

Effect of the Experimental Condition on AFM Electrochemical Dip-Pen Nanolithography

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Effect of the Experimental Condition on AFM Electrochemical Dip-Pen Nanolithography

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Abstract

Electrochemical Dip-Pen Nanolithography (EDPN) is a new SPM Lithography technique that uses the system of tip – condensed water meniscus – surface as a tiny electrolyte cell to directly “write” metallic features on the surfaces. We discussed the factors that may affect the EDPN. The effects of humidity and applied voltage were investigated.

Introduction

One hot topic in the area of nanoscience and technology is to get the nanofeatures with desired size, morphology, composition, and location by a precisely controlled procedure. Scanning Probe Nanolithography (SPL) has been very successful in this field. Many kinds of SPL based techniques have been developed and demonstrated to be very efficient in manufacturing designed nanostructures^[1]. Dip-Pen Nanolithography (DPN) was first established by Mirkin et al. in Northwestern University^[2].

In DPN, the small water meniscus formed between the AFM tip and the substrate due to the capillary effects of the sharp tip-surface system, which is very unfavorable to the AFM imaging, was applied as the transport media to deliver the solutes from the tip to the surface^[2].

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Long chain organic molecules with thiol ends were very successfully transferred from the tips to the gold surfaces^[2-4], and those with silazane ends could be transferred from the tips to the Si/SiO_x surfaces^[5], and formed monolayers of organic molecules on the surfaces with controlled shape and location. These organic patterns produced with DPN can be further used to absorb proteins and form protein nanoarrays^[6]. Based on the self-assembling properties of -SH containing organic molecules on gold surfaces, and -Si-OH containing organic molecules on silica surfaces, modified oligonucleotides with thiol or silazane groups can also be patterned on gold or Si/SiO_x surfaces^[7].

Li and Liu et al. first proposed to use the tip-water meniscus-surface system as a tiny electrolytic cell to pattern metal features on surfaces^[8]. As shown in Fig.1, water-soluble salts of metals are loaded on the tips. While the tip is approaching the surfaces, spontaneously formed water meniscus between the tip and the surface dissolves a little amount of salts. When a positive voltage is added between the tip and the surface, the metal ions dissolved in the small water droplet will be reduced and deposited on the cathode, i. e. the surface. By controlling the movement of the tip, many kinds of nanofeatures can be obtained with different shapes and sizes. This new DPN technique is called Electrochemical Dip-Pen Nanolithography (EDPN). The basic idea of this EDPN is to apply the small water droplet condensed on the tip as a tiny reaction vessel. Indeed, many kinds of reactions besides the electrochemical ones can also take place in this nano-sized reaction vessel, including the surface reduction of metals^[9], polymerization^[10], and sol-gel reaction^[11]. With this EDPN, we were able to directly “write” many kind of nanostructures made of gold, silver, platinum, palladium, germanium et al. on the silicon surfaces with a precise control over the shape and

location^[8]. In this paper, we discuss the important factors that may affect the EDPN.

Experimental

A Digital Nanoscope IIIa Multimode SPM was used in all experiments. We used the accessory nanolithography software to control the movement of the tip and the voltage applied between the tip and the surface. A humidifier and a dehumidifier were used together to control the humidity of the atmosphere. Before EDPN, a normal tapping mode silicon cantilever was dipped in the ink solution, and then blow-dry.

Results and Discussion

Many factors, such as the humidity, scan speed, applied voltage, character of tip (shape and conductivity), property of the wafer (conductivity and surface property), amount of salts on tip, property of metal salts, may affect the reduction of the metal ions, and then affect the formation of the nanostructures. Scan speed, humidity and applied voltage are three factors that are easier to handle. We have shown the effect of scan speed in the previous paper^[8]. Here, we further investigated the effect of humidity and applied voltage.

EDPN needs a somewhat humid atmosphere to form a tiny water droplet on the tip, which acts as the electrolytes. When the relative humidity was too high, “large” amount of water will be condensed on the tip and formed a “big” water droplet. Then almost all salts coated on the tip are dissolved. Therefore, when a positive voltage is applied between the tip and surface, the metal ions should be reduced spontaneously, and all metals deposits on the

surfaces immediately. When the atmosphere is too dry, there is not enough water condensed on the tip, then EDPN cannot be performed. Fig.2A shows the electrochemically produced germanium particles scattered on the surfaces within the area covered by a “large” water bubble when the relative humidity is as high as 50%. Saturated solution of GeO_2 in 0.05 M NaOH (pH=7) was used as the ink. When the relative humidity was reduced to 46%, the particle-scattered area became narrower, with a shape somewhat like a red pepper (Fig.2B). When the relative humidity goes to 41%, a continuous line of germanium can be obtained (Fig.2C). When the relative humidity is lower than 40%, we could not get any germanium nanostructures.

When the voltage applied between the tip and the surface is lower than a critical value, no electrochemical reactions can take place, then no nanostructures can be written on the surface. The critical value is decided by many factors, such as the resistance of the tip and the wafer, the property of the salts loaded on the tip, the humidity of the atmosphere, etc. When the applied voltage is higher than this critical value, the increasing of it will lead to the increase of the current of the system and then enlarge the amount of metals reduced per unit time. Therefore, the size of the nanostructures produced by EDPN should increase with the increase of the applied voltage. Unlike Au, Pd, Pt et al., EDPN of Cu with CuCl_2 or CuSO_4 as inks normally obtain a series of dots instead of a smooth line^[8]. This may be caused by the low surface affinity of copper on silicon. Fig.3 presents two copper dots produced at different voltages. When a voltage of 2 volts was applied, the height of the dot is 8 nm. But when the voltage increased to 5 volts, the produced copper dot is as high as 27 nm. This proves that the voltage applied between the tip and the surface will tremendously affect the EDPN.

In conclusion, scan speed, humidity and voltage applied are all important factors for EDPN. It needs a proper humidity to form a tiny water droplet to act as the transport media. Increasing the voltage applied will increase the size of the produced nanostructures. We can obtain nanostructures of various metals with desired shape, size, height and location on the surfaces by carefully control the lithography condition.

Acknowledgment

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Figure Captions:

Fig.1 Schematic drawing of the EDPN

Fig.2 AFM images of germanium features by EDPN at different humidity, A) 50%, B) 46% and C) 41%, bars in the pictures all represents 1 μ m.

Fig.3 Applied voltage dependence of the height of Cu dots by EDPN, A) 2V, B) 5V.

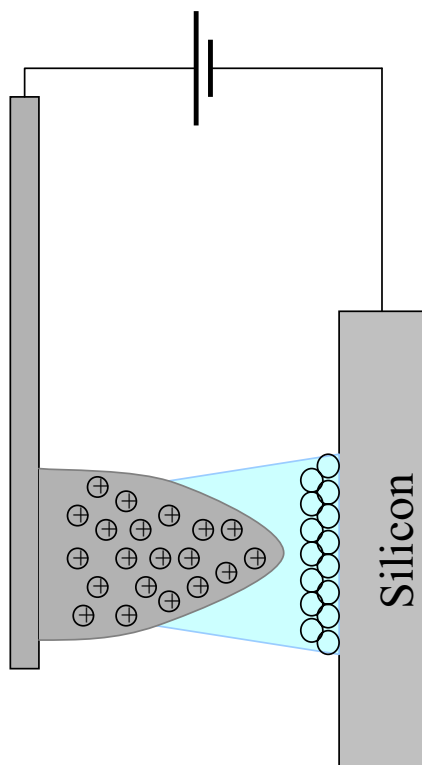


Fig.1

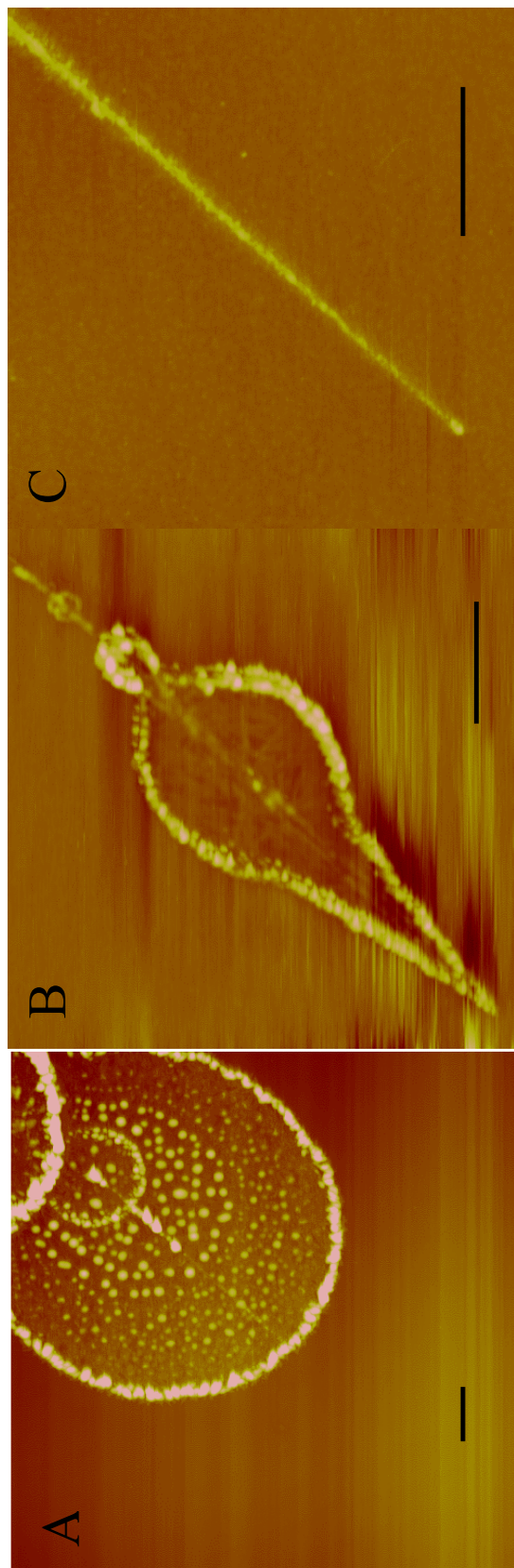


Fig.2

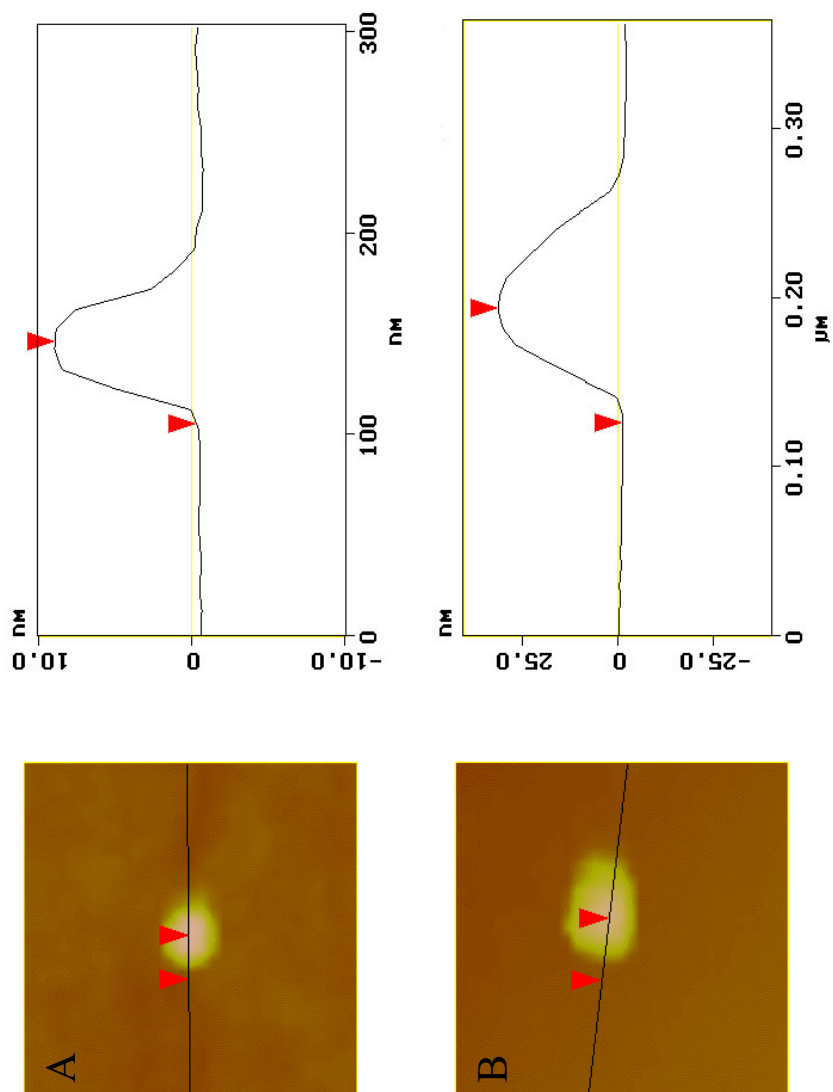


Fig.3