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电化学"沾笔"纳米刻蚀及其他

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本文提出了一种基于"沾笔"纳米刻蚀和电化学还原技术在表面上制备金属及半导体纳米结构的普适性方法。用这种方法可以在硅表面直接书写线宽度低于50纳米的多种金属和半导体组成的纳米结构。这种简单而有效的方法在精确控制位置和结构的功能化纳米器件制备中具有重要的潜在应用前景。

关键词: "沾笔"纳米刻蚀 电化学 AFM 纳米结构
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Electrochemical AFM "Dip-Pen" Nanolithography and More

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A general approach for fabricating metallic and semiconducting nanostructures has been developed based on "dip-pen" nanolithography combined with electrochemical reduction of water-soluble salts. This method can be used to directly write many different types of metal or semiconductor features on Si substrates with sub 50 nanometer linewidth. This simple but powerful method has great potential in fabricating functional nanodevices with high degree of control over their locations and structures.

Keyworks: dip-pen lithography electrochemical AFM nanopatterns

Fabrication of nanostructures with controlled geometry at specific locations is one of the key challenges in nanotechnology. Great effort has been put in discovering new ways to solve this problem. Many techniques, including electron beam lithography, Scanning Probe Microscope (SPM) lithography[1], microcontact printing etc., have been used by researchers to create structures with nanometer dimensions. Among them, SPM based lithography has attracted great attention because of its simplicity in operation and precise control on the structure and location. SPM lithography techniques based on mechanical scratching, anodization of Si surfaces, electrochemical decomposition of self-assembled monolayer, electric field induced chemical reaction and electrochemical reaction in solution using protected SPM tips have been developed in the last decade. More recently, a "dip-pen" lithography method has been reported that uses an AFM tip as a "nib" to directly deliver organic molecules onto an Au surface[2-4]. This technique used a tiny water droplet condensed on the AFM tip as the transfer media to dissolve the organic molecules and deliver them to the surface, much like the ancient "dip-pen" invented several thousands years ago. Here we report a more general method based on this AFM "dip-pen" technique that not only can deliver organic molecules on to Au

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surfaces, but can also be used to directly fabricate metal and semiconductor line and dots on to surfaces.

When AFM is used in air to image a surface, the narrow gap between the tip and surface behave as a tiny capillary that condenses water from the air. This tiny water droplet is actually an important factor that has limited the resolution of AFM in air. "Dip pen" AFM lithography was developed by utilizing the water droplet to transport organic molecules from the tip to surface. In our new techniques described here, we also use the tiny water droplets on the AFM tips as the transfer media. However, unlike in the previous AFM "dip-pen" method where water is just used as a solvent of the molecules, we turned this tiny water droplet into a small electrochemical cell in which metal salts could be dissolved, reduced into metals electrochemically and deposited on the surface (Fig. 1). This development significantly expended the scope of "dip-pen" lithography, making it a more general nano-fabrication technique that not only can be used to deliver organic molecules on to surfaces, but also capable to fabricate metallic and semiconducting structures with precise control of location and geometry. Because of the electrochemical nature of this new approach, we call this technique electrochemical "dip-pen" nanolithography (E-DPN).

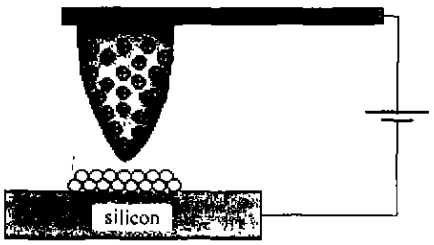

Fig. 1 Schematic draw of Dip-Pen nanolithography

We have investigated the deposition of several metals and semiconductors on Si surfaces using the E-DPN technique. Here we take the deposition of Pt metal as an example. The experiments were performed using a Nanoscape IIIa AFM (Digital Instruments) with the included lithography software. 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 a solution of H_2PtCl_6 water (0.5 ~ 1% by weight) and blown dry with compressed air. The substrate used in the experiments were P type Si(100) wafer after cleaning by a standard method: First the wafers were irradiated under UV light in air for 30 minutes to oxidize organic contaminants on the surface and to form a thin oxide layer, then it was dipped into 1: 10 HF aqueous solution to remove the oxide layer and contaminants. After that the wafers were oxidized again by UV irradiation for 10min to form a hydrophilic surface. In the E-DPN process, the surfaces were first imaged in tapping mode to find a suitable location. Then the scanning is stopped and the tip was brought into contact with the surface. To deposit Pt on the surface, a DC voltage was added between the tip and the surface with the surface being the cathode while the tip was being slowly moved across the surface in certain pattern controlled by the software. In this process, the $HPtCl_6$ molecules dissolved in the water droplet were electrochemically reduced into Pt metal on the cathode:

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

We have found that the relative humidity in the environment is one of the key factors for the process. We have found that a relative humidity between 40% and 60% is suitable for the process. The DC voltage needed for metal deposition depends on the type of salt we use and the surface resistivity. For Pt deposition, we normally chose to apply a DC voltage of 1V to 3V between the tip and the sample. Higher voltages tend to oxidize the Si wafers to create features made of SiO_2 rather then Pt metals. As shown in Fig. 2, a Pt line as thin as 50 nm can be created on Si surfaces with E-DPN technique. The height of the Pt line shown in the figure is ~0.4nm.

Many characteristics of the lines have convinced that they are metallic lines deposited electrochemically on the surfaces. Finally, the lines have catalytic activity towards the thermal decomposition of ethylene. As shown in Fig. 3, we have heated the Si wafer with one Pt line and one SiO_2 line created by E-DPN and AFM anodization in ethylene flow at 500℃ for 30

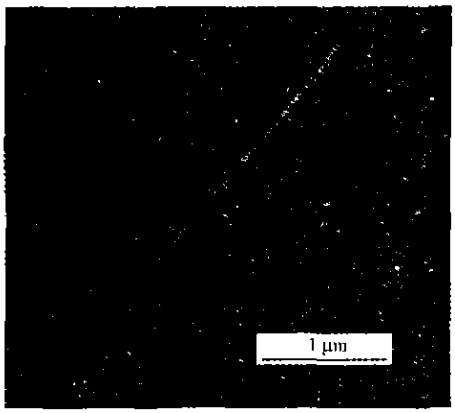

Fig 2　AFM image of a platinum line drawn by the E-DPN method under the condition of relative humidity 40% with a voltage of 4V and a translation speed of 5nm · s^{-1}

minutes. The Pt line showed a large amount of carbon deposition while the SiO_2 line showed no change. This observation is a strong proof that the features created with E-DPN technique are Pt lines since it is know that Pt is a good catalyst for the decomposition of ethylene. The height and width of the fabricated features using the E-DPN technique depend on several factors, including the humidity, scan speeds and applied voltages. We have shown that by varying these factors, we can change the height and width. An example is shown in Fig. 4, where by changing the scanning speed from 10 to 20nm · s^{-1}, we can change the height of the created features from 0.4nm to 0.2nm. However, controlling the height and width of the created features is not an easy task since they also depend on the shape of individual tips used for the fabrication and the relative humidity in the environment. Nevertheless, we have shown that some degree of control of the feature

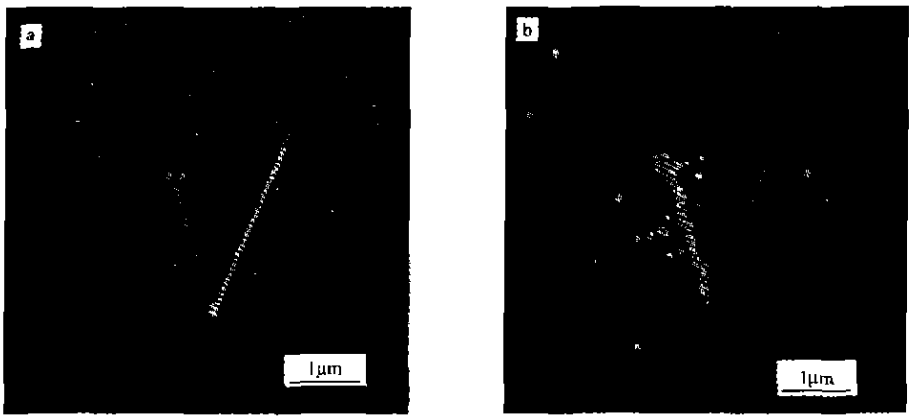

Fig. 3　(a) The character "V" composed of platinum (left) and silicon oxide (right). The Pt line is drawn with a voltage of +4V between the tip and the wafer and a scan speed of 10nm · s^{-1}. The SiO_2 line is created with a −10V voltage to oxidize the surface and the scan speed is 50nm · s^{-1}. The relative humidity is 58%

(b) The same area of the wafer after heated at 500℃ under the atmosphere of ethylene in argon for an hour

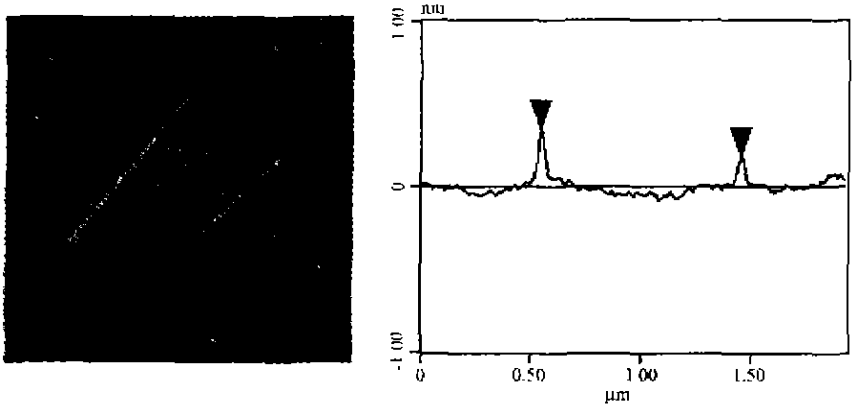

Fig. 4　AFM image and height profile of two Pt lines drawn at different scan speed. Left line at 10nm · s^{-1} and right line at 20nm · s^{-1}. The voltage applied at the tip is 3V for both lines and the relative humidity is 43%

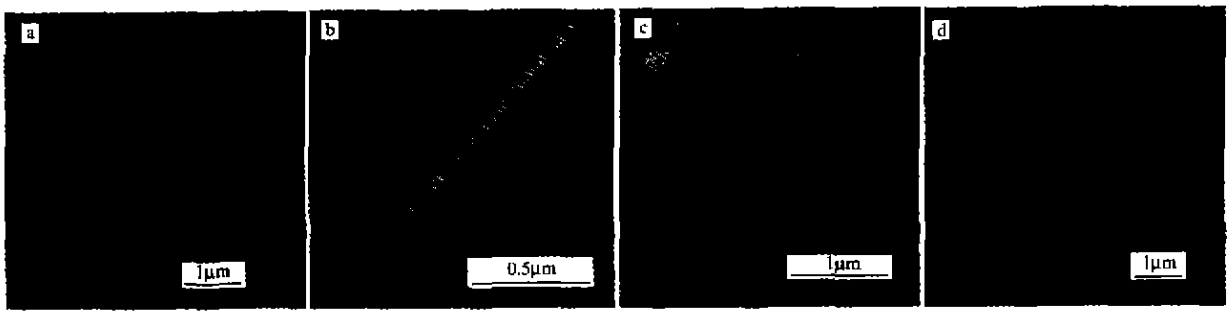

Fig. 5 (a) A silver line drawn by E-DPN method with $AgNO_3$ solution as the ink. Experimental conditions: relative humidity, 42%, voltage: 4V, translation speed: 20nm · s^{-1}

(b) A germanium line with the saturated solution of GeO_2 in 0.05mol · L^{-1} NaOH as the ink, relative humidity: 42%, voltage: 5V, translation speed 100nm · s^{-1}

(c) A palladium line using $PdCl_2$ as the precursor Relative humidity: 38%, voltage: 3.5V, scan speed: 10nm · s^{-1}

(d) A copper square with $CuCl_2$ as precursor. Relative humidity: 46%, voltage: 3V, scan speed: 50nm · s^{-1}

dimensions can be achieved using the E-DPN techniques. More works targeting on delivering known amount of metal atoms to the surfaces by monitoring the current between the tips and surfaces 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 succeded in created features made of Au, Ge, Ag, Cu etc. In principle, any metal or semiconductor that can be electrochemically deposited from water-soluble salts could be delivered to a surface with precise control of positions to form features with nanometer dimensions using this technique. A few examples are shown in Fig. 5.

In summary, we have developed a new E-DPN technique that can be used to directly fabricate metal and semiconductor features with nanometer dimensions. Comparing with previously reported DPN technique, the new technique has significantly expended the scope where DPN nanofabrication technology can be applied. Such a simple but powerful technique would enable us to fabricate simple nanoelectronic devices with sections made of different metals and semiconductors. It also allows us to deliver different chemicals to specific locations for localized chemical reactions. More importantly, the fundamental idea beneath this technique, which is to use the tiny water droplets between the tips and surfaces as the reaction vessels, could be applied to develop more powerful techniques that are based on localized chemical reactions rather than limited to electrochemical reactions. The only requirement for such reactions is that the reaction products to be water-insoluble. The large number of suitable reactions available will make AFM DPN nanofabrication of very powerful tool for making unique nanodevices as well as chemically modifying the devices made by more conventional nanofabrication techniques.

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