Fabricating artificial nanowells with tunable size and shape by using scanning tunneling microscopy

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The authors report a method of precisely fabricating the large-scale nanocrystals with well-defined shape and size. The (111) oriented Pb islands deposited on Si(111)-7×7 substrate were investigated with a manipulation technique based on scanning tunneling microscopy. By applying a series of voltage pulses on the as-grown islands, artificial center-full-hollowed or half-hollowed nanowells are created, and the thickness and shape can be precisely regulated via tuning the manipulation parameters. Artificial nanoarray patterns in micron scale are also constructed using this method.
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Constructing well-organized artificial nanostructures is of great importance not only in the understanding of physical and chemical properties at nanometer scale but also in nanodevice technology. Two commonly used approaches for fabricating nanostructures are the so-called "top-down" and "bottom-up" techniques.[1] The top-down techniques, including electron-beam lithography (EBL),[2,3] advanced lithography,[4] microcontact printing,[5] etc., are sophisticated on creating predesired surface features, but usually limited in resolution below 100 nm because of the nature of the processes. On the other hand, the bottom-up techniques have been developed to direct assembled atoms or molecules into the ordered patterns at nanometer scale.[6] The feature size of the nanostructures obtained through the bottom-up techniques can reach a scale less than ~10 nm. However, the geometric shape is mainly determined by either growth kinetic pathway, energetics, or their competition, as well as the properties of the substrates served as the template, and hence the bottom-up techniques are less controllable compared with the top-down techniques. One solution is to take a hybrid approach by combining the top-down lithographic patterning technique with the bottom-up self-assembly process. For example, the molecular ruler method has scaled down the nanostructure size on an EBL pattern to ~30 nm with high precision,[7] and the strain engineered self-assembly on patterned mesas has created well-aligned uniform quantum dots.[8]

Scanning tunneling microscopy (STM) has been applied to move and position single atoms/molecules since the early 1990s.[9–13] Recently, we have applied STM manipulation to precisely control the thickness of the nanostructures with single atomic layer precision.[14,15] In this letter, we present studies to extend our STM based nanofabrication of metallic structures to some further fronts. By applying a series of appropriate voltage pulses to the STM tip, rather than the single voltage pulse as used before,[14,15] we achieved to control the lateral shape as well as the exact location of the targeted Pb island grown on Si(111)-7×7 substrate through regulating the pulse parameters. The resulted nanostructures have interesting shapes and selected locations with atomic layer precision, implying the potential in the research and application of size- and shape-sensitive properties at nanometer scale.

The Pb islands were grown in an ultrahigh vacuum (base pressure of 2×10^{-10} Torr) molecular beam epitaxy (MBE) chamber. The high purity Pb (99.999%) was thermally evaporated from a homemade tungsten cell and deposited onto the Si(111)-7×7 substrate. The growth rate was controlled at ~0.5 ML/min. The clean Si(111)-7×7 substrate was prepared by cycles of flash annealing at 1000 °C followed by fast cooling down. The Si(111) substrate was cooled down to ~150 K by liquid nitrogen during the deposition, and then slowly warmed up to room temperature. The topography measurement was *in situ* performed at room temperature with an Omicron variable temperature scanning tunneling microscope connected to the MBE growth chamber. The detailed description of the instrument has been reported elsewhere.[16] For the STM imaging, the constant current mode was adopted with a typical tunneling current of ~0.02 nA and a bias voltage of ~1.0 V. The manipulation voltage pulse was applied from the STM tip.

Figure 1(a) shows a Pb island grown by depositing ~3 ML Pb at 150 K followed by slowly warming up to room temperature. The height of the island is 3.1–4.9 nm increasing from the upper left to the lower right. It has been reported previously that if charge is injected into the Pb island, the chemical potential of the Pb island is drastically dropped due to the so-called "Coulomb-sink" effect[15] and thus the Pb island is triggered to regrow accompanied by the mass transport between the charged island and the surrounding neutral ones. The charge injection can be easily performed through the bias voltage pulse applied to the STM tip. The Pb island growth, as also reported previously, can be controlled as precisely as atomic layer in the vertical direction to the surface, if a STM bias voltage pulse is applied near the Pb island edge.[14] Below, we elucidate that the Pb island growth can be easily controlled by tuning the STM pulse parameters, e.g., the amplitude or the time constant, and the Pb island is also possible to transform into some interesting shapes if a series

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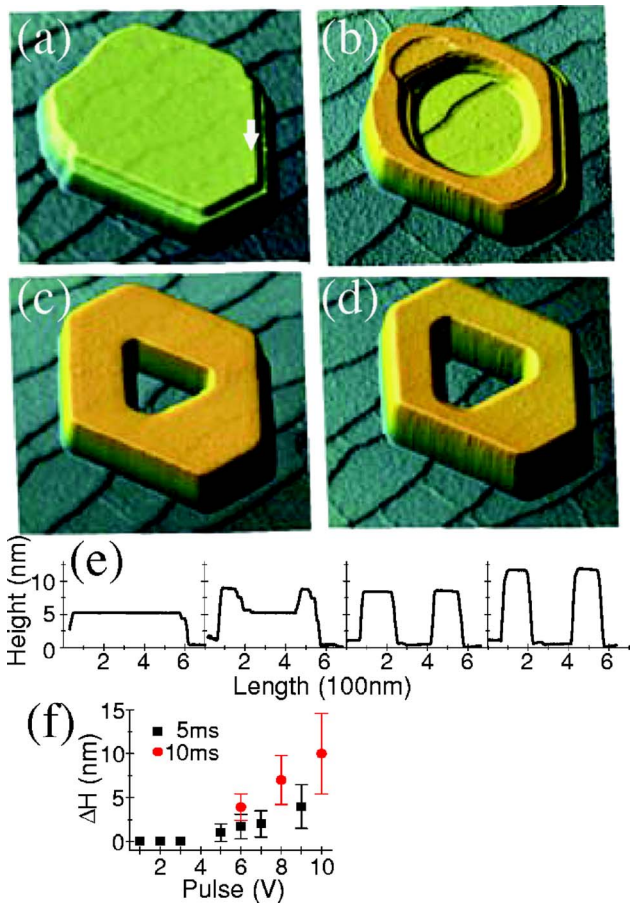

FIG. 1. (Color online) [(a)–(d)] Series of STM images (720×720 nm^2) showing the nanostructures fabricated by STM manipulation. The Pb coverage is ~3 ML. The images were recorded at a tunneling current (I_t) of 0.02 nA and a tip bias voltage (U) of 1.0 V. (a) Original Pb island before STM manipulation. (b) The center-half-hollowed nanowell formed by charging at the Pb island edge. (c) Center-full-hollowed nanowell formed by charging at the bottom of the well in (b). (d) Center-full-hollowed nanostructure with the different ratios of inner/outer diameter and thickness from the one shown in (c). (e) The cross-section profiles along the horizontal center lines in (a)–(d), respectively. (f) Dependence of the triggered growth height on the pulse amplitude.

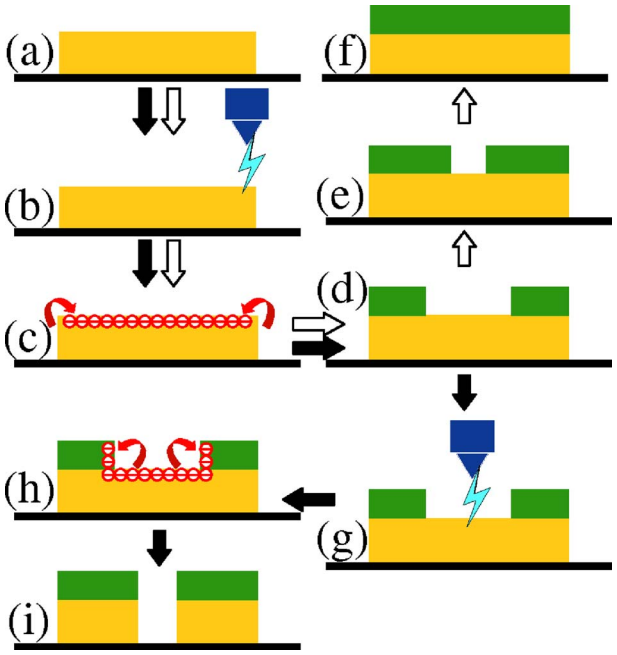

FIG. 2. (Color online) Schematic drawing of the STM manipulation process. The white arrows [(a)–(f)] show the process of fabricating flattop Pb island with different thicknesses. The black arrows [(a)–(i)] show the fabrication of hollow-centered nanostructures with different inner diameters and thicknesses.

of STM voltage pulses is applied at different sites on the top of the Pb island.

By applying a STM voltage pulse of ~10 V at the island edge [indicated by a white arrow in Fig. 1(a)] for 10 ms during scanning, the island was triggered to grow with 12 atomic layers around the edge simultaneously, and a stable center-half-hollowed nanowell is formed [Fig. 1(b)]. The outer side of the nanowell is nearly the same as that of the original island. The height of the bottom of the nanowell is the same as the original flattop island, and the thickness of the wall is 3.58 nm (~12 ML) from the bottom of the nanowell. For such center-half-hollowed structures, our STM observation indicates that it is very stable, taking a few days to recover the flattop configuration if no further perturbation is introduced.

If we manipulate the center-half-hollowed nanowell shown in Fig. 1(b) with another STM voltage pulse at the bottom, this time the growth starts from the inner edge side at the position where the charge is distributed. The bottom is completely broken up and the Pb atoms climb up to attach to the inner sidewalls to increase the lateral area and thus to decrease the Coulomb effect. The resulted center-full-hollowed structure is shown in Fig. 1(c). The height change of the island during the manipulation is more clearly seen in the cross-section profiles in Fig. 1(e). Different from the center-half-hollowed nanowells, the inner sidewalls of the center-full-hollowed nanowell form a triangle hole. This possibly indicates a transition of inner walls from a stepped structure in a center-half-hollowed well to a faceted structure in a center-full-hollowed well. The ratio of the inner diameter to the outer can be increased by charging the nanowell from the inner edge side which makes the inner Pb atoms climbing up [see Figs. 1(c) and 1(d)]. The thickness can be tuned by charging from the outer edge side which induces mass transport from the surrounding neutral islands to the charged one.[15] Figure 1(d) shows the same nanowell but with tuned inner/outer diameter ratio and thickness by a series of STM voltage pulses.

Assuming that the vacuum gap resistance is 5×10^{10} Ω (according to the typical bias of 1.0 V and tunneling of 0.02 nA), the injected charge is estimated to be $\sim1\times10^{7}$ electrons per Pb island for the 10 V pulse in 10 ms. Dependence of the triggered growth height on the pulse amplitude is shown in Fig. 1(f). The triggered growth height monotonically increases with increasing voltage. We also found that the triggered growth height beyond about 30 ms is no longer sensitive to the original pulse duration applied, which indicates that the charge injection is most possibly completed in the first 30 ms.

The elementary processes of the Coulomb effect driven nanofabrication are illustrated in Fig. 2. The white and black arrows represent the process flows for the growth of the flattop islands and the center-hollowed nanowells, respectively. To form thicker flattop island, the voltage pulses should be applied on the edge sites of the original island, while to form center-hollowed nanowells, the voltage pulses need to be ap-

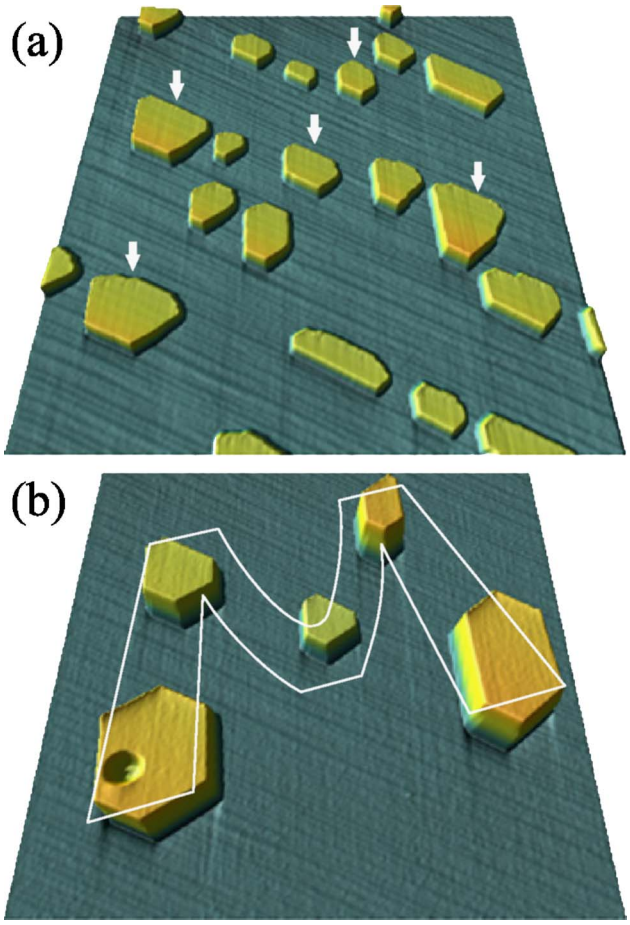

FIG. 3. (Color online) STM images (5000×5000 nm^2) showing fabrication of nanoarchitecture by the manipulation. (a) Initial Pb(111) island archipelago obtained by depositing Pb atoms on the Si(111) surface. The arrows indicate the selected Pb islands to be manipulated. (b) The character "M" written by growing five preselected Pb islands and erasing all others in (a) using STM. The elapsed time from (a) to (b) is 120 h.

plied at the center part of the center-half-hollowed nanowells.

We also extend this approach to fabricate predesigned nanoarray patterns even in the micrometer scale. Figure 3 shows an example where five selected islands [indicated by the five arrows in Fig. 3(a)] are made to grow while all the others are "erased," forming the character of "M" [white line in Fig. 3(b)]. We have checked mass conservation, confirming that the supply of atoms for the growth of selected islands comes from their neighboring islands. Compared with the other established techniques,[1–8] the final island locations in the fabricated nanoarray depend on the initial island distribution that is generated by the Pb deposition and cannot be controlled. Once the random initial distribution is generated, we are able to eliminate and grow the Pb islands in this particular distribution. In the process, millions of atoms are moved across microns under the direction of the STM baton, which is different from the operation mode used for a STM to push or pull single atoms.[9–13]

In summary, we have created various nanostructures by "massive" STM manipulation of millions of atoms via the Coulomb effect. This way, large-scale nanostructures can be fabricated with high precision. The nanostructures so obtained have controllable shapes and sizes. We have also manipulated an island array to build predesigned architectures by growing, moving, and erasing entire islands.

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