Nanometer-scale flow of molten polyethylene from a heated atomic force microscope tip

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Abstract
We investigate the nanometer-scale flow of molten polyethylene from a heated atomic force microscope (AFM) cantilever tip during thermal dip-pen nanolithography (tDPN). Polymer nanostructures were written for cantilever tip temperatures and substrate temperatures controlled over the range 100–260 °C and while the tip was either moving with speed 0.5–2.0 µm s⁻¹ or stationary and heated for 0.1–100 s. We find that polymer flow depends on surface capillary forces and not on shear between tip and substrate. The polymer mass flow rate is sensitive to the temperature-dependent polymer viscosity. The polymer flow is governed by thermal Marangoni forces and non-equilibrium wetting dynamics caused by a solidification front within the feature.

1. Introduction

The atomic force microscope (AFM) [1] has been widely explored as a tool for nanolithography. In dip-pen nanolithography (DPN), an ink flows from an AFM tip onto a substrate [2, 3]. DPN requires that the ink has sufficiently high mobility to flow from the tip to the surface, and generally results in monolayer-thick nanometer-scale patterns of small molecules [3, 4], polymers [5–7], biomolecules [8, 9], or inorganics [10]. It is possible to modulate the flow of ink from the tip to the substrate by varying the temperature, which affects the ink mobility [11, 12]. In thermal DPN (tDPN), an AFM cantilever with an integrated resistive heater at the tip deposits inks that are solid at room temperature but that can flow at elevated temperature. Heated AFM tips can deposit nanometer-scale patterns of polymers [13–16], metals [17], and polymer–nanoparticle composites [18].

Several published articles have investigated the transport mechanisms that govern ink flow during room-temperature DPN with liquid inks. In some cases, a water meniscus formed at the tip–substrate interface mediates the diffusion of ink to the substrate [19–22]. The rate of ink transport depends upon the meniscus size, the ability of the ink to diffuse across the meniscus, and on the interaction between the ink and the substrate. DPN can deposit polymer onto a surface by direct diffusion of polymer from the tip, which results in a polymer nanostructure no more than a few monolayers in height [6, 7]. In contrast, tDPN can deposit polymer nanostructures with thicknesses from a monolayer to several hundred nanometers [18, 23]. The mechanism for polymer transport between the tip and the substrate is not diffusion through a water meniscus, since the tip operating temperature typically exceeds the boiling point of water. Shear induced by the relative motion between the heated tip and substrate has produced polymer structures that are a few monolayers in height [23]. However, drawing features hundreds of nanometers in height requires significant mass flow down the tip, which cannot be fully explained by tip–substrate shear-dominated flow. This paper investigates the mechanisms of polymer melt flow during thermal DPN. The effects of cantilever tip speed, temperature, and dwell time on the resulting structures are explored.

2. Interfacial phenomena during thermal DPN

Figure 1 illustrates the thermal deposition of polyethylene (PE) nanowires from a heated tip. Figure 1 also shows experimental results for 20 µm long PE nanowires deposited...
Polymer flows from the tip to the substrate through either viscous forces during flow. The polymer viscous force scales as $F_{\text{visc}} \sim \pi rh \mu V$, by multiplying the polymer shear stress between the tip and substrate with the area of the polymer in contact with the substrate.

The shear force on the polymer is estimated by considering a no-slip condition and a characteristic velocity length scale $t$ between tip and substrate. The shear force scales as $F_{\text{shear}} \sim 2\pi rh \mu V$, by multiplying the polymer shear stress between the tip and substrate with the area of the polymer in contact with the substrate.

The line forces at the top and bottom of the meniscus involve thermal Marangoni effects and substrate surface wetting. A large temperature gradient exists between the cantilever heater and the substrate [26]. The magnitude of the line force scales as $F_{\text{line}} \sim 2\pi r T \Delta \gamma$, which may be non-zero due to the temperature-dependent surface tension $\gamma(T)$ driving flow down the tip toward colder temperatures. The contact angle between the meniscus and the substrate dictates the direction of $F_{\text{line}}$, with high surface wettability leading to a larger radial force.

The local curvature $\kappa$ of the liquid–air interface determines the Laplace pressure. The force between the top and bottom of the meniscus scales as $F_{\text{pressure}} \sim 2\pi r T (\gamma_s \kappa_s - \gamma_b \kappa_b)$, where $\kappa_s$ is the curvature of the polymer at the substrate and $\kappa_b$ is the curvature at height $h$. A wetting substrate can create a curvature that locally decreases Laplace pressure, which would drive flow toward the substrate.

The shear and surface driving forces must be balanced by viscous forces during flow. The polymer viscous force scales as $F_{\text{visc}} \sim 2\pi rh \mu V_p$, where $V_p$ is the characteristic velocity.

Figure 1. (a) Graphic of molten polymer flowing from a heated tip. (b) 20 µm long PE nanowires written with a hot tip. The lines are 600 nm wide and 300 nm tall. (c) PE nano-dots patterned by dwelling the hot tip at a single point. (d) Array of PE nanowires written at different speeds.

on a silicon substrate. The PE nanowires are 600 nm wide and 300 nm tall. The dimensions of patterned features are controlled by varying the tip temperature, speed, and dwell time during the writing process.

Polymer flows from the tip to the substrate through either shear or surface tension stresses. The relative importance of viscous stress to surface tension stress is given by the capillary number, $Ca = \mu V / \gamma$, where $\mu$ is the polymer viscosity, $V$ is the cantilever tip velocity, and $\gamma$ is the polymer surface tension. For 52 kg mol$^{-1}$ molecular weight PE, the viscosity is 360–1840 Pa s and the surface tension is 0.022–0.028 N m$^{-1}$ over the temperature range 160–260°C [24, 25]. When the tip speed is 1 µm s$^{-1}$, $Ca \sim 0.1$, indicating that surface tension is significant during tDPN.

Figure 2 shows the stresses and capillary contact line forces acting on polymer on and near the tip during tDPN. The relative motion between the tip and substrate induces shear stress in the polymer, $\tau_{\text{shear}}$. A temperature gradient between the hot cantilever and the room-temperature substrate induces a thermocapillary stress existing along the polymer free surface, $\tau_{\text{th}}$. For a liquid that wets both the tip and substrate, there are capillary forces at the polymer contact lines at the heater, $F_{\text{heater}}$, and the substrate, $F_{\text{substrate}}$. Finally, the local polymer surface curvature governs the internal Laplace pressure, $\Delta p$.

A simple model identifies the forces that drive polymer flow. The tip is modeled as a cylinder with radius $r$ and the polymer as a thin film encompassing the cylinder with a height $h$ and thickness $t$. The tip is in contact with the substrate, and the polymer film meets the substrate at an angle $\theta$. The force balance on the polymer control volume surrounding the cylindrical tip is

$$F_{\text{shear}} + F_{\text{line}} + F_{\Delta p} + F_{\text{visc}} = 0,$$

where $F_{\text{shear}}$ is the shearing force between the tip and substrate, $F_{\text{line}}$ is the net line force acting along the free surface, $F_{\Delta p}$ is the force due to Laplace pressure gradients within the meniscus, and $F_{\text{visc}}$ is the resisting force due to viscosity. Inertial effects are negligible as the Reynolds number is at most $Re = 10^{-10}$.

The shear force on the polymer is estimated by considering a no-slip condition and a characteristic velocity length scale $t$ between tip and substrate. The shear force scales as $F_{\text{shear}} \sim 2\pi rh \mu V$, by multiplying the polymer shear stress between the tip and substrate with the area of the polymer in contact with the substrate.

The line forces at the top and bottom of the meniscus involve thermal Marangoni effects and substrate surface wetting. A large temperature gradient exists between the cantilever heater and the substrate [26]. The magnitude of the line force scales as $F_{\text{line}} \sim 2\pi r T \Delta \gamma$, which may be non-zero due to the temperature-dependent surface tension $\gamma(T)$ driving flow down the tip toward colder temperatures. The contact angle between the meniscus and the substrate dictates the direction of $F_{\text{line}}$, with high surface wettability leading to a larger radial force.

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The shear and surface driving forces must be balanced by viscous forces during flow. The polymer viscous force scales as $F_{\text{visc}} \sim 2\pi rh \mu V_p$, where $V_p$ is the characteristic velocity.
of the polymer, which is not the tip velocity. This equation assumes a no-slip condition on the tip.

Although the local polymer curvature and 2D temperature gradients must be known to estimate the surface forces, some qualitative observations can be made. Viscous forces which impede flow must be balanced by $F_{\text{shear}}$, $F_{\text{line}}$, and $F_{\text{pressure}}$. Polymer mass flow due to $F_{\text{shear}}$ should depend linearly on the tip speed, and should be zero for a stationary tip. Thermal Marangoni effects in $F_{\text{line}}$ increase with increasing heater temperature, and are zero when the substrate and heater temperatures are equal. The Laplace pressure force $F_{\text{pressure}}$ requires a non-equilibrium fluid geometry, such as a moving solidification front within the polymer feature.

3. Experiment and results

We measured the amount of polymer transferred from the tip while varying tip temperature, tip dwell time, and surface chemistry. The tip speeds ranged between 0.5 and 2 $\mu$m s$^{-1}$ and the temperature ranged between 100 and 260 °C. Polymer was written on either silicon dioxide or PTFE to study the effect of surface wettability. For dot writing (zero tip velocity), the tip dwell times ranged from 0.1 to 100 s. Polymer was written on native silicon with either a hot tip and room-temperature substrate, or hot tip and hot substrate.

The heated tip was made from ultra-nanocrystalline diamond (UNCD) coated doped single crystal silicon, with a tip radius of 100 nm. The tip can reach temperatures exceeding 1000 °C and the temperature response can be calibrated to within 1 °C. The UNCD tip coating serves to both minimize wear and to improve adhesion of the ink to the tip compared to bare silicon tips [27]. The polymer was PE with a molecular weight of 52 kg mol$^{-1}$. The PE melting point was 140 °C with a degradation temperature of 280 °C. The cantilever was coated by dipping the end into molten PE and quickly removing it. After writing, the cantilever can be either immediately re-inked for further writing or it can be cleaned with an oxygen plasma.

The polymer–substrate and polymer–tip contact angles were expected to play a significant role in heated tip mass transfer. The contact angle of a molten PE drop was measured for three different solids: ultra-nanocrystalline diamond (UNCD), native silicon oxide (SiOx), and polytetrafluoroethylene (PTFE). These surfaces were chosen because the cantilever tip material was UNCD, while the substrate was either SiOx or PTFE. Figure 3 shows the results, giving PE wetted UNCD with a contact angle of 9°, SiOx with an angle of 44°, and PTFE with an angle of 88°. In general, a UNCD tip performs polymer deposition better than a silicon tip, presumably owing to the higher wettability of PE on UNCD compared to silicon.

The polymer mass on the cantilever must be significantly larger than the deposited feature mass to ensure uniform mass flow throughout an experiment. Figure 4 shows resonant frequency measurements used to determine the polymer mass on the cantilever during deposition. Inking the cantilever deposited 1300 pg of PE onto the cantilever end, of which 1000 pg was removed before the tip patterned stable lines. The tip then patterned 5000 $\mu$m of lines at 40 fg s$^{-1}$, which consumed 200 pg of material. These values are typical and
allow the tip to continuously write features for 2 h before requiring additional polymer ink.

Figure 5 shows an AFM image of polymer lines written at a speed of 0.5 μm s⁻¹ and a linear temperature ramp between 100 and 260°C. The tip did not write any polymer until reaching 150°C, at which point a large amount of polymer deposited onto the substrate. The flow was intermittent from 150 to 200°C and became steady between 200 and 260°C. The temperature was held constant for the final 5 μm of travel, resulting in steady flow, which indicated that thermal transient timescales are small compared to the experiment timescale. The flow of polymer ceased after turning off the heater.

Figure 6 shows the mass flow rate of PE from a hot tip to a room-temperature substrate as a function of temperature, speed, and substrate type. Polymer nanowire lines were drawn at constant speed while ramping the cantilever heater temperature between 100 and 260°C, and then the nanostructures were measured with a cold tip. Mass flow was calculated by multiplying the measured nanostructure cross-sectional area by the velocity of the tip and the PE density (ρ = 950 kg m⁻³). Figure 6(c) shows the PE mass flow rate onto SiOx for a tip speed of 0.5 or 2 μm s⁻¹. The polymer began to flow steadily at 190°C with a mass flow rate of 40 fg s⁻¹. The average mass flow rate increased to nearly 200 fg s⁻¹ when the temperature of the cantilever heater reached 260°C. Figure 6(d) shows the PE mass flow rate onto PTFE for the same conditions. The polymer flow on PTFE was 20 fg s⁻¹ at 140°C, and 80 fg s⁻¹ at 260°C.

The results of figure 6 reveal several aspects of the polymer flow. First, the mass flow rate does not depend upon tip speed for speeds between 0.5 and 2.0 μm s⁻¹, indicating that substrate shear force does not dominate mass transport. Second, higher substrate wettability leads to more polymer

Figure 5. (a) AFM image of PE lines written at 500 nm s⁻¹ while increasing the cantilever heater temperature from 100 to 260°C. (b) Profile of a PE deposit written during the temperature ramp. PE begins to flow at 150°C, with an unsteady flow until roughly 200°C and then steady flow above 200°C.

Figure 6. (a) AFM image of PE lines drawn with a linearly increasing temperature. (b) Cross-section of the lines at 200°C. Mass flow rate for 10 lines as a function of temperature on (c) SiOx and (d) PTFE for speeds of 0.5 μm s⁻¹ (gray squares) and 2 μm s⁻¹ (blue circles). Data averages shown for writing speeds of 0.5 μm s⁻¹ (black) and 2 μm s⁻¹ (blue) guide the eye. The mass flow rate did not depend on tip speed, but was at least two times lower for PTFE.
deposition. Polymer flow onto the PTFE was much lower than polymer flow onto SiOx, owing to the difference in surface wettability. Finally, the mass flow rate increases nonlinearly with increasing temperature, which can be explained by the strong (logarithmic) viscosity reduction with temperature, since both thermal and Laplace forces depend only linearly on temperature [24].

In order to eliminate shear forces and study surface capillary forces on mass flow, polymer was deposited from a stationary tip in contact with a substrate. Figure 7 shows AFM images of features deposited onto room-temperature SiOx at tip temperatures of 180 and 240°C for dwell times between 0.1 and 100 s. Figure 7(c) shows polymer feature radii as a function of time, with a least-squares fit to the data revealing a \( \sim t^{0.5} \) time dependence. Figure 7(d) shows the feature height growing with time as \( \sim t \). For polymer to flow, a negative radius of curvature, \( r_s \), must form between the polymer and the substrate to counteract the positive radius of curvature of the cylindrical tip. Note that the pressure cannot be less than zero absolute pressure. For \( r_s = -50 \text{ nm} \), \( \gamma_s = 0.032 \text{ N m}^{-1} \), \( \gamma_h = 0.025 \text{ N m}^{-1} \), \( \kappa_h = 1 \times 10^6 \text{ m}^{-1} \), and \( \kappa_s = -1 \times 10^7 \text{ m}^{-1} \), the mass flow is \( \sim 10 \text{ fg s}^{-1} \). An estimation of shear-driven flow is given by \( \dot{m}_{\text{shear}} = 2\rho \pi \eta V \), and a tip speed \( V = 1 \text{ mm s}^{-1} \) gives a mass flow of \( \sim 1 \text{ fg s}^{-1} \). Thus, both thermal Marangoni forces or Laplace pressure forces likely drive polymer flow during tDPN.

The substrate temperature was controlled using an external heater such that the substrate and the tip were at the same temperature, thus removing a temperature gradient near the tip. Figure 8 shows PE dots written when the tip and a SiOx substrate were both maintained at a temperature of 200°C. The dwell times were from 0.1 to 60 with a tip speed of 1 mm s\(^{-1}\) between dots. The radius of the written features varied between 1200 and 1400 nm, and the height of the features varied between 5 and 8 nm. The height of the deposited feature was two orders of magnitude smaller for a heated substrate than for a room-temperature substrate (cf figure 7). Small but visible streaks between the written dots

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**Figure 7.** Mass flow onto room-temperature SiOx surfaces from a hot tip held stationary for different dwell times and temperatures. PE dots written at (a) 180°C and (b) 240°C with dwell time 0.1–100 s. The dots are asymmetric due to tip motion after deposition. (c) Radius of the dots written at 180°C (blue circles) and 240°C (red circles). (d) Dot height for both cases. (e) Feature volume for both temperatures. Lines in (c)–(e) are power-law fits as described in text.
suggested that the meniscus quickly reached equilibrium on the tip and brushed material onto the substrate.

Figure 9 shows scanning electron microscope images of heated tips after writing. Figure 9(a) shows a tip after writing at 200°C on a substrate at room temperature. Figure 9(b) shows a tip after writing at 200°C on a substrate at 200°C. The dwell time was 30 s, and both the tip and substrate were cooled before lifting from the surface. For the cool substrate, the polymer around the tip was a disc shape of diameter ∼500 nm and height ∼200 nm. For the heated substrate, the polymer around the tip had a smooth contour along the entire height of the tip, with diameter ∼400 nm.

Polymer mass flow rate and written feature geometry were compared for both lines and dots on hot and cold substrates. Figure 10 shows PE lines and PE dots written on a SiOx substrate. The tip was 200°C and the substrate was either at room temperature or 200°C. Polymer nanowire lines were written at 1 μm s⁻¹ and polymer dots were written with dwell times of 50 s. The line written on the hot surface was 3 μm wide having a rough 10 nm tall dendritic structure. In contrast, the line written on the room-temperature substrate was 700 nm wide and 450 nm tall, with a mass flow rate 7.5× larger compared to the hot substrate. The dot written on the hot substrate had a 20 nm tall dendritic structure in the center, a 10 nm tall hemispherical droplet, and a thin, 0.4 nm tall flat layer extending 1.2 μm in radius. The dot written on the cold substrate had a radius of 1.3 μm and a height of 500 nm, which was 1–2 orders of magnitude taller than the dot written on the hot substrate.

This series of experiments illustrates several aspects of polymer flow from a heated AFM tip. For a hot substrate, the absence of thermal Marangoni forces allows the liquid meniscus to quickly come to equilibrium between the heater and substrate. Feature heights less than 10 nm suggest that long-range surface forces are responsible for the mass
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Figure 10. Comparison of lines and dots on hot (200°C) and cold SiOx substrates (20°C). (a) A 3 µm wide, dendritic polymer line written on a hot substrate at 1 µm s⁻¹. (b) Polymer line written at 200°C on a room-temperature substrate at 1 µm s⁻¹. Line topography on a (c) hot and (d) cold substrate. (e) PE dot written on a hot substrate. (f) PE dot written at 200°C on a cold substrate. Dot topography on a (g) hot and (h) cold substrate.

transfer. For a cold substrate, mass flow could be explained by Marangoni forces pumping material down the tip onto the substrate. Additionally, the temperature gradient at the surface likely causes a solidification front to evolve during dot growth. Mass flow would occur as the contact line and Laplace pressure continually adjust to the moving front. While both Marangoni and Laplace pressure forces are influencing mass flow, more must be known about the temperature field around the tip and the polymer meniscus geometry to precisely identify the relative contributions.

Understanding how polymer inks transfer from a heated tip during tDPN can aid in improving the speed and duration of the transfer process. Polymer flow rates are most sensitive to the temperature-dependent viscosity of the polymer, so choosing low-viscosity inks can greatly increase flow. Additionally, increasing the thermal gradient between tip and substrate, pressure gradient within the polymer, and polymer–substrate wettability will increase mass flow. Further increases in mass flow could be obtained by exploiting tip–substrate shear to drive polymer flow in high molecular weight, highly entangled polymer melts. Optimizing these parameters improves patterning throughput, making large-area patterning feasible. As the flow rate increases, the tip must be re-inked with higher frequency. Polymer ink could be stored along the entire length of the cantilever and chip, and driven toward the tip with a temperature gradient.

4. Conclusions

We investigated the mechanisms of polymer flow of molten polyethylene during tDPN. Heated atomic force microscope tips operated between 100 and 260°C wrote polymer nanostructures at tip speeds between 0.5 and 2.0 µm s⁻¹ and dwell times between 0.1 and 100 s. The independence of mass flow rate with tip velocity showed that mass flow was driven by capillary forces and not substrate shear. Mass flow was most sensitive to the polymer viscosity. Additionally, a higher contact angle between polymer and substrate decreased the amount of mass transfer. Polymer was also patterned on a hot surface at 200°C to eliminate thermal gradient effects (Marangoni forces and polymer solidification). The mass flow rate was 7.5× less on the hot substrate than for a cold substrate for a moving tip. When the substrate was hot, the meniscus quickly came into equilibrium between heater and substrate and little mass flow occurred. The large mass flow onto the cold substrate could be due to both thermal Marangoni force and non-equilibrium wetting dynamics caused by a solidification front within the feature.

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