

Deposition of metal nanostructures onto Si(111) surfaces by field evaporation in the scanning tunneling microscope

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Islands of gold or copper having dimensions as small as 200 Å in diameter and 10 Å in height were prepared by field evaporation from a tip of the appropriate metal in a scanning tunneling microscope (STM). The field emission of metal is induced by the application of tip-negative bias pulses having amplitudes of 6–20 V, and durations of 2 μs to 2 ms. The metallic composition of the protrusions observed by STM are confirmed by *ex situ* elemental analysis using the field emission scanning Auger microprobe (FE-SAM). Tip-positive bias pulses also produce protrusions, however these are unstable either to STM imaging or to exposure to high-energy electron beams, as in the FE-SAM instrument. It is therefore probable that nanostructures formed via tip-positive bias pulses are not metallic. These data provide the first direct experimental evidence for metal transfer between an STM tip and a surface.

The transfer of metal islands composed of gold and copper from the tip of a scanning tunneling microscope (STM) onto hydrogen-terminated Si(111) surfaces which are in contact with either an air or a dry N₂ ambient is described in this letter. These islands have dimensions as small as 200 Å in diameter and 10 Å in height and may be positioned on the silicon surface with a lateral precision of ≈50 Å. Significantly, the field emission scanning Auger microprobe (FE-SAM) reveals that the transfer of metal occurs reliably in this experiment only for bias pulses having a *tip-negative* polarity despite the fact that STM images reveal the production of protrusions following the application of bias pulses having *either* polarity. Previously, Mamin *et al.*^{1,2} have reported the deposition of gold nanostructures via chemically assisted field evaporation (CAFE) onto Au(111) surfaces in ultrahigh vacuum; McBride and Wetsel³ have invoked electric field effects to explain the apparent transfer of metal between an STM tip and a surface.

The STM imaging and modification experiments described here were accomplished using a commercial air/liquid STM.⁴ Experiments were performed in an ambient of laboratory air or dry, purified N₂. Modified surfaces were transferred in air to a FE-SAM instrument⁵ for elemental analysis of nanostructures and scanning electron microscopy. Nominal operating conditions of 20 keV accelerating potential and 9 nA of beam current provided a spot size of approximately 300 Å. Copper and gold wire, both of ≥99.99% purity from Aldrich, were employed for the preparation of STM tips: Copper tips were prepared by mechanical cutting and gold tips by electrochemical etching in concentrated hydrochloric acid. Si(111) surfaces having root-mean-square roughness of 2–4 Å were obtained by etching in aqueous 40% NH₄F exactly as described previously.⁶ Constant-

current mode STM images were acquired using tip positive biases of 2 V and typical currents near 0.05 nA.

The application of bias pulses having amplitudes of 5–20 V, durations of 2 μs to 2 ms, and either polarity (tip positive or tip negative) produce modifications to a hydrogen-terminated Si(111) surface in air (or in pure N₂) which, in STM images, appear as protrusions having typical dimensions of 1000 Å diameter and 200 Å in height. Qualitatively similar protrusions are observed with STM tips composed of copper and gold. Figure 1, for example, shows an STM image of an ensemble of nanostructures produced with a gold STM tip: Each of the three protrusions clustered at the four corners of the image were generated using single tip-negative pulses of 12 V × 50 μs while each of the three protrusions at center was produced with a tip-positive bias pulse having the same amplitude and duration. It is readily apparent from Fig. 1 that nanostructures produced with tip-positive and with tip-negative polarities using the same tip are virtually indistinguishable in STM images of these features.

Despite the apparent similarity of tip-positive and tip-negative protrusions in STM images, however, the behavior of these structures when exposed to a high energy electron beam, as in the FE-SAM instrument, is distinctly different: Tip-negative protrusions are completely stable whereas tip-positive protrusions “evaporate” in the electron beam; disappearing completely within a few seconds of exposure. For single tip-negative protrusions, Auger spectra are readily acquired and representative spectra are shown in Fig. 2: Figure 2(a) is the FE-SAM spectrum for a region of the Si(111) substrate in which no nanostructures were deposited; Figs. 2(b) and 2(c) show spectra for single copper and gold nanostructures, respectively. All of these spectra show evidence of significant carbon contamination and oxide growth which are unavoidable consequences of exposure of the surface to air

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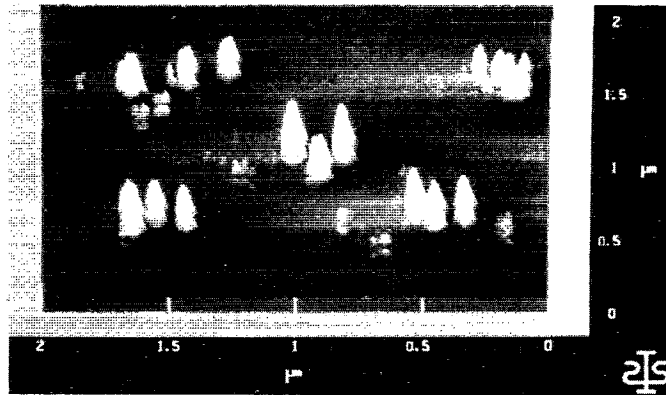


FIG. 1. STM image of an ensemble of nanostructures produced using either tip-negative (corners) or tip-positive (center) bias pulses having an amplitude of 12 V and a duration of 50 μ s (see text). The three nanostructures in the upper left corner were intentionally deposited with greater separation (≈ 1000 Å).

which occurs during transfer to the FE-SAM instrument. For the spectra of copper and gold nanostructures, the metal Auger signatures are well separated from these background signals. However, an enhanced oxygen signal for the copper structures in the differential spectrum of Fig. 2(c) [as com-

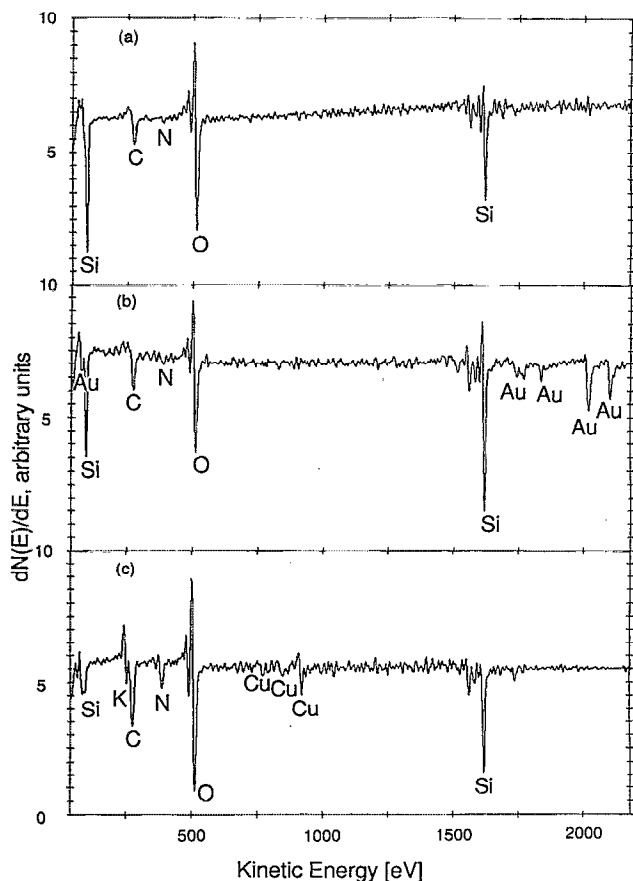


FIG. 2. Scanning Auger microprobe spectra of modified and unmodified Si(111) surfaces: (a) Unmodified region of a silicon surface, (b) Nanostructure generated using a gold STM tip, (c) nanostructure generated using a copper STM tip.

pared either to the spectra shown in Figs. 2(a) or 2(b)] suggests that oxidation of the deposited metal may have occurred. These data constitute the first *direct* evidence for the deposition by field evaporation of metal from an STM tip.

Tip-negative protrusions of either copper or gold are stable in height and diameter during repeated imaging in the STM for durations of hours. This stability contrasts with the fast surface diffusion for modifications on Au(111) surfaces observed previously,^{7,8} apparently indicating the existence of a barrier to the diffusion of gold atoms from the protrusions onto the Si(111) surface. Again, tip-positive protrusions exhibit poorer stability, becoming lower in height over several successive scans and eventually disappearing completely within an hour.

Based on the observed absence of stability in the FE-SAM and the STM, we speculate that protrusions produced with tip-positive bias pulses are not metallic, but derive instead from reactions of surface contaminants or, potentially, from the localized formation or removal of a thin surface oxide layer.⁶

A secondary effect which operates during some metal deposition experiments is the apparent localized melting of the silicon surface in the immediate vicinity of the metal deposit. A scanning electron micrograph and an STM image of two metal deposition sites which show evidence for surface melting are shown in Figs. 3(a) and 3(b), respectively. In Fig. 3(a), melting is apparent as a darkened (depressed) circular region ≈ 400 Å in diameter. An FE-SAM spectrum (not shown) reveals that the bright feature at the top of this pit (150 Å in diameter) is a gold deposit. The STM image of Fig. 3(b) shows a qualitatively similar depression surrounding another gold deposit (that at upper left). It should be emphasized that melt craters are only observed following the application of tip-negative bias pulses, and appear with the highest probability for amplitudes greater than 15 V.

For the gold deposition experiments, the observed bias polarity dependence for metal evaporation is in apparent agreement with the calculations of Tsong⁹ and Miskovsky *et al.*¹⁰ for the system of two proximal gold electrodes (i.e., tip and surface). The calculations of these authors predict

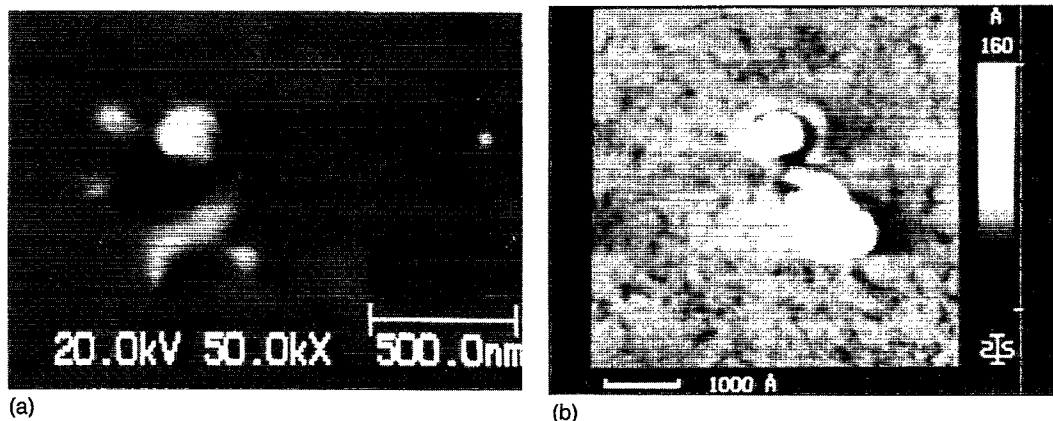


FIG. 3. (a) Secondary electron image from FE-SAM of a gold nanostructure (spheroid near top) deposited with apparent localized melting of the silicon surface. Deposition was effected using a tip-negative, $20\text{ V} \times 100\ \mu\text{s}$ bias pulse. (b) STM image of two gold nanostructures deposited using two tip-negative $15\text{ V} \times 50\ \mu\text{s}$ bias pulses. Evidence for localized melting about the left-most structure is visible as a depressed region.

that gold atom transfer ought to occur most readily (at the lowest field) for the anion Au^{2-} (i.e., for tip-negative bias, as observed experimentally here)—of course, the magnitude of the charge on the transferred species is not experimentally measurable from our data. The gold/silicon system has not so far been explicitly treated by theory. The mechanism of atom transfer has been discussed in context of the CAFE method by Avouris and co-workers^{11,12} and by Lang.¹³

The deposition of nanoscale metal structures on silicon surfaces or the surfaces of other semiconductors has not, to our knowledge, been demonstrated previously. This capability has immediate technological importance due to the fact that rectifying Schottky barriers ought to be formed at the metal-semiconductor contact. The current-voltage properties of these nanometer-scale diodes are currently under investigation.

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