TOPICAL REVIEW

Active nanocharacterization of nanofunctional materials by scanning tunneling microscopy

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Received 22 June 2007
Accepted for publication 9 October 2007
Published 13 March 2008
Online at stacks.iop.org/STAM/9/013003

Abstract

Recent developments in the application of scanning tunneling microscopy (STM) to nanofabrication and nanocharacterization are reviewed. The main focus of this paper is to outline techniques for depositing and manipulating nanometer-scale structures using STM tips. Firstly, the transfer of STM tip material through the application of voltage pulses is introduced. The highly reproducible fabrication of metallic silver nanodots and nanowires is discussed. The mechanism is thought to be spontaneous point-contact formation caused by field-enhanced diffusion to the apex of the tip. Transfer through the application of z-direction pulses is also introduced. Sub-nanometer displacement pulses along the z-direction form point contacts that can be used for reproducible nanodot deposition. Next, the discovery of the STM structural manipulation of surface phases is discussed. It has been demonstrated that superstructures on Si(001) surfaces can be reverse-manipulated by controlling the injected carriers. Finally, the fabrication of an atomic-scale one-dimensional quantum confinement system by single-atom deposition using a controlled point contact is presented. Because of its combined nanofabrication and nanocharacterization capabilities, STM is a powerful tool for exploring the nanotechnology and nanoscience fields.

Keywords: nanotechnology, nanocharacterization, scanning tunneling microscopy, scanning probe microscopy, nanomaterials, nanofabrication

(Some figures in this article are in colour only in the electronic version.)

1. Introduction

With the recent trend of miniaturization in electronics, magnetic devices, and nano electro-mechanical systems (NEMS), materials science researchers are now frequently confronted with nanostructured materials on a scale below ~100 nm [1]. It is well known that nanotechnology-driven materials research, or nanotechnology-assisted materials research, plays a key role both in basic science and in industrial innovations of novel nanometer-scale products such as nanoelectronics devices. The development of advanced fabrication and characterization technologies for novel nanofunctional materials is one of the most important subjects in advanced nanomaterials research. Since the dimensions of novel microscopic devices will shrink to true nanometer scale below ~10 nm in the near future, the development of a probe for fabrication and in situ characterization at true nanometer scale is urgently needed. Moreover, the merging of nanofabrication and nanocharacterization tools into a unified tool will enhance the productivity of nanomaterials
Figure 1. Active nanocharacterization using STM. (a) In the ‘seeing is creating’ type, nanofabrication and nanocharacterization are merged. (b) The ‘seeing is discovering’ type involves dynamic characterization in externally applied fields or environments.
Figure 2. (a) Schematic circuit diagram of a SET transistor. (b) Schematic representation of a nanometer-scale SET transistor in UHV. To fabricate a SET nanodevice, novel techniques for fabricating nanometer-scale circuit parts such as nanowires and nanodots on semiconductor substrates should be developed.

to those of conventional microelectronics devices. For example, a nanometer-scale circuit composed of conductive nanowires, tunneling barriers, and a conductive nanodot has a single-electron tunneling (SET) effect, which can be applied to the fabrication of microscopic transistors and memories [14]. A nanometer-scale SET transistor, an important candidate technology for high-speed, low-power large-scale integrated circuits (LSIs), is schematically shown in figure 2. To develop such nanodevices, reproducible nanofabrication techniques for the fabrication of metallic nanostructures on clean substrates must first be developed.

Although conventional methods of fabricating artificial metallic nanostructures are mainly based on electron-beam lithography (EBL) [15], various STM-based methods have been developed due to the versatility of STMs [9–13]. One of the most intensively investigated STM-based nanofabrication techniques is the electric-field-induced material transfer of a tip to a substrate through the application of voltage pulses [16–29]. Because the pulse width applied is less than ~1 ms, this method is fast. Mamin et al [13] were the first to demonstrate the electric-field-induced deposition of tip materials in 1990. They demonstrated that atomic emission from a gold tip to a gold substrate through the application of voltage pulses in air can be used to write gold nanodot patterns with no apparent degradation of the tip. During the early 1990s, many researchers reported the field-induced transfer of tip materials through the application of voltage pulses in various environments, such as in air [16–19], UHV [20, 21], or liquid [22]. By these tip-material-transfer methods, various sizes of nanomounds can in principle be deposited at the desired position. However, atomic-resolution STM imaging with a tip used for field-induced deposition was not achieved until 1996.

In 1996, Fujita et al [23] demonstrated the field-induced deposition of gold nanodots on an atomically resolved Si(111)-(7 × 7) surface using a gold-coated tip in UHV. Typical STM images of gold nanostructures fabricated at room temperature (RT) are shown in figure 3. Gold nanodots ~10 nm in diameter and ~1 nm in height were deposited by applying a single negative voltage pulse...
to a gold-coated tungsten tip, as shown in figure 3(a). In contrast, upon applying a voltage pulse with positive polarity to the tip, a larger nanomound, typically ∼50 nm in diameter and ∼3 nm in height, was deposited, as shown in figure 3(b). Only with a negative polarity tip was deposition controllable and the fabrication of an arbitrary pattern of gold nanodots in accordance with a specified design possible. The threshold voltage for gold atom transfer is approximately ∼5 V. The corresponding electric field of ∼5 V nm⁻¹ is significantly lower than the reported threshold value for the field evaporation of Au⁺ (∼17 V nm⁻¹) [30]. Although the deposition of gold nanodots on clean Si surfaces in UHV was successfully demonstrated by applying voltage pulses and has been extensively studied [24, 29], the formation of continuous nanowires was found to be difficult due to the low deposition probability of gold (∼60%) [23].

An STM tip-material transfer study on a new material (silver), in which metallic nanodots on a clean Si(111) surface were obtained with much higher reproducibility, was recently reported [28]. The STM tip was made of an electrochemically etched tungsten wire (99.99% purity) on which a thin silver film was deposited by magnetron sputtering. Although it was possible to transfer silver at both polarities, a negative polarity was again found to be more suitable for nanofabrication because of the higher probability of deposition (up to 100%) and smaller nanodot dimensions. The observed threshold voltage for negative polarity is about 3.5 V, which is significantly smaller than that for gold. Above the threshold, the deposition probability reaches ∼100%. Figure 4(a) shows an STM image of silver nanodots after applying several voltage pulses. Its line profile, as shown in figure 4(b), clearly indicates that the nanometer-scale dots can be created with a relatively small voltage. Owing to the nearly perfect deposition yield, nanodots, nanowires and nanocharacters can be created, as shown in figure 4(c), demonstrating the versatility of STM tip-material transfer for developing nanometer-scale circuits. Tunneling spectroscopy performed above a silver nanodot showed linear I–V characteristics around zero bias indicating a metallic nature. I–V curves observed above the neighboring silver nanodots showed that there was a decrease in tunneling current, indicating the presence of a carrier depletion layer. If a high-work-function metal comes in contact with an n-type semiconductor, electrons flow from the semiconductor to the metal, depleting the characteristic surface region of the semiconductor of electrons. Consequently, local electrical resistivity increases near the surface with respect to its bulk value. Similar space-charge regions under gold nanodots on n-Si(111) were also demonstrated by artificial point contact [31].

Despite these extensive studies on field-induced tip-material transfer, no consensus regarding the mechanism of nanodot deposition by applying voltage pulses has been reached. Generally, the proposed models can be categorized into two types. One is the field evaporation model [13, 16, 18–21, 26, 27], and the other is the mechanical point-contact model [17, 22, 25, 28, 29]. The combination of field evaporation and mechanical point contact has also been proposed [23]. The field evaporation model was first proposed by Mamin et al [13] in the case of atom emission from a gold tip on a Au(111) surface in air. A detailed physical
A negative voltage pulse is applied, causing field-induced diffusion of Ag towards the apex of the tip. The elongated tip apex may cause a spontaneous point contact during the pulse. Immediately after the pulse ends, feedback is recovered, causing the tip to retract and the point contact to break. Because of the relatively strong chemical bond, a metallic Ag nanodot is left, forming a nearby depletion layer.

The voltage pulse method described above is suitable for fabricating nanodots of various dimensions. If tip-material transfer is mainly caused by the spontaneous formation of a point contact, then it will be possible to deposit the tip material by artificial point-contact formation. On the basis of this idea, the so-called ‘z-pulse method’ was developed. This technique uses the controlled approach of the tip to the surface to form an atomic point contact by applying a voltage pulse to a z-direction piezo-actuator. An example of tip-material transfer using the z-pulse method with a pure gold tip is given here.

When a small z-axis-displacement pulse (∆z) corresponding to a tunneling gap distance of less than 1 nm is applied to a gold tip located in the tunneling region, a gold nanodot can be formed on the surface under certain conditions, as shown schematically in figure 6(a). In the initial stage, the tip is located at a regulated height. The gap distance is typically approximately 0.5 nm, depending on the tunneling conditions, such as applied gap voltage and feedback current. By applying a z-pulse, the gold tip typically approaches to within ~0.3 nm of the surface. When the gap distance is close to a typical bond length of ~0.2 nm, an atomic-sized point contact is spontaneously formed by the formation of an atomic-scale protrusion, which may be caused by field-induced diffusion or by the formation of a chemical bond. According to the dimer–adatom–stacking-fault (DAS) model, the Si(111)-(7×7) surface contains surface adatoms, which have dangling bonds protruding into the vacuum. Therefore, it is possible to form an atomic-sized point contact through chemical bonding with these dangling bonds if the gap distance is sufficiently small for both wave functions to overlap. After extracting the tip, because of the chemical bonds between the gold and silicon atoms a nanoscale gold dot is left on the surface.

An image of a typical gold nanodot formed after applying a single z-pulse (∆z = ~0.3 nm, Tpulse = 1 ms) at 50 K is shown in figure 6(b). The image clearly shows a gold nanodot protruding from the Si(111)-(7×7) surface, whose dimensions are about 6 nm in diameter across the base and 0.9 nm in height. Compared with the voltage pulse method, the advantage of the z-pulse method is its higher deposition efficiency.

3. Nanostructure fabrication by tip-material transfer using z-direction pulses

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probability. If tip conditions, such as the shape of the apex, are suitable, a gold nanodot almost always forms after a single $z$-pulse is applied. By measuring the gap current between the gold tip and the Si(111) surface against the change in the gap distance ($I$–$z$ curve), it is possible to demonstrate that the tip-material transfer is actually caused by point-contact formation. Figure 7 shows a typical $I$–$z$ curve obtained at RT. To measure the current flow, a small constant voltage $V_t$ was applied to the tip. At first the observed current showed an exponential increase because the tip was still in the tunneling regime. At approximately $-0.2$ nm closer to the surface than the regulated position, the current suddenly jumped to a much higher value (about 25 nA), after which the current was almost constant up to $-0.3$ nm. This discrete change in current clearly suggests the formation of a point contact between the gold tip and the Si(111) surface. Point-contact formation using an STM configuration has been studied for various metal surfaces (Au, Ni, Cu, Pt, Al) [17, 33–35], and the conductance $G$ showed jumps of multiples of $2e^2/h (=77.5\mu S)$ as the contact was stretched. Using the Landauer–Büttiker formula, the quantum conductance of a nanowire can be expressed as

$$G = \frac{2e^2}{h} \sum_{i=1}^{N_C} T_i$$

where $N_C$ is the number of conduction channels supported by the point contact and $T_i$ is the transmission probability of the $i$th channel. If a point contact with a few channels forms and the transmission probability is unity ($T_i = 1$), then the contact resistance should show a quantized value $R_c = R_Q/N_C$, where quantum resistance $R_Q$ is defined as $h/2e^2 (=12.9k\Omega)$. The total resistance $R_{\text{total}}$ at the observed current plateau in figure 7 is about $80k\Omega$, which is on the same order as the quantized resistance. Therefore, the observed jump in the $I$–$z$ curve can be partially attributed to a consequence of the quantized conductance, which suggests that a nanometer-scale point contact was formed between the gold tip and the Si(111) surface. The significant deviation from $R_c$ can be explained by the spontaneous formation of a depletion region underneath the contact and by the relatively large reflection caused by the mismatch of Fermi wavenumbers in the two media.

The insert in figure 7 is an STM image taken immediately after $I$–$z$ curve measurement and clearly shows the formation of a gold nanodot. Its size is about the same as that obtained by the single $z$-pulse shown in figure 6, which suggests that nanodot formation by tip-material transfer is caused by the formation of a nanoscale point contact.

4. STM phase manipulation by carrier injection

The Si(001) wafer is the most important material in semiconductor technology. Although its surface structure has been extensively studied for decades, the ground state of the Si(001) surface at low temperatures was not clearly understood until recently. Since uncertainty about the ground state of such an important material may have a significant effect on the development of precise simulation methods of semiconductor processing, research in this area should be of the highest priority. With the rapid development of low-temperature UHV–STM, various structures, such as static (2×1) [36], dynamic (2×1) [37, 38], p(2×2) [39], and c(4×2), have been...
proposed as the ground state of the Si(001) surface [40]. Here, the static (2×1) structure is composed of symmetric dimers. The dynamic (2×1) structure is thought to be composed of apparently symmetric dimers. This structure is normally observed at temperatures near RT and is composed of buckled dimers in fast flip–flop motion. Since the flip–flop motion is a thermally activated phenomenon, lowering the temperatures to ~120 K freezes the motion and causes asymmetric dimer structures of p(2×2) or c(4×2) to appear. First, the static and dynamic symmetric dimer structures were ruled out for the Si(001) surface by precise STM and NC-AFM measurements at approximately 5 K [41, 42]. Very low temperature STM measurement (670 mK) [43] and a low-temperature LEED study performed by Mizuno et al [44] clearly showed that c(4×2) is the most stable ground state. This conclusion is consistent with the result of first-principles DFT calculation [45].

Sagisaka et al [40] discovered a new method of STM manipulation while investigating the ground state of the Si(001) surface. By controlling the energy of carriers injected by an STM tip, it is possible to reverse-manipulate periodic surface superstructures at temperatures below ~40 K [46]. As shown in figure 8, it is possible to manipulate the Si(001) surface phase between c(4×2) and p(2×2) by precisely controlling the sample bias in STM at such low temperatures. When the surface is scanned at a relatively low positive bias, it shows a single c(4×2) phase or the ground state. Gradually increasing the positive sample-bias voltage causes the surface dimer rows to fluctuate individually. This fluctuation was attributed to the flip–flop motion induced by the injected electrons. A further increase in the positive bias voltage caused the surface to shift to a single p(2×2) phase or to the quasi-ground state.

The reconstructed Si(001) surface exhibits low-dimensional surface electronic states originating from the dangling bonds of the dimer rows. The empty dangling bond state (π∗) is situated within the bulk band gap and reveals energy dispersion along the dimer-row direction. The filled dangling bond state (π) overlaps with the bulk valence band [47, 48]. Electron injection into the empty surface state (π∗) from the STM tip is responsible for the structural change from the ground state, c(4×2), to the quasi-ground state, p(2×2) [49]. In contrast, hole injection into the filled surface state (π) causes a structural change from the quasi-ground state, p(2×2), to the true ground state, c(4×2).

The observed structural manipulation by controlling the gap voltage provides a reasonable explanation as to why previous researchers reported different structures as the true ground state of the reconstructed Si(001) surface. Similar structural manipulation through STM carrier injection has been also discovered for Ge(001) surfaces at low temperatures by Takagi et al [50]. To obtain a unified mechanism for STM structural manipulation, further comparative studies between Si(001) and Ge(001) (with the help of theoretical modeling) should be carried out.

5. 1D quantum confinement by STM atom deposition using point contact

As described above, the reconstructed Si(001) surface at low temperatures exhibits interesting features such as a 1D electron state in which the surface electrons are preferably transported along individual dimer rows. The quantum interference of the 1D electron waves can be visualized by UHV–STM at low temperatures [51, 52]. Confinement of the 1D electrons using the dimer rows of the reconstructed Si(001) surface was first demonstrated by Yokoyama and Takayanagi [51], by evaporating aluminum onto the surface to form aluminum ad-dimer chains. These chains acted as potential barriers, confining 1D electron waves to along the dimer rows. The next challenge is to create artificially controlled structures at atomic scale to confine 1D electrons to a designed length along a single dimer row.

For this purpose, further improvement of the above-mentioned tip-material transfer technique by creating an artificial point contact between the STM tip and the surface is required. The obvious advantage of this method is that it enables the fabrication of atomic-scale scattering centers at desired positions. By transferring tungsten atoms from the STM tip of a sharpened tungsten wire, Sagisaka and Fujita have succeeded in fabricating a quasi-1D quantum well on a single dimer row [53]. Tungsten atoms were deposited through the formation of a point contact from the apex of a tip to the surface, as shown schematically in figure 9(a). Stable LT-STM operation in UHV is required for the reproducible positioning of the tip. The point contact was formed by moving the tip closer to the down atom of a buckled dimer. An STM image of a typical tungsten atom deposited on a Si(001) surface at 79 K is shown in figure 9(b). The observed protrusion in the center of the image is thought to be a tungsten atom deposited on the down atom of a buckled silicon dimer.

Using this atom deposition technique, the fabrication of two tungsten dots along a single dimer row with a suitable separation (~10 nm) for effective quantum confinement was attempted, the result of which is shown in figure 10(a). If the tungsten atoms act as effective scattering
barriers to the dangling-bond-state ($\pi^*$) electrons, then the quasi-1D electron waves along the dimer row should be confined between the two scattering barriers, fully realizing an artificially fabricated 1D quantum well.

The LDOS at surfaces can be visualized by differential conductance ($dI/dV$) mapping using a lock-in technique. As shown in figure 10(b), the $dI/dV$ maps obtained from the dimer row with two tungsten dots clearly reveal confined electron waves. As the sample bias is increased, several quantized states are observed. This observation indicates that a single dimer row surrounded by two tungsten dots functions as a quasi-1D quantum well. These results clearly suggest that the STM atom deposition technique is compatible with high-resolution STM/STS imaging. The combination of fabrication and characterization techniques operable at atomic scale will further advance the exploration and clarification of novel quantum phenomena and functionalities.

6. Conclusion

Recent developments in nanofabrication and nanocharacterization technologies using STM were reviewed. Special emphasis was placed on the various fabrication techniques of nanometer-scale structures using STM tips acting as both nanofabrication and nanocharacterization tools. Firstly, an STM nanofabrication method based on tip-material transfer by applying voltage pulses was introduced. The highly reproducible fabrication of metallic silver nanodots and nanowires using a silver-coated tip was demonstrated. The mechanism of tip-material transfer through the application of voltage pulses can be explained by the spontaneous formation of a point contact due to field-enhanced diffusion to the apex of the tip, for which most of the previous reports assigned field evaporation as being the dominant process. Secondly, another method of transferring STM tip material by applying $z$-direction pulses was introduced. Sub-nanometer displacement pulses along the $z$-direction ($z$-pulses) form point contacts resulting in reproducible nanodot deposition. Then, the discovery of the STM structural manipulation of surface phases was discussed. It was demonstrated that the superstructures on reconstructed Si(100) surfaces can be reverse-manipulated between the ground states and quasi-ground states by controlling the energy of the injected carriers. Finally, the fabrication of an atomic-scale 1D quantum confinement system was presented using a single-atom-deposition technique by controlling the point contact formation by the STM tip. Because of its combined nanofabrication and nanocharacterization capabilities, STM is a powerful tool for exploring the nanotechnology and nanoscience fields.

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