Ultramicroscopy 110 (2010) 733–736

Contents lists available at ScienceDirect

Ultramicroscopy

journal homepage: www.elsevier.com/locate/ultramic

Fabrication of ionic liquid thin film by nano-inkjet printing method using atomic force microscope cantilever tip

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ARTICLE INFO

Keywords:
Local deposition
Ionic liquid
Thin film
Atomic force microscopy

ABSTRACT

We demonstrate the fabrication of thin films of ionic liquid (IL), 1-butyl-3-methyl-imidazolium tetrafluoborate, by nano-inkjet printing method using an atomic force microscope (AFM) cantilever. The IL filled in a pyramidal hollow of the AFM cantilever tip was extracted from an aperture at the bottom of the hollow and deposited onto a Pt substrate when the bias voltage was applied between the cantilever and the substrate. We succeeded in fabricating IL thin films with a thickness of 4 nm. The areas and thicknesses of IL thin films were controlled by the fabrication conditions in this method, which is also useful for the investigations of nanometer-scale properties of ionic liquid.

1. Introduction

Ionic liquids (ILs) are salts composed of cations and anions, which form stable liquids at room temperature. They have unique characteristics such as extremely low volatility, high ionic conductivity, and so on [1]. Their typical applications include reaction and extraction solvents [2,3] and electrolytes for dye-sensitized solar cells [4]. Since ILs have favorable properties for lubricants, the applicability of ILs as lubricants has been investigated by several research groups [5–7]. Some ILs are good electrical and heat conductors with chemical stability in various circumstances including vacuum environments at high temperatures. They are especially suitable as the lubricants for micro/nano electromechanical systems (MEMS/NEMS) [8]. It is essentially important to study structures and mechanical properties of IL thin films in order to apply ILs for the lubrication of MEMS/NEMS.

Atomic force microscopy is not only a powerful imaging tool but also a tool for investigation of friction, wear and lubrication on a nanometer scale. The lubrication characteristics of the IL thin film prepared by the dip coating technique have been studied using AFM [5,7,8]. They reported that the IL films, which are partially bonded with the atoms of the substrate surface, showed good lubrication properties. Development of the fabrication techniques of the IL thin films with a designed area and thickness is indispensable for further investigations of lubrication mechanisms. Fabrication of IL thin films by dip-pen nanolithography (DPN) technique using AFM cantilever tip [9] has been recently reported [10,11]. However, those films made by the DPN were not as uniform as those prepared by the dip coating technique and not ideal for the precise investigation of lubrication characteristics. In addition, producing multiple films with different areas and thicknesses by DPN in a single experiment could be a problem because of a relatively small liquid volume on its tip.

We recently developed a nano-inkjet printing method using an AFM cantilever, which allows us to deposit ultrasmall liquid droplets onto a conductive substrate from the atomic force microscope tip by applying an electric field between the cantilever and the substrate [12], as schematically shown in Fig. 1. In this study we employed the nano-inkjet printing method to deposit multiple IL droplets to fabricate ultrathin films. We investigated the structures of the deposited IL thin films depending on the voltage pulse duration and also discuss the mechanisms of the coalescence of the droplets into a continuous thin film.

2. Experimental methods

We used silicon nitride cantilevers (Olympus Co., OMCL-HA100WS) with a pyramidal hollow tip for the nano-inkjet printing and the subsequent characterization. The nominal spring constant and the resonance frequency were 15 N/m and 160 kHz, respectively. The backside of the cantilever was coated with Au, which was used for electrically grounding the cantilever. We drilled an aperture with a diameter of about 200 nm at the bottom of the hollow using a focused ion beam (FIB) system (SII NanoTechnology Inc., SMI-2050MS). The aperture, located several hundred nanometers away from the tip, was drilled from the backside of the cantilever such that the tip was not damaged.

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doi:10.1016/j.ultramic.2010.02.041

The typical height of the aperture from the tip apex was about 400 nm. We also removed the Au coating inside the hollow by the FIB to have the hydrophilic silicon nitride as an inner hollow surface. The cantilever was finally cleaned by a UV-ozone cleaner for 10 min before placing the liquid in the hollow.

We used water-miscible ionic liquid, 1-butyl-3-methyl-imidazolium tetrafluoroborate, $[BMIM]BF_4$ (KOKUSAN CHEMICAL Co. Ltd), as received from the manufacturer. The liquid has a conductivity of about 3.5 S/cm, which is high enough for the nano-inkjet printing. The IL was put into the hollow of the cantilever using a hand manipulator with a tapered glass pipette. The IL volume in the hollow was several picoliters.

We used a 4-nm-thick Pt film sputtered onto an atomically-flat Al_2O_3(0 0 0 1) surface as a substrate for this study. The Al_2O_3(0 0 0 1) surface was prepared by annealing at 1000 °C for 2 h in air [13]. The atomic terrace of the Al_2O_3 substrate was maintained on the Pt film surface and the root-mean-square (RMS) roughness on the terrace on the Pt film measured by AFM was about 70 pm over a 500 nm^2 area.

We used a commercially available AFM system (SII NanoTechnology Inc., SPA300 and Nanonavi Station). All experiments were performed under nitrogen atmosphere to avoid the formation of water meniscus between the tip and sample surface. The cantilever was vibrated at a frequency close to its resonance and the distance between the tip and sample was regulated by the amplitude modulation (AM) method, in which the damping of the vibration amplitude was kept constant. The nano-inkjet process including the tip positioning and the voltage application to the substrate was controlled by a script program. Although the nonlinear and asymmetric behavior of the piezoelectric tube scanner was not compensated during the script program control, it was compensated during the subsequent AFM imaging. The deposition positions were not calibrated, and the patterned areas in the AFM images appeared elongated in the vertical direction. To avoid causing a complicated movement of the tip during the application of the voltage pulses, the tip-sample distance feedback was turned off for the period from 1 s before the onset of the voltage pulse to 1 s after the pulse.

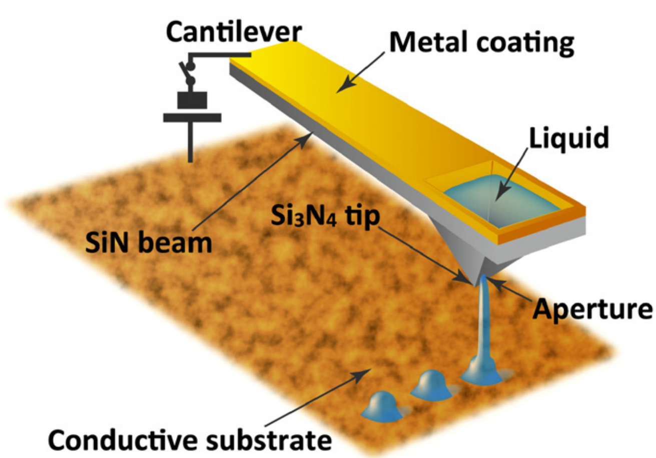

Fig. 1. Schematic of nanoscale inkjet printing method. The droplet was deposited from an aperture onto a conductive substrate by applying a voltage pulse between the substrate and the backside of the cantilever.

3. Results and discussion

We applied a series of voltage pulses of 9 V with a 2 s duration to make 5 × 5 arrays of the IL droplets while the average distance between the vibrating tip and the sample surface was kept about 7 nm. Fig. 2(a and b) shows AFM images of IL droplet arrays deposited under the same experimental conditions except that they were deposited using different cantilever tips and different separations, which were 300 and 200 nm, respectively. Scanning electron micrographs taken on the tip side of the cantilever showing the shapes of the apertures were shown in the insets of both figures. In Fig. 2(a), we can see circular deposits whose typical diameter is about 100 nm. The cross-sectional profile of the deposits (not shown) indicates that the shape of deposits is a plateau with a flat area on top whose height is about 2.5 nm. On the other hand, we can clearly see smaller but multiple deposits at each position where we applied the voltage pulse in Fig. 2(b). It is natural to think that the plateau droplets in Fig. 2(a) were deposited as a result of the continuous flow of the IL from the aperture during the voltage application, as shown schematically in Fig. 1. In contrast, we speculate that the multiple small droplets in Fig. 2(b) were deposited from several multiple asperities near the tip. The difference in the deposition mechanism between the two cases can be ascribed to a slight difference in the geometry of each tip and/or each aperture. In fact the shapes of the apertures on the two tips were different as shown in the insets of Fig. 2(a and b), where we can see that the latter was not an ideal circle but it was distorted.

Figures from Fig. 2(c to h) are consecutive AFM images of some multiple IL deposits. As shown in Fig. 2(c), we focused on two groups of multiple small droplets, and they were repeatedly imaged to investigate the change of the droplet structures. It is generally difficult to image liquid droplets without deformation or coalescence of the droplets by the conventional AM-mode AFM [14]. The structures of the droplets can be easily modified by the tip scans. We observed that the droplets in each group coalesced to form large droplets by the continuous tip scans as shown in the figures. The two large droplets shown in Fig. 2(h) finally

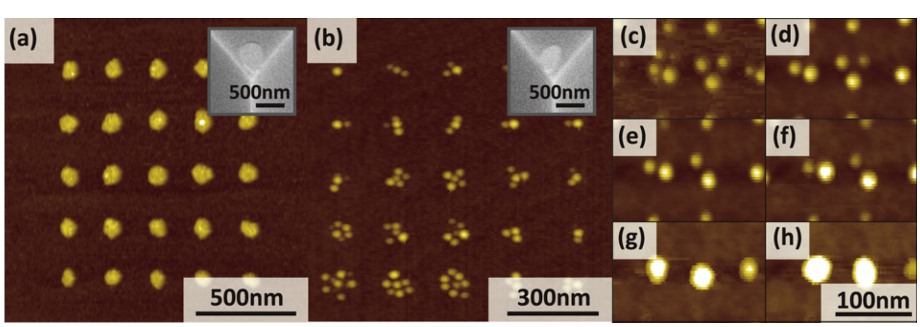

Fig. 2. (a and b) are topographic AFM images of 5 × 5 droplet arrays deposited using different cantilever tips. Voltage pulse of 9 V with the duration of 2 s was applied at each deposition position. (c–h) are consecutive AFM images of two groups of multiple IL deposits. The images show that the droplets in each group coalesced to form large droplets by the continuous tip scans.