Measurement of DPN-Ink Viscosity using an AFM Cantilever

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ABSTRACT

The Dip-Pen Nanolithography (DPN) process uses a chemically coated scanning probe tip (the "pen") to directly deposit a material ("ink") with nanometer precision onto a substrate. Several experimental parameters have been observed to influence the ink transport in DPN. Among these, viscosity and density of the ink are the two important parameters which play a crucial role in ink transport in DPN. It is necessary to understand and control these parameters in order to optimize DPN processes for a particular application. Here we report on studies employing Atomic Force Microscopy (AFM) to measure the viscosity of DOPC used as ink for DPN. It is difficult to measure the viscosity of this ink using standard processes of measuring viscosity because the DOPC is not dissolved into some organic solution while writing. Therefore, we have employed the shift in resonance frequency of a vibrating cantilever in air and in DOPC to measure the viscosity of the DOPC ink as used in DPN.

Keywords: Dip-pen nanolithography, Atomic Force Spectroscopy, viscosity, resonance frequency

1 INTRODUCTION

Dip-pen nanolithography (DPN) [1, 2] has shown potential as a fast and simple surface patterning technology applicable for a variety of molecular "inks". In order for DPN to be developed for industrial applications, a better understanding of the process must be established. The degree of patterning reproducibility and effects of environmental parameters, such as temperature, humidity, and concentration of vapours or co-adsorbed solvents must be determined. The nanoscopic patterning behaviour of each molecular ink correlates well with the macroscopic behaviour of the substance. Macroscopic observations such as melting, solubility, viscosity, and adhesion are useful in predicting the nanoscopic patterning behaviour of a substance [3]. Although DPN has emerged as a useful tool for fabricating nanostructures, the mechanism of ink transport is far from understood, and a data-consistent, quantitative analysis of the factors that influence it has not been carried out. Some researchers have proposed that the meniscus is central to the transport process [1, 4] while others have concluded that in some cases water plays no role in the transport process [5].

The patterning process in a DPN experiment can be broken into two elementary processes – The first step is molecular transport from the tip to substrate, which in many cases involves dissolution of ink into the meniscus that naturally forms between the tip and sample under ambient conditions. The second step is ink adsorption onto the surface and monolayer formation. Both the transport and adsorption of ink molecules often depend on several variables, including temperature, humidity, the physicochemical properties of the ink and surface, writing speed and tip-substrate contact force. Among the other parameters mentioned above viscosity and density of the ink are the two very important parameters which play a crucial role in transporting the ink from the tip of the cantilever to the substrate. Viscosity determines the flow rate of a fluid. In case of DPN the transport rate of molecules of more viscous ink will be slower and vice a versa. Therefore, in order to have better control over the patterning process using DPN, it is essential to know the viscosity of the ink.

A widely used way to deliver the ink to the tips to coat them prior to writing is by so called "ink wells". The ink wells are microfluidic chips that allow depositing the desired ink dissolved in an appropriate solvent (chloroform) into an ink reservoir. The ink reservoir is large enough for convenient handling with pipettes and is connected to the actual micro wells for dipping the tips via micro channels (typical width ~ 6 µm). The ink wells are dried for few hours to allow for evaporating of the chloroform before using them for coating the tip of the cantilever. It is difficult to measure the viscosity of this ink using standard processes of measuring viscosity at experimental conditions. Therefore, to measure the viscosity of the ink, we have compared the resonance frequencies of a vibrating cantilever in air and in the viscous ink. From the shift in resonance frequency in viscous fluid we have found the product of viscosity and density of the fluid using a theoretical formula provided by Chen *et al.* [6].

It is shown earlier that the cantilever of an AFM can be utilized to measure the viscosity of a fluid [7, 8]. In dynamic mode of AFM, the resonance spectrum of the cantilever is determined by the mechanical and geometrical properties of the cantilever, as well as by forces exerted by the medium surrounding the cantilever. In fluid, the oscillations of the cantilever are damped as a result of the added drag on the cantilever [9]. The resulting increase in effective mass shifts the resonant frequency to a lower value, relative to its resonant frequency in air or vacuum. According to theoretical models, the resonant frequency of the cantilever is a function of the density and viscosity of the surrounding medium [6].

Here we report on studies aimed at employing the AFM to measure the viscosity of DOPC ink used for DPN. We have particularly used this ink because it can be used as a carrier ink for the multiplexed and/or massively parallel patterning of functional lipophilic materials. DOPC is also shown to be a suitable carrier for simultaneous deposition of multiple functional lipids, including biotinylated and nickel chelating lipids mixed in different stoichiometric ratios [10, 11]. We have also studied the effect of temperature and relative humidity (RH) on the viscosity of the ink.

2 EXPERIMENTAL METHODS

We have determined the viscosity of 1, 2-Dioleoyl-sn-Glycero-3-phosphocholine (DOPC) by measuring the change in resonance frequency of the cantilever of AFM in viscous fluid. We have used two different cantilevers for our experiments. Measurements were carried out using rectangular shaped silicon cantilevers from Applied NanoStructures, Inc., [12]. The nominal spring constant (k) values of the two cantilevers were 40 N/m (referred as cantilever I) and 45 N/m (referred as cantilever II) and the resonance frequencies (ω_0) were 300 KHz and 190 KHz respectively according to the manufacture's datasheet. All experiments were conducted on a NANOINK DPN 5000 system and at T = (20±1)°C and RH = (40±2)% unless otherwise stated. This system is combined with an AFM. The viscous fluid (DOPC) has been kept into the ink well (purchased from NANOINK [13]). An optical microscope image of the experimental set up has been shown in figure 1. The diameter of the micro wells where the tip of the cantilever has been dipped is 20 µm and the depth is 85 µm. Sample volumes were ~ 0.03 nl. The ink has been prepared from a DOPC solution (DOPC in chloroform, concentration 20mg/ml) purchased from Avanti Polar Lipids Inc [14]. It has been diluted to 10mg/ml for our experimental purpose. We have also studied the effect of temperature and RH on the viscosity of the ink solution. Measurements were performed at five different temperature values – 20°C, 25°C, 30°C, 34°C and 38°C. The temperature has been increased from 20°C to 38°C while keeping the RH fixed at (40±2)%. We have waited for approximately 2 hours before starting the measurements at a particular temperature so that the system reaches to its equilibrium state. The RH has also been varied from 10% to 75% in steps of 15 while keeping the temperature fixed at (20±1)°C. The resonance frequency of the cantilever in water at 20°C was used to calculate the constant K for a given cantilever using equation 3.

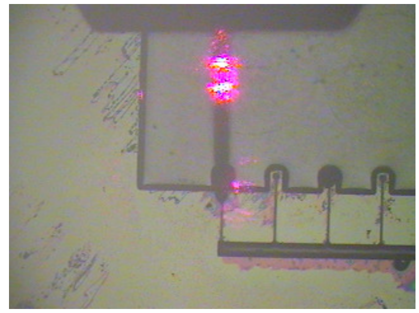

Figure 1. Optical microscopic image of the cantilever tip dipped in the micro wells containing DOPC ink.

3 EXPERIMENTAL RESULTS AND DISCUSSIONS

In the current study, we employed the AFM to measure the viscosity of the ink used for DPN. This technique is based on the shift in resonant frequency of the AFM cantilever submerged in a viscous medium [9]. As known from fundamental equations of fluid mechanics [15] when a body of arbitrary shape oscillates in a liquid, inertial and viscous forces acting against the motion scale with the size of the body and a characteristic length that defines the thickness of a viscous skin around the body. Chu [16] showed that the resonance frequency of a rectangular cantilever vibrating in a fluid could be approximated as (assuming the viscous fluid as inviscid one)

$$\frac{\omega_{fluid}}{\omega_0} = (1 + \frac{\pi \rho b}{4 \rho_C h})^{-\frac{1}{2}} \tag{1}$$

Where ω_{fluid} and ω_0 are the resonance frequencies in fluid and in air, respectively, ρ_c is the density of the beam, b and h are the width and thickness of the beam, and ρ is the density of the fluid. Later Sader [17] showed that equation 1 is not valid for viscous fluids and further modifications had been done. To simplify the numerical calculations, the dynamics of the cantilever can be treated as a one dimensional harmonic oscillator [18]. In this approximation, the resonant frequency of the oscillator in air, ω_0, is proportional to the square root of the spring constant of the cantilever, k, over the effective mass m*, i.e.,

$$\omega_0 = \sqrt{\frac{k}{m^*}} \tag{2}$$

Moreover, Chen *et al.* [6] theorized that the resonant frequency of the damped cantilever in a viscous medium is

$$\omega = \frac{1}{8}\left(\sqrt{9(K\eta\rho)^4 + 64\omega_0^2} - 3(K\eta\rho)^2\right), \qquad (3)$$

where ρ and η are the density and viscosity of the medium, respectively, and K is a constant for a given cantilever.

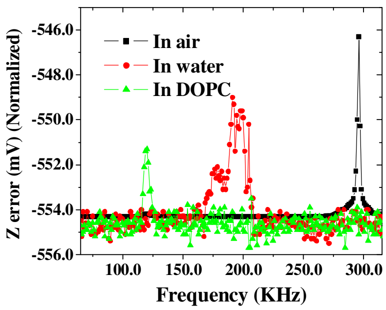

Figure 2. Resonance curves of cantilever I in air, water and DOPC. As the viscosity of the medium increases, the resonance frequency shifts to lower value.

In our experiments, we have first checked the resonance frequencies of both cantilevers (cantilever I and II) in air. The measured resonance frequency of cantilever I in air is 296 KHz which is very close to the nominal resonance frequency value of the cantilever according to manufacturer's datasheet. For cantilever II, the resonance frequency in air is measured to be 176.3 KHz whereas the nominal value of the resonance frequency in air is 190 KHz according to the manufacture's datasheet. To check the resonance frequency in the fluid, the cantilever was slowly brought down to the surface of the ink solution (DOPC) using the stepper motor. Figures 2 and 3 present the resonance response of the two AFM cantilevers in air, water, and DOPC. The corresponding resonance frequencies of cantilever I in air, water, and DOPC are 296 KHz, 191 KHz, and 123 KHz, respectively. The resonance frequencies of cantilever II in air, water, and DOPC are 176.3 KHz, 136.8 KHz and 83.8 KHz, respectively. This

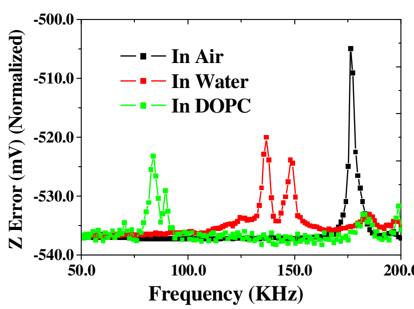

Figure 3. Resonance curves of cantilever II in air, water and DOPC.

shift in resonance frequency from air to water and DOPC can be attributed to a viscous dampening of the cantilever's oscillation. As we can see from figures 2 and 3 that when the cantilever vibrates in a viscous fluid mainly two changes occur to the resonance curve. Firstly, as the viscosity of the solution increases, it shifts the resonance frequency of the cantilever to lower values and secondly, the amplitude at resonance also decreases because of viscous damping. Figures 2 and 3 therefore, show the normalized amplitude values vs. driving frequencies to fit the data in a single graph.

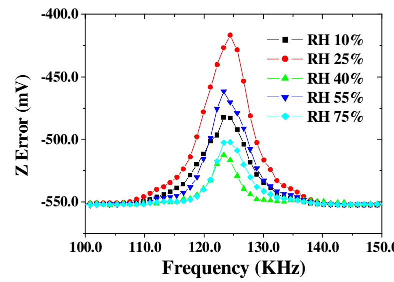

Figure 4 Resonance curves of cantilever I at different RH values.

Next we have studied the effect of RH and temperature on the viscosity of the ink. It is known that RH plays a crucial role in patterning the surface using DPN and the adsorbed water layer on a surface increases as the RH increases. Generally, in case of DPN, the water meniscus formed between the tip and the substrate helps the ink molecules to get transported to the surface. Specially, in case of DOPC, it has been observed that for writing with these molecules, RH should be $\geq$ 50% [10, 11]. In our experiment, we have first started with very low RH = 10% and then slowly increased the RH up to 75% in steps of 15. Figure 4 shows the resonance curves of cantilever I at different RH values.

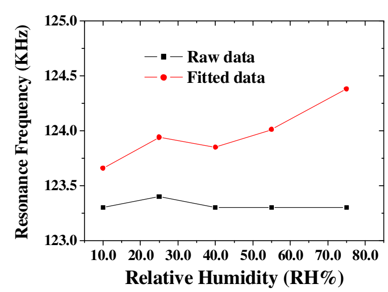

Figure 5 Resonance frequencies of cantilever I vs. RH. There is no significant shift in resonance frequencies for different RH values (both for raw and fitted data).

In figure 5 we have plotted the resonance frequencies vs. the RH (both raw and fitted data). The fitted data have been obtained by fitting the raw resonance curves using Lorentzian fit. For the raw data, the resonance frequency is the frequency corresponding to the highest measured amplitude. As we can see from figures 4 and 5 that there is no noticeable change in the resonance frequency as we increase the RH. Another important factor for studying the viscosity of a fluid is temperature. Generally, for liquid, viscosity decreases as we increase the temperature.

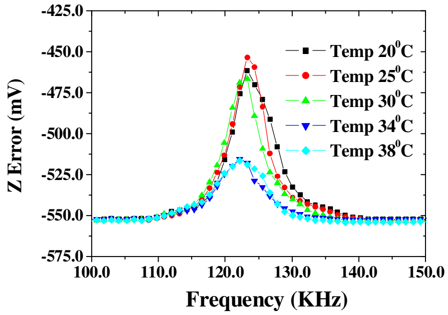

Figure 6 Resonance curves of cantilever I at different temperature values.

Therefore, we have also studied the effect of temperature on the viscosity of the DOPC ink. We have started from room temperature (T = 20°C) and increased it up to 38°C. The maximum temperature that we can achieve with our instrument is 40°C. We were particularly interested in the temperature range of 37°C ≤ T ≤ 40°C because for DOPC bilayer (on a solid surface) the L_β (lamellar gel) – L_α (liquid crystalline) phase transition occurs at this temperature range according to Leonenko et al. [19]. Figure 6 shows the resonance frequency curves for cantilever I at five different temperatures. As we can see from figures 6 and 7 there is no noticeable change in the viscosity of DOPC ink at this temperature range. It is important to mention here that the molecular orientation of DOPC inside the micro wells is not known but cannot be expected to be a well ordered bilayer structure but rather a random distribution. Finally, we have calculated the product of ρη for both the cantilevers using equation 3. For cantilever I, ρη is found to be 1.58 $Kg^2/m^4 \cdot s$ and for cantilever II it is 1.75 $Kg^2/m^4 \cdot s$.

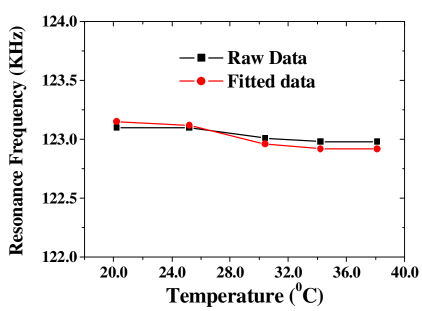

Figure 7 Resonance frequencies of cantilever I vs. temperature. There is no significant shift in resonance frequencies for different temperature values (both for raw and fitted data).

4 CONCLUSIONS

In this paper we have shown that the viscosity of inks used for DPN can be determined from the shift in resonance frequency of a cantilever vibrating in the ink as compared to that in air. This method for monitoring viscosity is of relevance to all biorheologic and microfluidic applications where functionalized cantilevers have to be used and it is a simple, yet reliable nondestructive procedure. We have also studied the effect of RH and temperature on the viscosity of the ink using the same method. In future studies we will apply this technique to screen broader range of different inks and ink mixtures to understand the influence of admixing (e.g. cholesterol in DOPC) on the viscosity.

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