$ as a function of the tunneling current measured at 18 mV bias is presented in Fig. 3(a). Tunneling resistance is a measure of both the tip-cluster distance and the interaction strength. For example, lowering the tunneling resistance causes a reduced tip-cluster distance (increased tip-cluster interaction). The $L_{\mathrm{atom}}/L_{\mathrm{tip}}$ is initially zero below 400 nA, and thus no atom has been extracted. The $L_{\mathrm{atom}}/L_{\mathrm{tip}}$ is ~ 1 above 400 nA, implying that the atom can be successfully extracted [Fig. 3(a)]. In a few cases, $L_{\mathrm{atom}}/L_{\mathrm{tip}}$ remains zero even at higher currents, indicating that not all extractions are successful ($\sim 85\%$ success rate). The plot in Fig. 3(a) shows a step-function characteristic with a current threshold of 400 nA. Next, we repeat the procedure by changing biases, and the results are displayed as a threshold current vs bias plot in Fig. 3(b), where each data point is determined by plotting the curves as shown in Fig. 3(a). $R_{\mathrm{th}} = 47 \pm 2$ kΩ is measured from the slope of the curve, which can be related to the threshold tip-cluster distance for atom extraction via a tip-height vs tunneling resistance curve [Fig. 3(c)] [22]. We find that the threshold tip-cluster distance corresponds to $R_{\mathrm{th}} = 47 \pm 2$ kΩ as 0.6 Å [Fig. 3(c)]. Thus, a ≤ 0.6 Å distance be-

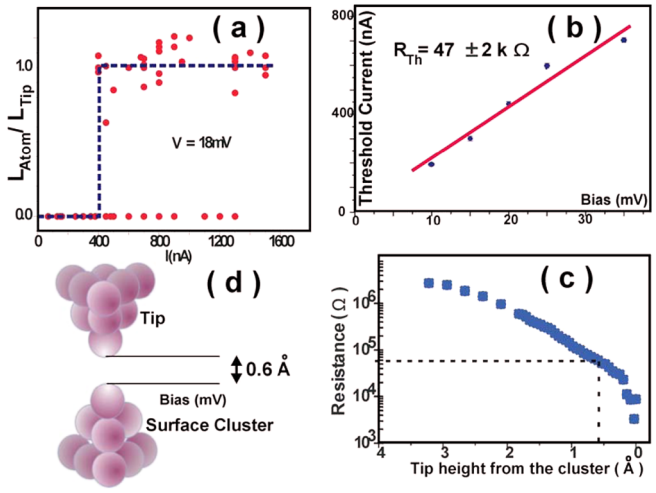

FIG. 3 (color online). Threshold resistance and tip height. (a) L_{atom}/L_{tip} versus tunneling current at a fixed bias of 18 mV shows a characteristic step function at 400 nA. (b) The threshold tunneling current versus bias plot shows a linear relationship. R_{th} is determined from the slope of this curve. (c) The tip-cluster distance of 0.6 Å corresponding to $R_{th} = 47 \pm 2$ kΩ is obtained (shown with a dashed line) from the tunneling resistance versus tip-height plot. (d) A model demonstrates the tip-cluster distance of 0.6 Å to extract the topmost cluster atom.

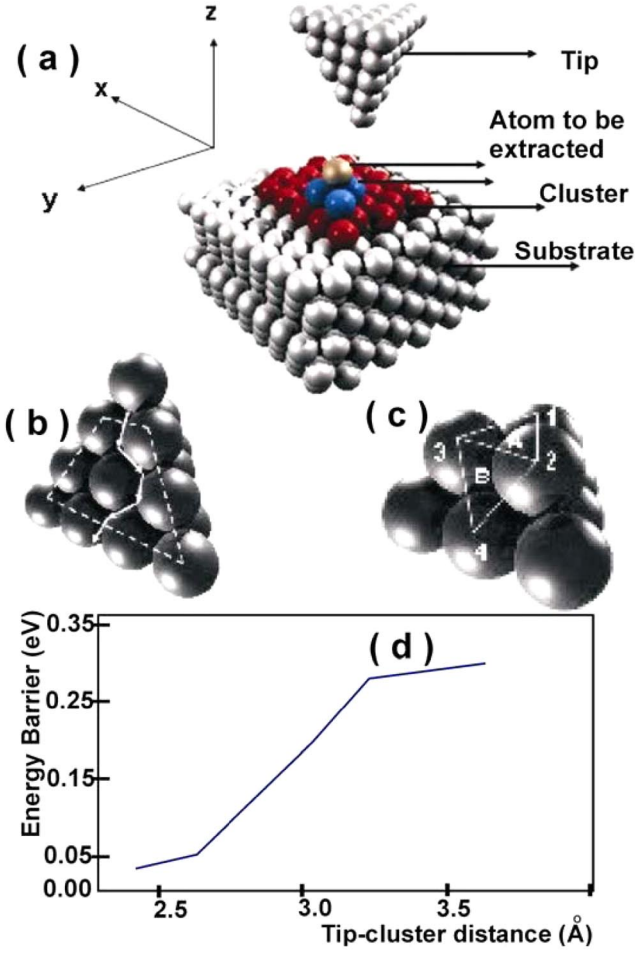

FIG. 4 (color online). Theoretical modeling. (a) The geometry of the tip, adatom, cluster, and silver substrate used for the calculation. (b) The minimum energy diffusion path of the atom after extraction. (c) Transfer of the atom from *A* to *B* and from *B* to *A* will cost the same energy. (d) The energy barrier for atom extraction vs the tip-cluster distance plot.

tween the van der Waals edges of the tip-apex atom and the cluster atom is necessary for the extraction [Fig. 3(d)]. For the manipulation of silver atoms on a flat Ag(111) terrace, $R_{th} = 210 \pm 19$ kΩ (1.3 ± 0.2 Å tip-atom distance) is required [6].

If local heating or electron-induced excitation are involved in the process, the curve in Fig. 3(b) would deviate from linearity [14]. The observed linearity indicates that the influence of such effects is not significant. Furthermore, since very low voltages (<35 mV) are used, the electric field contribution is negligible [3,14]. Therefore, the tip-cluster interaction should be the central element in this case. Here the threshold resistance is a well-defined and reproducible quantity for the atom extraction as in the case of atom manipulation [6].

To obtain a qualitative picture of the process, a combined theoretical investigation using molecular dynamics and molecular static simulations with interaction potentials obtained from the embedded atom method [15,16] has been performed. The prototype system used for the calculations consists of a 35-atom silver tip and a 28-atom silver cluster [Fig. 4(a)] on the 6-atomic-layer Ag(111) substrate having 80 atoms in each layer. Initially, the entire system is allowed to relax to its minimum energy configuration using the conjugate gradient method. Since only small biases are used in the experiment, the electric field effect is not considered. The molecular static calculations provide the potential energy landscape, while the molecular dynamics simulations reveal the atom's path during the extraction.

The energy required to extract the atom is the energy barrier to move the atom from its original location *A* to the next site *B* [Figs. 4(b) and 4(c)]. In the absence of the tip, the energy barrier for a silver atom to diffuse over the Ag(111) step edge is 300 meV, which is higher than the 100 meV barrier for atom diffusion on a flat terrace. The calculation reveals that the tip height has a dramatic effect on the potential energy landscape of the topmost cluster atom. By lowering the tip height, the atom-extraction energy barrier is greatly reduced [Fig. 4(d)]. Thus, we conclude that the location of the tip in close proximity of the cluster is sufficient to extract the topmost atom by overcoming the binding of the atoms within the cluster [23].

In summary, we have demonstrated a reproducible atom-by-atom extraction process using tip-cluster interaction. The required tip-cluster distance (0.6 Å) for atom extraction is also experimentally determined. Theoretical calculations reveal that the location of the tip near a cluster can

effectively reduce the atom-extraction barrier and that the tip-cluster interaction alone is sufficient to knock out an atom from the cluster. This work not only provides a fundamental understanding of the influence of distance-dependent tip-cluster interaction but also opens a novel route to produce single atoms for future nanoscale experiments or for atomistic constructions.

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[21] See EPAPS document No. E-PRLTAO-97-001651 for the STM movie. A direct link to this document may be found in the online article's HTML reference section. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
[22] In Fig. 3(c), an abrupt decrease in tunneling resistance occurs at the tip-cluster contact point. The *I-V* spectroscopy measured at this point shows an Ohmic relationship [14].
[23] The calculated values describe a qualitative measure only and not for a quantitative comparison with the experiment. We use (111) geometry for both the top and the side of the cluster. The barriers for the atom to jump over or jump back, depending on the geometry of these facets, since the number of bonds binding the atom will change according to the geometry.