Embossed and Intaglio Nano-Patterning using Nanopipette based on the QTF-AFM System

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ABSTRACT

We demonstrated embossed and intaglio nano-patterning using Nanopipette based on the QTF-AFM (Quartz Tunning Fork-Atomic Force Microscopy) system. Used materials in the patterning system were nanoparticles solution and acetone for delivery solution mica and flat plastic for substrate mica. By realizing the nano-scaled liquid ejection technique with the pulled nanopipette conbined QTF-AFM, various lithography systems can be realized with any liquid solution and sample, such as embossed and intaglio nanolithography. After filling the target solution, the inserting side of aperture was closed with commercial epoxy for the purpose of protection from the evaporation of liquid solution and control of the ejected liquid volume. After forming of capillary condensation between nanopipette tip and surface, we applied electric field to extract out the inside liquid to the substrate. The nano-patterned size could be controlled by the nanopipette's size and applied electric field.

Keywords: Nano-Patterning, Nanopipette, Emboss, Intaglio

1 INTRODUCTION

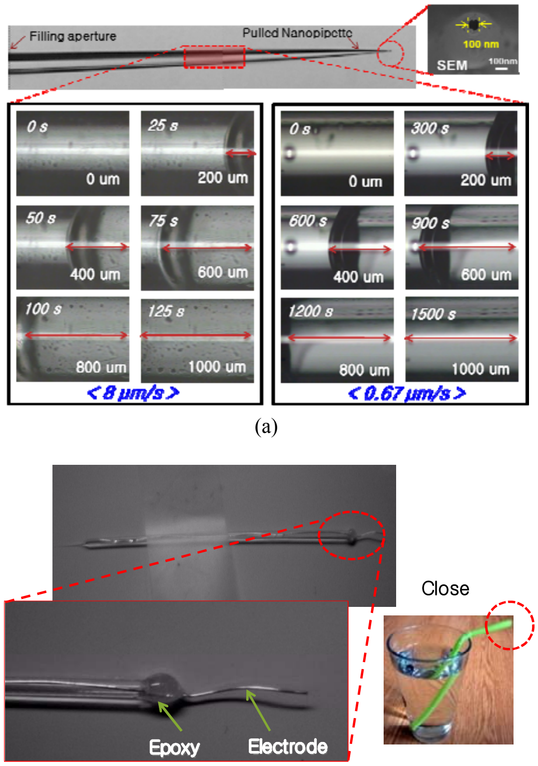
Nanolithography system is the versatile apparatus to fabricate the nano-patterning directly on the substrate with various different materials [1]. There have been many different approaches to realize the nanolithography system, such as nano-imprint [2], electron beam lithography [3], dip-pen lithography [4], molecular self-assembly technique [5], and so on. However, the liquid solution transport mechanism through nano-aperture is not well established. In this work, we demonstrate the nano-liquid delivery system using nano-apertured pipette combined with QTF-AFM to transport the target liquid solutions into the substrate. The control of a small amount of liquid ejection is hart to realize cause of fluidic property of liquid itself. Once extrusion occurs from the nano-aperture, it is hard to stop the flow continuum behavior without an extraordinary treatment. We proposed controllable nano-patterning system using simple closing treatment of the filling side of aperture with commercial epoxy in order to suppress the extraction behavior of inside liquid. With this technique, any liquid solution can be used to fabricate nano-patterning on the desired region. Especially, intaglio patterning is available using acetone for solution and flat plastic for substrate. We used amplitude mode QTF-AFM feedback system to control the distance between tip and surface [6]. To measure the amount of ejected solution, we choose the current detection technique using generally used IV converter (LF356). We can also control the patterning size with Nanopipette size and Humidity, approach time, distance, applying voltage. Used substrate was coated with Au using Commercial Metal Sputter on the SiO_2 substrate.

2 LIQUID EJECTION VIA THE PULLED NANOPIPETTE COMBINED QTF-AFM

Nanolithography was performed by simply fabricated pulled nanopipette attached quartz tuing fork – AFM system. We can investigate the field-induced nanoscaled liquid ejection and transport of the liquid, and finally nano-scaled patterning on the substrate. Any kind of nano-materials can be used in this system.

2.1 The pulled nanopipette

The pulled nanopipette was fabricated by commercial puller (Sutter Instrument, Co.). We chose borosilicate (outer diameter; 1 mm, inner diameter; 0.7 mm) in order to make smaller apertures and thinner shapes. Furthermore, we found that the borosilicate nanopipette tip had the least impact on a quality factor. With variation of pulling parameter, various sizes of pulled pipette’s aperture can be made (30 nm ~ 20 μm). And the aperture size can be defined by typical current measurement system and scanning electron microscopy (SEM) images. Fig. 1 (a) shows the shape of the 100 nm aperture nanopipette and SEM image. After fabrication of the pipette, evaporation behavior was tested using optical microscope through open side (filling aperture, in Fig. 1 (a)) of pipette for control of the ejected nano-liquid’s volume. Filling the nanopipette can be easily completed by capillary force, which formed between filament and inner surface of the pipette. After filling of target liquid solutions (18MΩ pure deionized water and acetone), we measured the evaporation rate of inside liquid out to the air through filling aperture. Measured evaporation rate of acetone (8 μm/s) was faster than deionized water case (0.67 μm/s). It is because acetone has higher order of volatilization rate. To prevent the evaporation of liquid and control of ejected liquid, filling



(a)

(b)

Figure 1: (a) The pulled nanopipette and the captured evaporation behavior using optical microscope. (b) After filling of liquid solution, the filling aperture is closed using commercial to prevent the liquid evaporation into the air.

aperture was closed with epoxy in Fig. 1 (b). This idea came from straw in the water. The water can be sustained inside of straw and is not extruded out into the air cause of inner pressure by closing the upper side of aperture.

2.2 QTF-AFM system

The QTF can be used as a high sensitive force sensor. But it has a nonlinear effect due to the stray capacitance itself. Thus, we remove this capacitance effect with electronic circuit see in Fig. 2 (a). Using another leg tied QTF which has same value of stray capacitance and opposite phase, the nonlinear effect was removed [7]. Therefore, this sensor can be used as a simple harmonic oscillator. The resonance frequency of used quartz tuning fork was 32,768Hz, which frequency can be changed by attaching the pulled nanopipette and driving amplitude was about 0.1 mV. Even the liquid filled nanopipette attached to the one side of QTF's prong, the quality factor of QTF is not decreased deeply. Because the nanopipette was made by borosilicate pipette, which tip apex was relatively soft compared to quartz pipette. As this tip approach to the sample, the frequency of QTF increased cause of perturbation of nucleation of water meniscus. This phenomenon can be expressed by followed equation of motion,

$$m\ddot{x} + b\dot{x} + kx = F\cos\omega t + F_{perturb} \qquad (1)$$

where m is the effective mass of the probe, b is the damping coefficient, k is the spring constant, F is the amplitude of the drive, and $F_{perturb}$ is the interaction force. As the forces interact on the tip of QTF as approach to the surface within 10 nm, the signal is changed and force can be interpreted using this equation of motion. After solving of this equation, perturbed force's elasticity and viscosity can be derived,

$$\begin{pmatrix} k = \dfrac{F}{A}\sin\theta + m\omega^2 - k_{\text{int}} \\ b = \dfrac{F}{A\omega}\cos\theta - b_{\text{int}} \end{pmatrix} \qquad (2)$$

where ω is the resonance frequency due to the perturbation and A is the free oscillation amplitude. Using this equation, we can study about nano-scaled liquid's mechanical properties.

2.3 Experimental setup (Nanopipette combined QTF-AFM)

Fig. 2 (b) shows diagram of proposed nano-patterning system. For nano-scaled patterning we used liquid droplet by electro ink-jet ejection method with keeping distance using distance regulated AFM system. We employed the non-contact, small-modulation (< 1 nm) shear-mode QTF-AFM system, because it easily detect only shear motion force, which can be formed by confined condensed nano-scaled water meniscus between apex of nanopipette and surface. The experimental procedure is consisted of three steps: approaching, applying electric field, and liquid election. We could measure the current response with typical IV-converter (LF356, 10MΩ). Real image of experiment was shown in Fig. 2 (c), the tip can be easily approached to the surface with monitoring the reflection image with CCD camera and QTF's output signal. For displacement of surface, we used the small PZT-tube which could be moved to 400nm (z-direction), 600nm (y-direction), 600nm (x-direction).

3 EXPERIMENTAL RESULTS (EMBOSSED AND INTAGLIO NANO-PATTERNING WITH NANOPIPETTE COMBINED QTF-AFM)

To measure the distance between tip and sample, we engage to shear mode QTF-AFM system which was acted like shear motion of vertical side to the substrate. Thus, we can define the existence of naturally condensed nano-water meniscus. Fig. 3 (a) shows an approach curve with applying electric or no field. After forming of condensed water the tip retracted immediately to the opposite direction to stop the liquid extrusion. In the case of no electric field, the rupture distance, which present the volume of liquid formed between tip and sample, was 10 nm. However, the rupture distance extremely increased in the presence of electric field (about 270 nm). This is evidence of liquid extrusion from inside of nanopipette.

Temperature and humidity are important factors in the experiment. The humidity variation leads to the change of the resonance frequency of QTF and the temperature variation can affect the whole system due to thermal expansion. To maintain the temperature and humidity within the required control range, a double chamber setup was employed by inserting an acryl chamber inside the Faraday cage chamber for shielding against electromagnetic noise. In particular humidity is more important. At low humidity condition & small apex size of Nanopipette, the patterning size could be small. On the contrary, at high humidity condition & big apex size of nanopipette, the patterning size could be large enough. Approach time, distance, applying voltage also influence to the size of patterning.

Fig. 3 (b) shows the results of embossed nano-patterning on the clean Au-coated substrate with nanoparticles liquid solution. After ejection of liquid solution on the substrate, the solution was evaporated onto the air, and nanoparticles can be remained. After forming of nano-patterning, AFM image can be gained using same nanopipette combined QTF-AFM system. Using this technique, any target nanomaterial can be taken. In the case of intaglio process of nano-patterning, we choose the acetone solution to remove the surface materials with flat plastic, in Fig. 3 (c). The plastic surface can be deformed with contact of several femtoliter volume of acetone solution. After process, we took the SEM image with this plastic sample. This technology can be applied with the selective biomolecule's removing system.

4 CONCLUSION

In this paper, we demonstrated that emboss and intaglio nano-patterning using nano-scaled water ejection nanopipette QTF-AFM, such as nano ink-jet. We have to progress further more small and more stable work about nano-patternings. Nano-aperture sizes of pulled nanopipette can be reduced by optimizing the pulling parameters. Organic/inorganic materials research can be avaiable using this technology combining with a fluorescence microscope Combining We expect that this system could be used in researching of nano-patterning of a variety of liquid solution in bio-nanotechnology.

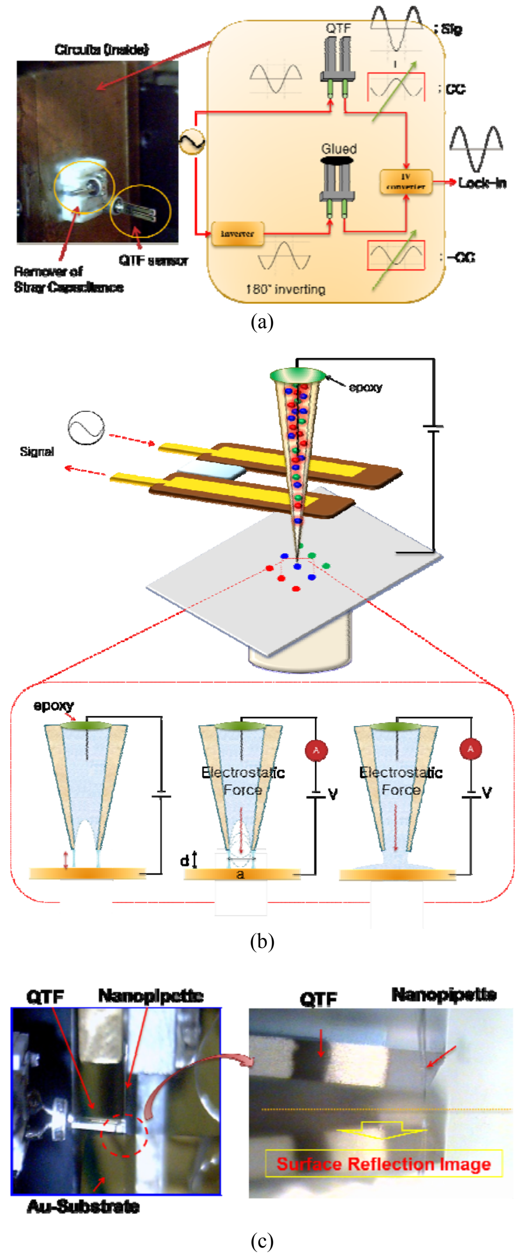
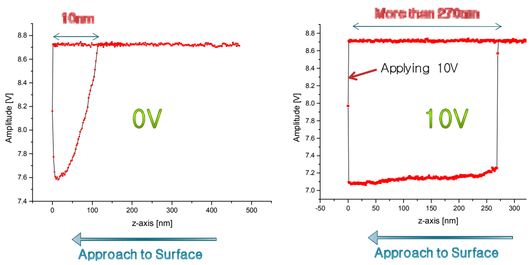


Figure 2: (a) Removing QTF's nonlinear property with another tied leg QTF and electronic circuit. (b) Diagram of experimental system and procedure (approaching, applying electric field, ejection). (c) Nanopipette combined QTF-AFM system. Side view of nanopipette attached QTF. While approaching, the tip can be easily controlled with monitoring the reflection image with CCD camera and the QTF's output signal.



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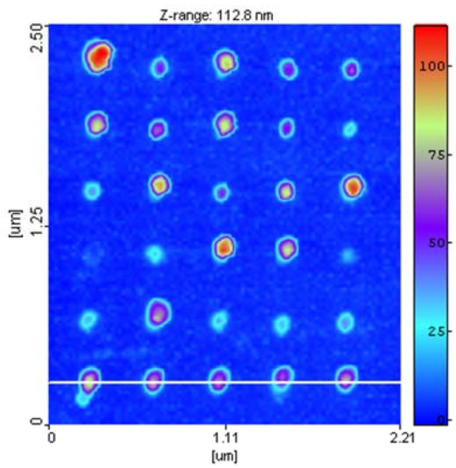

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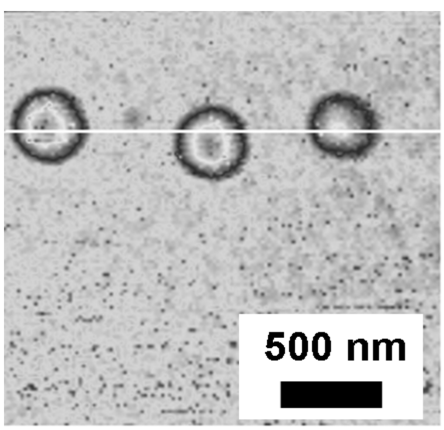

(c)

Figure 3: (a) Approach curve of system. At no electric field, the rupture distance was 10 nm. However, at +10 V, the confined water meniscus was elongated over 270 nm. This is evidence for liquid ejection from inside of nanopipette. (b) Embossed nano-patterning on the Au-surface. (c) SEM image of intaglio nano-patterned surface. (approaching, applying electric field, ejection).

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