Comparative Study of fabrication patterns of a ferroelectric polymer P(VDF-TrFE) on gold thin film and gold ball via Dip-pen Nanolithography

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ABSTRACT

A Gold ball with many atomically flat facets was prepared using melting method, and a gold thin film was prepared by sputtering. A comparative study of fabrication of a ferroelectric polymer poly(vinylidene fluoride-trifluorethylene) [P(VDF-TrFE)] patterns on the gold ball and gold thin film via dip-pen nanolithography (DPN) was presented in this paper. The transport rate of P(VDF-TrFE) to the gold ball was greater than that to the gold thin film due to less friction force.
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Key Words: dip-pen nanolithography, gold thin film, gold ball, atomic force microscopy, [P(VDF-TrFE)]

1 INTRODUCTION

Atomic force microscopy (AFM) was invented in 1986 by Binnig et al. At that time the main function of AFM was to visualize surface morphology at high spatial resolution [1]. In the following years, it was found that AFM tip could change the surface property mechanically or chemically. With the development of cantilevers, several AFM-based nanotechnologies, such as nanooxidation, nanomanipulation, nanografting, force nanolithography, nanocatalysis and dip-pen nanolithography, were developed rapidly, making AFM a promising technique for nanofabrication [2].

Dip-pen nanolithography [3] has drawn great attention and obtained rapid development since its invention due to its simplicity and high resolution. Arbitrary nanostructures composed of chemical(s) were fabricated at ambient condition by the deposition of chemical(s) from a coated tip to the substrate of interest during the contact between the tip and the substrate. The line width constructed via DPN was reported to be as narrow as 15 nm. Various materials such as thiols [3], biomaterials [4], inorganic materials or sol-based inks [5-6], and organic materials [7] were used as DPN inks. Nanostructures of some conducting polymers were also created by direct surface patterning or in situ polymerizing the generated patterns composed of monomer ink [8-9]. The substrate was extended from gold to Si, SiOx, glass and mica, and the tip was developed from a single tip to tip array [10], thus making DPN a versatile and efficient nanolithography.

Ferroelectric polymer is an important class of functional materials, which has potential applications in electrical, optical, biomedical, robotic, and sensing devices [11]. P(VDF-TrFE) was reported to show the highest ferroelectric polarization and electromechanical response among the known ferroelectric polymers [12], therefore, it was widely used as acoustic sensors and transducers [13-14]. Micro- and nanostructures of P(VDF-TrFE) were fabricated onto polycrystalline gold film via DPN. P(VDF-TrFE) molecules in these patterns are highly oriented and hold ferroelectric property [15].

The quality of DPN can be affected by many parameters, such as temperature, relative humidity, chemical affinity between the ink and the substrate, and surface property of the substrate. Temperature and relative humidity effect on DPN have been extensively studied in the thiol (ink) - gold (substrate) system [16-18].

In present study, we studied the effect of surface property on DPN by comparing the results of P(VDF-TrFE) transferred to a gold ball and a polycrystalline gold thin film. It is found that surface property plays important role in DPN process.

2 EXPERIMENTAL

2.1 Materials

P(VDF-TrFE) with a mole ratio of VDF/TrFE as 4/1 (Piezotech S. A), 99.5% acetone (Ajax Finechem), 30% hydrogen peroxide solution (BDH Laboratory), concentrated sulfuric acid (Aldrich) were used as received. 99.99% gold wire was supplied by TSL Jewelry Shop.

2.2 Preparation of Polycrystalline Gold Thin Film

Initially 10 nm Ti and then 30 nm gold were coated on *n*-Si (100) wafer by sputtering with ExplorerTM 14 Denton Vacuum.

2.3 Preparation of the Gold Ball

The preparation process of the gold ball is referred to literatures [19-20] with minor modification. A gold wire with diameter of 0.15 mm was rinsed with acetone and dipped in piranha solution (V/V=7/3 concentrated sulfuric acid / 30% H_2O_2. **Note**: piranha solution reacts violently with organic solvents) for 15 min to remove organic materials on gold surface. The wire was melted in CH_4 flame, and a small ball about 3 mm diameter was formed when the melted gold left the flame and re-solidified in the atmosphere.

2.4 DPN with P(VDF-TrFE)

A solution of 3.6 mg of P(VDF-TrFE) dissolved in 5 mL of acetone was used as the ink. The AFM tip was coated by dipping the cantilever in the above solution for 1 min, and blown dry with nitrogen, a thin film of P(VDF-TrFE) was coated on the cantilever surface after the volatilization of acetone, as visualized with a field emission scanning electron microscopy. DPN patterning and AFM imaging were performed with the coated tip and a commercial AFM (Solver P47H, NT-MDT, Russia). The silicon cantilever (contact "golden" silicon cantilever, CSG11) used for DPN was purchased from NT-MDT company, its typical spring constant, tip curvature radius and resonance frequency were about 0.03 N/m, 10 nm and 10 kHz, respectively. DPN patterning was operated in
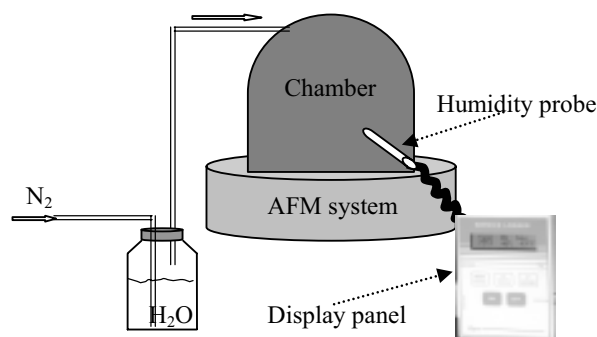

Figure 1: Schematic diagram of the AFM experimental system for DPN. AFM was placed in a chamber. Purge dry N_2 in to the system to obtain low relative humidity, whilelet N_2 pass through a water bottle to obtain high relative humidity.

contact mode with a contact force of 2.0 nN. The AFM system was placed in a chamber. The relative humidity (RH) was controlled by dry N_2 or humid N_2 purged into the chamber at a rate of 0.2 L/min and measured with a humidity and temperature sensor with an accuracy of ±2% (Cole-Parmer Instrument Company). Fig. 1 is the schematic diagram of the DPN experimental system. All the experiments were conducted at room temperature (about 22^oC) unless otherwise stated. Each data was averaged from five independent measurements.

3 RESULTS AND DISCUSSION

The surface topology of the flat facets on the gold ball was characterized using AFM, as shown in Fig. 2, some surface steps can be seen clearly, and the step height is ranged from 0.25 nm to 0.30 nm, close to the reported theoretical inter-atomic distance of gold, 0.288 nm [21]. Within each
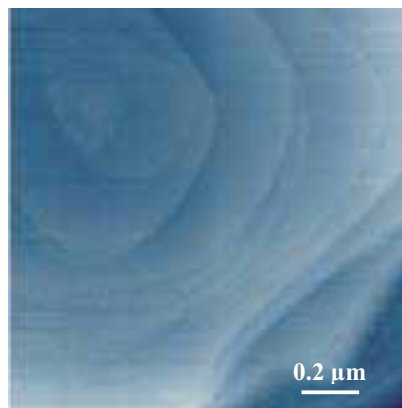

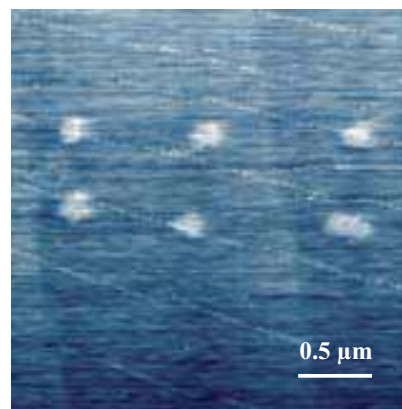Figure 2: topography of flat facets on a gold ball

Figure 3: topography of a P(VDF-TrFE) point array on gold ball via DPN (contact time: 60s, 80% RH, 22^oC).

step the surface is atomically flat with a roughness of less than 1 Å, while the roughness of the gold thin film prepared by sputtering is about 0.6 nm.

The topography and lateral force microscopy (LFM) images of the P(VDF-TrFE) patterns on a gold thin film fabricated via DPN may be referred to literature [15]. P(VDF-TrFE) was deposited on flat facets of the gold ball during the contact between the coated tip and the gold substrate and formed desired nano- to microstructures, which could be recognized in topography and LFM images. Fig. 3 gives a clear topography of a P(VDF-TrFE) point array on gold ball. The contrast is better and the pattern is more uniform than the patterns on a gold thin film due to less roughness, and the thickness of P(VDF-TrFE) in the patterns is about 1 nm, the same as that on the gold thin film. This indicates that P(VDF-TrFE) patterns on gold ball fabricated via DPN contain two layers of molecules [22].

Like on the gold thin film [15], hydrophobic polymer P(VDF-TrFE) on the gold ball exhibited darker contrast, i. e., smaller friction force between the tip and the substrate was produced, as illustrated in Fig. 4, the LFM image of a point array of P(VDF-TrFE) with nearly identical diameter shows darker contrast compared with gold substrate.
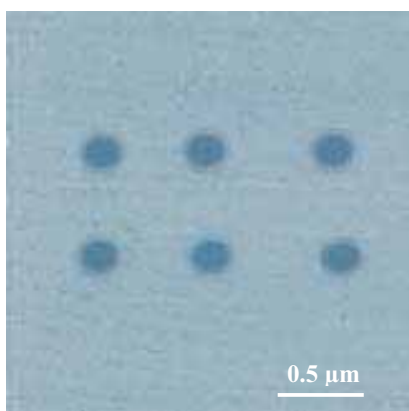

Figure 4: LFM images of a P(VDF-TrFE) point array fabricated via DPN on gold ball (contact time:60s, 80% RH, 22°C).

Fig. 5 is the curve of dot area (A) as a function of contact time (t) for the P(VDF-TrFE) patterns on the gold ball and gold thin film. The area was measured with an error of less than 10%. It can be found that A changes linearly with the contact time for both the gold ball and the gold thin film but with different rates. The slope of $A - t$ curve on the gold ball, 380 ± 34 nm^2 / s, is greater than the slope of $A - t$ curve on gold thin film, 150 ± 13 nm^2 /s. (Here we defined the slope of $A - t$ curve as the transport rate of

ink, υ, and $\upsilon = \dfrac{dA}{dt}$). Therefore, at the same condition, the transport rate of P(VDF-TrFE) to gold ball is greater than that to gold thin film. The reason caused the difference is believed to be the surface topography of substrate. As described above, the roughness of the polycrystalline gold film (about 0.673 nm) is greater than the roughness of the facets on the gold ball (less than 0.1 nm). Kasupke and Henzler have proved that roughness strongly influences the sticking coefficient (S_0) of molecule on solid surface, and

S_0 increases greatly with increasing surface roughness [23], Daikhin and Urbakh also reported that roughness increases the frictional force in confining system [24]. The increased sticking coefficient or friction force on the rough surface make the diffusion of the ink molecules more difficult, resulting in slower transport rate compared with less rough surface.
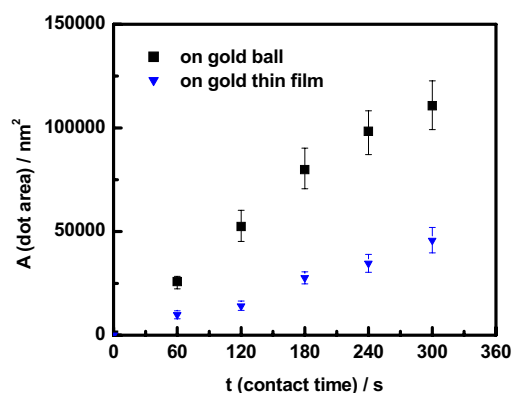

Figure 5: Plot of point area (A) as a function of contact time (t) at 80% RH, 22°C.

In addition, the gold ball can be reused for two more times for DPN after cleaned using a simple procedure. In this procedure, the gold ball was copiously rinsed with acetone, subsequently immersed in piranha solution for 15min, then copiously rinsed with deionized water, followed blown dry with N$_2$, finally cauterized on CH$_4$ flame to orange color. There is little difference between the patterns transferred to a fresh gold ball, and a gold ball cleaned once or twice. However, surface roughness increases with cleaning times. A gold ball is not suitable for DPN after being cleaned above three times.

In present work, the methods to prepare the gold film and gold ball were different, which results in different surface property. In order to study the quantitative relationship between surface roughness and the transport rate of ink, we

will prepare a series of gold substrates with various surface roughness using the same method in future.

4 CONCLUSIONS

The paper reported the effect of substrate surface on DPN using a ferroelectric polymer P(VDF-TrFE) as ink. Two kinds of gold surfaces, polycrystalline thin film and atomically flat facets were prepared by sputtering and melting methods, respectively. A comparative study of P(VDF-TrFE) patterns fabricated onto a gold ball and gold thin film via dip-pen nanolithography was presented. The surface roughness plays important role in DPN. The transport rate of ink to a rough substrate is slower than that to a relative flat substrate due to the increased friction force or sticking coefficient of molecules.

5 ACKNOWLEDGEMENT

REFERENCES

[1] G. Binnig, C. F. Quate and Ch. Gerber, Phys. Rev. Lett. 56, 930,1986.

[2] Q. Tang, S. Q. Shi and L. M. Zhou, J. Nanosci. Nanotech. 4, 948, 2004.

[3] R. D. Piner, J. Zhu, F. Xu and C. A. Mirkin, Science 283, 661, 1999.

[4] J. Hyurk, D. S. Ginger and K. B. Lee, Angew. Chem. Int. Ed. 42, 2309, 2003.

[5] L. M. Demers and C. A. Mirkin, Angew. Chem. Int. Ed. 40, 3069, 2001.

[6] L. Fu, X.G. Liu, Y. Zhang, V. P. Dravid and C. A. Mirkin, Nano Letters 3, 757, 2003.

[7] P. Manandhar, J. Jang, G. C. Schatz, M. A. Ratner and S. Hong, Phys. Rev. Lett. 90, 115505-1, 2003.

[8] P. Xu and D. L. Kaplan, Adv. Mater. 16, 628, 2004.

[9] M. Su, M. Aslam, L. Fu, N. Q. Wu and V. P. Dravid, Appl. Phys. Lett. 84, 4200, 2004.

[10] M. Zhang, D. Bullen, S. W. Chung, S. Hong, K. S. Ryu, Z. F. Fan, C. A. Mirkin and C. Liu, Nanotechnology 3, 212, 2002.

[11] H. S. Nalwa, Ferroelectric Polymers: chemistry, physics, and applications (New York: Marcell Dekker, Inc), 1995.

[12] H. Ohigashi and K. Koga, Jpn. J. Appl. Phys. 21, L455, 1982.

[13] P. Lum, M. Greenstein, C. Grossman and T. L. Szabo, IEEE Transactions on Ultrasonics Ferroelectrics and Frequency Control 43, 536, 1996.

[14] M. Toda, IEEE Transactions on Ultrasonics Ferroelectrics and Frequency Control 49, 299, 2002.

[15] Q. Tang, S. Q. Shi, H. T. Huang and L. M. Zhou, Superlattices and Mircostructures 36, 21, 2004.

[16] P. V. Schwartz, Langmuir 18, 4041, 2002.

[17] S. Rozhok, R. D. Piner and C. A. Mirkin, J. Phys. Chem. B 107, 751, 2003.

[18] S. Rozhok, P. Sun, R. D. Piner, M. Lieberman and C. A. Mirkin, J. Phys. Chem. B 108, 7814, 2004.

[19] T. Hsu and J. M. Cowley, Ultramicroscopy 11, 239, 1983.

[20] C. B. Ross, L. Sun and R. M. Crooks, Langmuir 9, 632, 1993.

[21] V. M. Hallmark, S. Chiang, J. F. Rabolt, J. D. Swalen and R. J. Wilson, Phys. Rev. Lett. 59, 2879, 1987.

[22] A. V. Bune, V. M. Fridkin, S. Ducharme, L. M. Blinov, S. P. Palto, A. V. Sorokin, S. G. Yudin and A. Zlatkin, Nature 391, 874, 1998.

[23] N. Kasupke and M. Henzler, Surf. Sci. 92, 40, 1980.

[24] L. Daikhin and M. Urbakh, Phys. Rev. E 49, 1424, 1994.