Electrochemical AFM "Dip-Pen" Nanolithography

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In recent years, SPM-based lithography has attracted great attention because of its simplicity and precise control of the structure and location. Many SPM lithography techniques based on mechanical scratching,[1] anodization of Si surfaces,[2] electrochemical decomposition of self-assembled monolayers,[3] electric field-induced chemical reactions,[4] electrochemical reactions in solution using electrochemical STM tips[5] have been developed in the past decade. Comprehensive reviews of SPM-related lithography can be found in the literature.[6] More recently, a "dip-pen" nanolithography (DPN) method has been invented that uses an atomic force microscope (AFM) tip as a "nib" to directly deliver organic molecules onto suitable substrate surfaces, such as Au.[7] By using this technique, organic monolayers can be directly written on the surface with no additional steps, and multiple inks can be used to write different molecules on the same surface. However, the current "dip-pen" method can only be used to deliver organic molecules to the surface. The long-term stability of the created structures is a potential problem. Here we report a new electrochemical "dip-pen" lithography technique that can be used to directly fabricate metal and semiconductor nanostructures on surfaces. This technique has all the advantages of the previous "dip-pen" technique and improves the thermal stability and chemical diversity of the structures because they now could be made of various inorganic materials. Furthermore, the ability to directly fabricate metal or semiconductor nanostructures on surfaces with a high degree of control over location and geometry is of significant interest in nanotechnology. Potentially, one could use this method to fabricate nanodevices with multiple metal and semiconductor components.

When AFM is used in air to image a surface, the narrow gap between the tip and surface behaves as a tiny capillary that condenses water from the air. This tiny water meniscus is actually an important factor that has limited the resolution of AFM in air. "Dip-pen" AFM lithography uses the water meniscus to transport organic molecules from tip to surface.[7] In our new technique, we also use the tiny water meniscus on the AFM tip as the transfer medium. However, unlike in the previous AFM "dip-pen" method where water is only used as a solvent for the molecules, we have used this tiny water meniscus as a nanometer-sized electrochemical cell in which metal salts can be dissolved, reduced into metals electrochemically, and deposited on the surface (Figure 1). Although electric field-induced chemical reactions,[4] electrochemical reactions in solutions using electrochemical STM,[5] and electrochemical deposition using self-assembled monolayer as resist[3c] have been previously used to create metallic nanostructures, our method is the first that combines the versatility of electrochemistry with the simplicity and power of the DPN method to produce nanostructures with high resolution. Electrochemical STM-based methods require that the substrates be metallic, but substrates used in our method do not have to be metallic since the control feedback of the AFM does not rely on the current between the tip and surface. Si wafers coated with native oxide provides enough conductivity for the reduction of the precursor ions. This development significantly expands the scope of DPN lithography, making it a more general nanofabrication technique that not only can be used to deliver organic molecules to surfaces but is also capable of fabricating metallic and semiconducting structures with precise control over location and geometry. Because of the electrochemical nature of this new approach, we call this technique electrochemical "dip-pen" nanolithography (E-DPN).

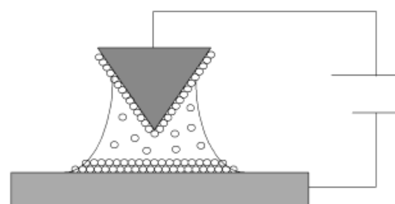
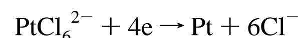


Figure 1. Schematic sketch of the E-DPN experimental setup.

We have investigated the deposition of several metals and semiconductors on Si surfaces at room temperature using the E-DPN technique. Here we show the deposition of Pt metal as an example.[8] The experiments were performed using a Nanoscape IIIa AFM (Digital Instruments). In a typical experiment, an ultrasharp silicon cantilever coated with H_2PtCl_6 is scanned on a cleaned P-type Si (100) surface with a positive DC bias applied on the tip. During this lithographic process, H_2PtCl_6 dissolved in the water meniscus is electrochemically reduced from Pt(IV) to Pt(0) metal at the cathodic silicon surface and deposits as Pt nanofeatures according to the following equation:



$$PtCl_6^{2-} + 4e \rightarrow Pt + 6Cl^-$$

The relative humidity in the environment is one of the key factors for the E-DPN process. Normally, the relative humidity

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(1) For example: (a) Liu, G. Y.; Xu, S.; Qian, Y. L. *Acc. Chem. Res.* **2000**, *33*, 457−466. (b) Kunze, U.; Klehn, B. *Adv. Mater.* **1999**, *11*, 1473−1475.

(2) For example: (a) Sugimura, H.; Nakagiri, N. *J. Vac. Sci. Technol. A* **1996**, *14*, 1223−1227. (b) Legrand, B.; Stievenard, D. *Appl. Phys. Lett.* **1999**, *74*, 4049−4051.

(3) For example: (a)Sugimura, H.; Takai, O.; Nakagiri, N. *J. Vac. Sci. Technol. B* **1999**, *17*, 1605−1608.(b) Sugimura, H.; Nakagiri, N. *Thin Solid Films* **1996**, *282*, 572−575. (c) Zamborini, F. P.; Crooks, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 9700−9701. (d) Gorman, C. B.; Carroll, R. L.; He, Y. F.; Tian, F.; Fuierer, R. *Langmuir* **2000**, *16*, 6312−6316.

(4) For example: (a) Maoz, R.; Frydman, E.; Cohen, S. R.; Sagiv, J. *Adv. Mater.* **2000**, *12*, 424−429. (b) Maoz, R.; Frydman, E.; Cohen, S. R.; Sagiv, J. *Adv. Mater.* **2000**, *12*, 725.

(5) For example: (a) Kolb, D. M.; Ullmann, R.; Will, T. *Science* **1997**, *275*, 1097−1099. (b) Forouzan F. and Bard, A. J. *J. Phys. Chem. B* **1997**, *110,* 10876-10879. (c) Hofmann, D.; Schindler, W.; Kirschner, J. *Appl. Phys. Lett.* **1998**, *73*, 3279−3281. (d) Randler, R. J.; Kolb, D. M.; Ocko, B. M.; Robinson, I. K. *Surf. Sci.* **2000**, *447*, 187−200. (e) Schindler, W.; Hofmann, D.; Kirschner, J. *J. Appl. Phys.* **2000**, *87*, 7007−7009. (f) Yang, R.; Evans, D. F.; Hendrickson, W. A. *Langmuir* **1995**, *11*, 211−213. (g) Li, C. Z.; Tao, N. J.; *Appl. Phys. Lett.* **1998**, *375*, 767.

(6) For example: (a) Nyffenegger, R. M.; Penner, R. M. *Chem. Rev.* **1997**, *97*, 1195−1230. (b) Wlieth, W., Lorenz, W. J., Eds.; *Electrochemical Nanotechnology - in situ Local Probe Techniques at Electrochemical Interfaces*; Wiley-VCH: Weinheim, 1998.

(7) (a) Piner, R. D.; Zhu, J.; Xu, F.; Hong, S. H.; Mirkin, C. A. *Science* **1999**, *283*, 661−663. (b) Hong, S. H.; Mirkin, C. A. *Science* **2000**, *288*, 1808−1811. (c)Hong, S. H.; Zhu, J.; Mirkin, C. A. *Science* **1999**, *286*, 523−525.

(8) In a typical experiment, a noncontact ultrasharp silicon cantilever (Silicon-MDT Ltd., NSCS15 cantilever) was coated with H_2PtCl_6 by dipping the cantilever into an aqueous solution of H_2PtCl_6 (∼2 wt %) and blown dry with filtered compressed gas. The substrates used in the experiments were P-type Si (100) wafers after cleaning by a standard method: First the wafers were immersed in piranha solution (2:1 H_2SO_4: H_2O_2 by volume) for 1 h to oxidize organic contaminants on the surface and to form a thin oxide layer, then were dipped into 1:10 HF aqueous solution to remove the oxide layer and contaminants. Clean H-terminated Si surfaces were obtained after HF treatment. The surfaces were then used for E-DPN. They were first imaged in tapping mode to find a suitable location for lithography. The scanning was then stopped, and the tip was brought into contact with the surface by reducing the tapping setpoint to 10% of the original value and a positive DC bias was applied on the tip while it was slowly moved across the surface in a preprogrammed pattern. The typical resistance of the circuit while the tip is in contact with the surface is ∼10 GΩ and the typical current ∼0.3 nA.

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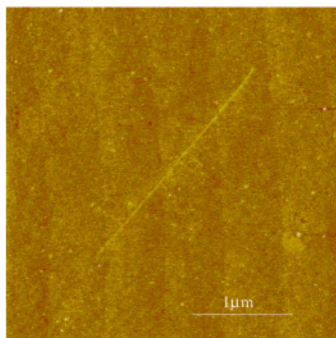

Figure 2. AFM image of a platinum line drawn by the E-DPN method under the condition of relative humidity 40% with a voltage of 4 V and a scan speed of 5 nm/s.

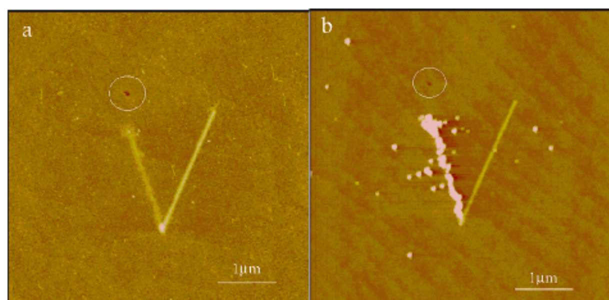

Figure 3. (a) The character "V" composed of platinum (left) and silicon oxide (right). The Pt line is drawn with a voltage of +4 V between the tip and the wafer and a scan speed of 10 nm/s. The SiO_2 line is created with a −10 V voltage to oxidize the surface and the scan speed is 50 nm/s. The relative humidity is 58%. (b) The same area of the wafer after heated at 500 °C under the atmosphere of ethylene in argon for an hour. The white circles highlight a surface defect as the landmark.

was maintained between 35 and 60% using a commercial humidifier and dehumidifier. The DC voltage needed for metal deposition depends on the type of precursor salt and the resistivity between the AFM tip and the surface. For Pt deposition, a DC voltage of 1−4 V was used; higher voltages tend to oxidize the Si wafers to create SiO_2 features rather than Pt nanostructures. As shown in Figure 2, a Pt line with 30 nm line width was created on a Si surface with the E-DPN technique. The height of the Pt line shown in the figure is ~0.4 nm.

Many characteristics of the nanofeatures prove that they are composed of the deposited metals rather than other materials, such as SiO_2. First, the lines are higher than the surrounding surface, proving that they are not mechanical scratches caused by the AFM tip. Second, the lines are stable in air at elevated temperatures. Heating the sample in air to 300 °C did not cause any changes in the morphology of the lines, which proves that the lines are not made of organic molecules or condensed water. Furthermore, heating to higher temperature (~500 °C) in Ar turns the lines into a series of small dots, indicating that the metal line melts at high temperature and aggregates due to surface tension. Third, unlike SiO_2 features made by AFM-tip-induced anodization, the lines are resistant to HF etching. Finally, the lines have catalytic activity toward the thermal decomposition of ethylene. As shown in Figure 3, we have created a Pt line with the E-DPN method and a SiO_2 line by AFM anodization on a Si wafer. We then heated the wafer in ethylene flow at 500 °C for 60 min. The Pt line shows a large amount of carbon deposition, while the SiO_2 line shows no change. This observation is a strong proof that the features created with the E-DPN technique are Pt lines since it is known that Pt is an active catalyst for the decomposition of ethylene. Figure 3b also showed that there is additional carbon deposition around the Pt line. This is probably due to unintentional deposition of Pt salt during imaging with the salt-coated AFM tip. We are currently working on eliminating these "defects" to fabricate nanostructures with clean background.

The height and width of the fabricated features using the E-DPN technique depend on several factors, including the humidity, scan speed, and applied voltage. We have shown that by varying these factors, we can change the height and width of the created features.[9] More work focusing on delivering a known amount of metal atoms to the surface by monitoring the current between the tip and surface and adjusting the scanning speed is currently under way in our lab.

The technique described here is not limited to Pt; other metals as well as semiconductors can also be delivered to the surface in a similar manner. We have succeeded in creating features made of Au, Ge, Ag, Cu, Pd, etc.[10] In principle, any metal or semiconductor that can be electrochemically deposited from an aqueous solution of salts could be delivered to a surface with precise control of position to form features with nanometer dimensions.

In summary, we have developed a new E-DPN technique that can be used to directly fabricate metal and semiconductor features with nanometer dimensions. This new technique has significantly expanded the scope where DPN nanofabrication technology can be applied. Such a simple but powerful technique would enable us to fabricate nanoelectronic devices with sections made of different metals and semiconductors or deposit nanostructures for site-specific CVD growth. More importantly, the fundamental idea behind this technique, which is to use the water meniscus between the AFM tip and surface as a reaction vessel, could be applied to develop more powerful techniques based on localized chemical reactions instead of only electrochemical or surface reactions. The only requirement for such reactions is that the reaction products be insoluble in the transport medium. The large number of suitable reactions will make AFM DPN nanofabrication a very powerful tool for making unique nanodevices as well as chemically modifying devices made by more conventional nanofabrication techniques.

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Supporting Information Available: Image showing the height of the features created by E-DPN can be varied by changing experimental conditions.; more images of metal and semiconductor nanostructures created by E-DPN nanolithography technique (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Please see supporting materials for an example whereby changing the scan speed from 10 nm/s to 20 nm/s, we can change the height of the created features from 0.35 to 0.2 nm.
(10) See Supporting Information.