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Thermomechanical formation and thermal detection of polymer nanostructures

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Abstract

In thermomechanical data storage, a heated atomic force microscope (AFM) cantilever tip scans over and melts small data bit indentations with radius of curvature as small as 20 nm into a thin polymer film. Small changes in the cantilever temperature, which correspond to changes in the thermal resistance between the cantilever and the data substrate, can detect the presence of previously written data bits. This chapter reviews work on modeling and measurement of heat and mass transfer during thermomechanical formation and thermal detection of polymer nanostructures for data storage. A study explores the impact of molecular confinement on viscous polymer flow in nanostructured thin films that finds a two order of magnitude increase in polymer viscosity and a shift from a no-slip to a slip in the polymer-substrate contact condition. Modeling and measurement of bit formation show that a cantilever temperature of 200 °C is required for bit formation at times greater than 1 ms, increasing to 500 °C for bit formation near 10 μ s. A study of cantilever thermal reading sensitivity shows that the cantilever compares well with other AFM-based metrology approaches, with a sensitivity exceeding 10⁵ μ V / nm . This chapter reviews work on heat and mass transfer that governs the processes of thermomechanical data write, read, and erase.

1 Introduction

Atomic force microscopy (AFM), invented in 1986 [1], has emerged as the most common tool for sensing and actuating at the nanometer scale. The basic

architecture of an AFM system consists of a micromachined tip at the end of a cantilevered beam. A motion control stage, attached to the cantilevered beam, brings the tip into contact with, and moves the tip laterally over, the surface. As the tip follows the shape of the surface, small changes in the vertical position of the cantilever beam are detected, shown in Fig. 1. AFM can produce topographic maps of the surface with resolution limited by shapes of the cantilever tip and the surface, and the quality of the scanning and sensing system, typically near 1 nm in all three dimensions. Schemes for vertical detection include piezoresistive activation of the beam [2], optical detection [1], and thermal detection [3]. A large number of local probe and cantilever-based instruments are based on this basic concept, including optical probes [4], force sensors [2], and biochemical sensors [5].

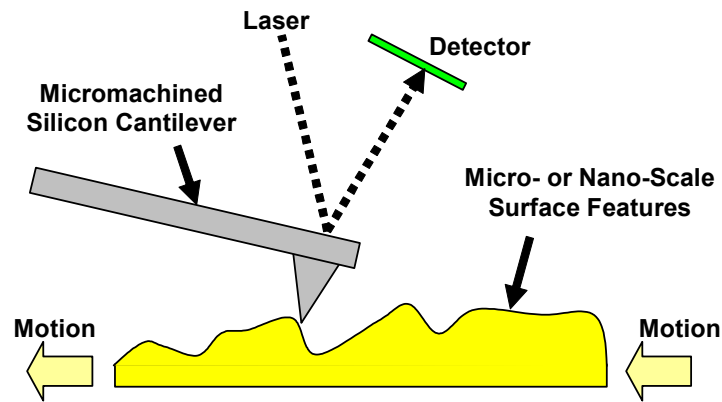


Figure 1: Schematic of AFM operation.

The cantilever tip can be used to intentionally modify the surface over which it scans. The various AFM surface modification research includes AFM cantilevers designed for guiding electromagnetic radiation into photoreactive polymer [6], cantilever tips which direct electrostatic discharge to locally oxidize a reactive surface [7], local chemical delivery with the AFM tip [8], direct indentation of soft materials [9], and the present approach of thermally-assisted indentation of soft materials [10].

1.1 Motivation for AFM data storage

The rapid advancement of magnetic data storage can be measured by continuous increases in the area density of data bits in commercial disk drives, currently growing at an annual rate of 100% [11]. The superparamagnetic effect, which governs the thermal stability of a magnetic data bit, will likely limit data density in current magnetic data storage technology near 100 Gbit / in² [12]. Several efforts show promise for expanding this limit even further, for example patterned magnetic media for perpendicular recording [13], which increase domain stability

through domain separation, or thermally assisted magnetic recording [14], which increases the magnetic susceptibility of the recording media such that magnetic bits can be written only at high temperature. Despite the data storage densities possible with these technology advancements, it remains unclear which technology will permit data storage devices capable of 1 Tbit / in² and beyond.

Several AFM-based data storage technologies that employ surface modification can produce feature sizes that are significantly smaller than magnetic recording data bit sizes [3,10]. Mamin and co-authors [15] have written a review on AFM for data storage. Lithographic patterning of extremely small features also drives progress in technology surface modification, and in general many of the probe-based data storage approaches offer promise for lithography.

Despite the progress and promise of these many AFM data storage technologies, there remain pervasive challenges to transferring this technology to a commercial product platform. These challenges include:

- **Speed.** Typical single-cantilever mechanical time constants are close to 100 kHz [16], which is small compared to a system-level data rate of 200 Mbit / sec for a commercially available disk drive [17]. Scanning probe data storage with competitive data rates are accomplished through single-cantilever optimization [18] and more recently the development of cantilever arrays [19].
- **Ability to “close the loop”** and detect the presence of or even the size and shape of the modified feature. The first design work for AFM cantilevers used in thermomechanical data storage wrote and read data bits with separate, individually optimized cantilevers [20]. Lithographic patterning that uses an AFM cantilever tip or STM tip as a waveguide requires wet chemistry to realize the features [6]. In general, the best AFM cantilever for patterning features or writing data bits is not necessarily the best cantilever for sensing the features written.
- **Reversibility,** as in erasing data or mending a lithographic mistake. While there exist successful data storage approaches, such as DVD-ROM, the magnetic-type recording scheme that offers many rewrites is often preferred.
- **Robustness.** Several approaches for probe-based surface modification and feature detection require high voltage [6], sophisticated feedback electronics, or careful alignment and preparation of a tunneling tip or a carbon nanotube [7]. The realization of a commercial product must overcome or avoid components that require laboratory equipment or high vacuum to operate reliably.

Very recent progress in thermomechanical data storage has provided promising solutions to each of these challenges. The present approach [21] aims to provide a large, functional array of AFM cantilevers, each capable of high data rates and high sensitivity. Elsewhere this group has reported data erasing [3,22], thus satisfying the reversibility requirement. Continuous contact between the AFM cantilever and the polymer surface, the sharp onset of bit formation [10], and the reliable stability of the data bits at temperatures below the bit-writing temperature [23] make thermomechanical data storage very robust.

1.2 Review of thermomechanical data storage

In thermomechanical data writing, a resistively heated AFM cantilever is in contact with and scans over a substrate coated with a thin polymer film. Heat generated in the cantilever flows along the cantilever tip into the thin polymer film, locally raising the polymer film temperature and causing the polymer to soften. Force applied to the softened polymer from the heated cantilever tip causes the polymer to deform, thus forming an indentation, with a radius of curvature as small as 20 nm [3,10]. Figure 2 illustrates thermomechanical data writing and Fig. 3 shows data bits in a 35 nm thick film of polymethyl methacrylate (PMMA). At 20-50 nm in diameter, these small data bits correspond to data density of up to 1 Tbit / in².

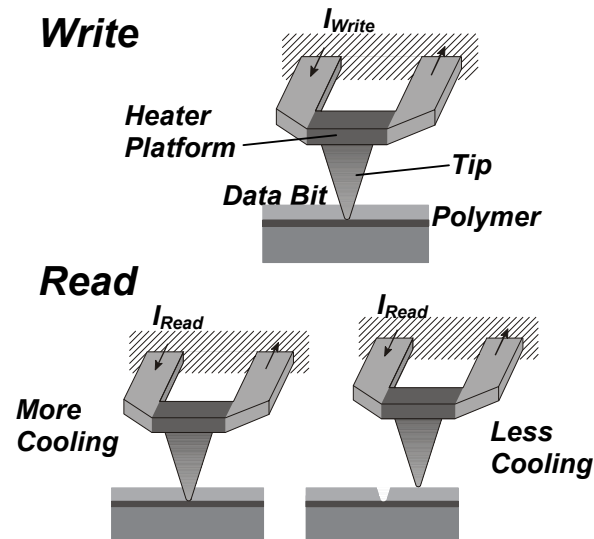


Figure 2: Schematic of thermomechanical data writing and thermal reading.

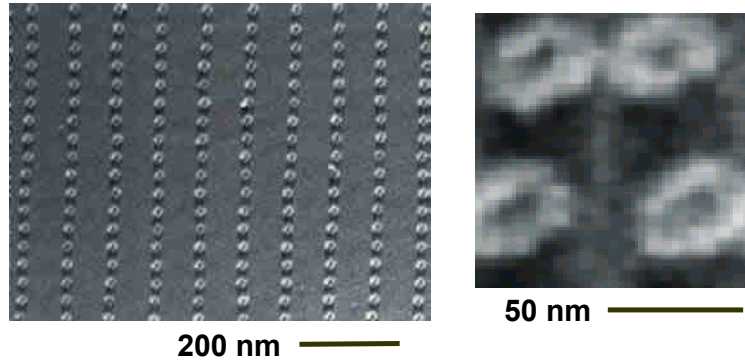


Figure 3: Indentations written and read with a heated AFM cantilever [3].

Several realizations of thermomechanical modification of polymer surfaces preceded the current approach. Mamin [24] first demonstrated thermomechanical data writing with the AFM by using an infrared laser to heat the cantilever. Further work used a commercial piezoresistive silicon cantilever that self-heated during brief electrical pulses [25]. While these resistively heated piezoresistive cantilevers could thermally write without the optical access of the first design, the entire cantilever was heated during an electrical heating pulse, resulting in cantilever thermal time constants as long as 0.45 ms. In order to reduce the thermal time constant for heating, Chui [20] designed and optimized AFM cantilevers with a heating time of less than 1 μ s, and a cooling time of near 10 μ s. The design improvement consisted of preparing the silicon cantilever with regions of differential impurity doping, such that only a small region of the cantilever near the tip was highly resistive, therefore creating a small heater region with significantly reduced heat capacitance.

A resistively heated silicon cantilever can be used to thermally detect the presence of a previously written data bit, allowing data reading. In reading operation, the cantilever is heated to a temperature that is well below the threshold temperature for bit formation. As the warm cantilever follows the contour of a previously written data bit, the change in the thermal resistance between the cantilever and the substrate produces a change in the temperature of the cantilever, measured through change in the electrical resistance of the cantilever heating element. By recording the dynamic temperature signal as the cantilever tip moves over the polymer surface, a surface contour map can be made. Figure 2 illustrates thermomechanical data reading. Binnig [3] measured the vertical sensitivity of thermal data reading to be between 10^{-4} and 10^{-5} per vertical nanometer for a cantilever that had not been optimized for thermal data reading.

This thermal data reading technique is distinct from techniques that use a thermocouple tip for topographic surface profiling [26] or make highly local temperature measurements [27]. Temperature mapping with a thermocouple-

tipped AFM, known as scanning thermal microscopy (SThM) is significantly better than the present implementation for high-resolution thermometry, while the present thermal proximity sensing yields extremely high vertical sensitivity for topographic imaging.

A crucial stage in the development of thermomechanical data storage technology was the development of fabrication techniques to reliably make AFM cantilevers with uniform mechanical and electrical properties [20,21,28]. Figure 4 shows a recent cantilever, which is 50 μm in length and has a tip height of 1 μm . More recent versions of this cantilever have a smaller tip height and are thinner for improved reading sensitivity [29].

A cantilever array can write and read data bits with higher speed than a single cantilever operating alone. While much work has been done to design and optimize individual AFM cantilevers [for example 18], only recently has there been significant progress in the development of cantilever arrays. Lutwyche [30] reports the fabrication and operation of a 5 X 5 cantilever array, which measured features of characteristic size 2 μm . A larger device with 1024 cantilevers in a 32 X 32 square array, known as the “Millipede” [21] and shown in Fig. 4, demonstrated successful thermomechanical and thermal data reading at a data density of 100-200 Gbit/in² [29].

1.3 Chapter overview

This chapter reviews studies of heat and mass transport in the cantilever, cantilever tip, and polymer layer during data bit formation and detection. A major challenge in this study is understanding the flow of polymer films of thickness comparable to the polymer molecule radius of gyration. Section 2 reviews a fundamental study of intrinsic polymer viscosity at nanometer length scales that reveals remarkable increase in the polymer viscosity compared to bulk polymer. Performed on thin polymer films identical to those used as data storage media, this study informs bit stability at elevated temperatures. In section 3, a model of heat transfer in the cantilever tip accounts for aspects of sub-continuum heat conduction in the silicon cantilever tip and nearby air, and illustrates the basic mechanisms of data bit writing and reading. Measurement and modelling of thermomechanical data bit formation finds the time and temperature dependence of onset bit writing conditions. Predictions show the effect of changes in the tip shape and tip loading force on onset writing conditions. Section 4 describes modeling of cantilever operation and design of cantilevers for improved thermomechanical data bit writing and thermal data reading, and investigates the thermal data reading approach for topographic sensing. The conclusion describes future applications of this work, including AFM materials processing and metrology.

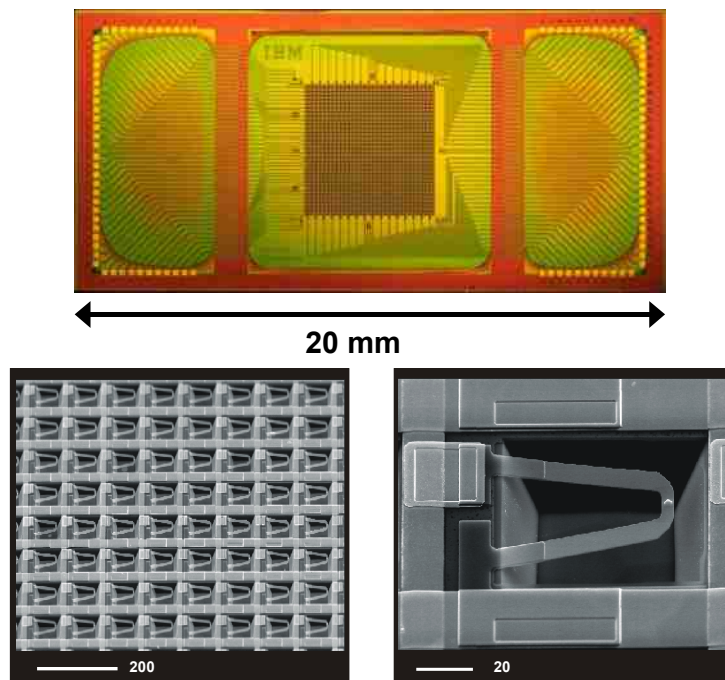


Figure 4: Picture of the Millipede cantilever array data storage chip and scanning electron microscope images of individual cantilevers in the array. Fabrication details can be found in Refs. [21,28] and successful operation of the array is reported in Ref. [30].

2 Relaxation Kinetics in Nanostructured Polymer Films

The physical properties of thin polymer films can differ from bulk properties, particularly at lengths comparable to or thinner than the radius of gyration of a molecule in bulk polymer [31]. Examples of polymer orientation, confinement, and frustration at small scales are observed as shifts in measured glass transition temperature T_g , [32,33,34], changes in polymer thermophysical properties [35], or changes in mechanical viscoelastic properties [36,37]. Of particular importance for understanding these observed phenomena are the chemical and mechanical influence of interfaces on polymer molecular motion. This section reviews the impact of confinement and bounding effects on thin polymer films.

2.1 Fundamentals of mass transport in confined soft materials

The length scale for a macromolecular material is the radius of gyration, R_g , which is the root mean squared distance between the mass centroid of the unperturbed molecule to each of the monomers in the macromolecular chain [31,38]. Typical values for R_g range from 5 nm to 100 nm. For macromolecular films of thickness comparable to or smaller than R_g , [32] or for single molecules confined on a surface or in a microfluidic channel [39], the radius of gyration concept is less useful, as the molecule will orient in the direction of confinement and will no longer be spherically symmetric.

Two relaxation mechanisms determine polymer molecular motion: a) monomer migration, which depends upon the free volume near each monomer and cooperative motion of nearby monomers, and b) reptation of the polymer chain, which requires migration of the polymer end. DeGennes [31] proposed a model of local macromolecular motion known as reptation, in which macromolecules in a condensed system move along the path of their own molecular backbone. More force or longer time is required for a macromolecule to locally move perpendicular to its path compared to motion through reptation. For free-standing or uncapped thin films, chain reptation is the dominant molecular transport mode [40,38].

Changes of phase in macromolecular systems are second order transitions [41], rather than the first order phase transition of melting. Macromolecular materials do not have a discontinuity in the heat capacity-temperature relation, but rather have a slow, continuous change in heat capacity over a temperature range. The onset temperature for this heat capacity change is known as the glass transition temperature, T_g . Because the macromolecular materials are inhomogeneous at the molecular level, with many overlapping, intertwining molecules, there exists an energy barrier for each chain interaction with itself or another chain. The apparently continuous material change above T_g is in fact a large number of closely spaced energy barriers. The link between highly local molecular mobility and temperature allows glass transition phenomena to be observed through changes in mechanical, electrical, or optical properties.

Measurements of the glass transition temperature of thin polymer films show that molecular confinement and nearby surfaces can affect polymer molecular motion. Studies show a thickness-dependence of T_g in PMMA films, with a T_g increase for PMMA on silicon dioxide surfaces, and a T_g decrease for PMMA on gold surfaces [33]. Studies of free-standing Polystyrene films show a large T_g depression below the bulk value of over 60 °C, which is a function of film thickness and molecular weight, indicating the impact of confinement in the absence of a bounding surface [34]. The same films capped by a nearby bounding surface of silicon dioxide demonstrate a reduced T_g depression at 10 °C, and only 4 °C depression for a sandwiched film.

Local measurements of glass transition in polymer films indicates the possibility of local glass transition effects even within the layer: the molecules closest to a bounding or free surface may have a different mobility or differing degrees of freedom than molecules farther from a surface [42]. For example,

polymer tacticity has been shown to affect T_g , since variation in the density of polymer-surface interactions locally influence molecular mobility [43]. A positron lifetime spectroscopy study of thin polystyrene films on hydrogen-passivated silicon showed a glass transition temperature close to the surface that was lower than the glass transition in the film, which were both lower than the glass transition expected for bulk polystyrene [44].

Closely related to glass transition temperature is the local mobility of polymer molecules in a thin film, which also depends upon molecular confinement and proximity to nearby surfaces. The diffusion of polymer layers in a supported thin film structure can be substantially reduced due to the presence of a nearby bounding surface. Indirect measurements of polymer diffusivity by monitored decreased activation energy required for phase separation in thin polymer films, due to surface energy provided by nearby surfaces [45]. Direct measurements of polymer interdiffusion made by fluorescent labeling of polymer sub-layers showed that inter-polymer friction coefficients in thin polystyrene films can be 10^2 to 10^3 times greater than the bulk coefficients, depending upon the support material [46]. The self-diffusivity of polymers is also thickness dependant, demonstrating a factor of two reduction in PS films at thickness well above R_g [47]. Measurements made with neutron scattering show over an order of magnitude reduction in self-diffusivity of polystyrene films at distances up to $10 R_g$ away from a bounding interface [48], and a similar reduction in PMMA films, but only up to distances of $4 R_g$ from the bounding surface [49].

Simulations of macromolecular motion allow for prediction of behavior of single molecular behavior near a surface and in confined geometries. Predictions show that even in the presence of a strongly attractive surface, molecular centroids are most closely bunched at a distance of R_g from the surface, as strong molecular alignment parallel to the surface prohibits molecules from moving any closer [50]. A simulation of polymer dynamics at a solid-melt interface showed that the interfacial region in the melt is extremely small at only a few tube diameters, and was independent of chain length. The direct impact of the interface was to anchor the molecular chains but this effect did not propagate far into the melt [51]. However, longer range surface forces and confinement effects did induce molecular anisotropy and affect diffusivity. A study of molecular chains of varying lengths [52] showed that while molecular anisotropy depends upon chain length and the energetics of the nearby surface, local chain-chain interactions are affected only weakly. Simulations of block copolymers showed that thermodynamic interactions between polymer blocks add a third complication which can locally affect molecular mobility [53].

Mechanical motion in thin polymer films is also restricted by confinement and bounding effects [54]. Films of Polyphenylmethylsiloxane sandwiched between atomically flat mica surfaces undergoing small oscillatory motions demonstrate strong rubber elasticity at thickness below five to six R_g [36]. This elasticity could be due to ‘bridging’ of polymer molecules with portions of individual molecule near both sandwiching surfaces [55].

A two-fluid model of polymer motion near interfaces proposes that some molecules are trapped near a bounding surface while molecules away from the

bounding surface or near a free surface have a different mobility [56] and experiments support this model [57]. More detailed models consider a local mobility, varying near interfaces but not discontinuously [34, 48].

2.2 Measuring flow characteristics in thin, nanostructured polymer films

In one recent measurement [58], a light scattering technique locally probes the temperature-dependant relaxation characteristics of a surface wave structure fabricated in a thin polymer film. Electron beam lithography forms spatially periodic three-dimensional polymer nanostructures in Poly methyl methacrylate (PMMA). This polymer has an unperturbed radius of gyration of 35 nm, and experiments are conducted for thickness at and above 35 nm. Heating induces a surface-tension driven flow that results in decay of the surface wave amplitude, observed through measurement of the scattering signal from an incident laser. Atomic force microscope (AFM) scans of the polymer surface aid interpretation of the scattering intensity signal evolution. The measurement shows long-range polymer cooperative motion during flow onset, and larger than expected viscosity for the thinnest polymer structures.

The sample material is a standard electron beam poly methyl methacrylate (PMMA) photoresist, with a number average molecular weight of 3.5×10^5 g / mol, and a measured bulk sample reveals a glass transition temperature at 120 °C. The substrate for the PMMA optical grating structures is a silicon wafer that is first prepared with a spin-coating of 100 nm of hard-baked SU8 epoxy. A grating pattern on PMMA is fabricated using an electron microscope exposure. The pattern consists of periodic rectilinear trenches spaced at 360 nm. Polymer samples are prepared at thicknesses 35 nm, 70 nm, 130 nm, and 300 nm, which correspond to approximately 1, 2, and 3, and 10 times the unperturbed radius of gyration.

Figure 5 summarizes the experimental setup. Hamdorf [59] used a similar technique to measure the surface properties of thick polystyrene films. The polymer grating structure is mechanically attached to a temperature-controlled heating stage, and is interrogated with a laser. The scattered light intensity is proportional to the spatial Fourier transform of the density autocorrelation function of the optically probed sample volume. The grating may be represented by a surface density modulation and the scattered intensity $S(\mathbf{k})$ is just proportional to the 2-dimensional Fourier spectrum of the local film topography. To first order, the intensity of the scattered signal is proportional to the square of the trench volume.

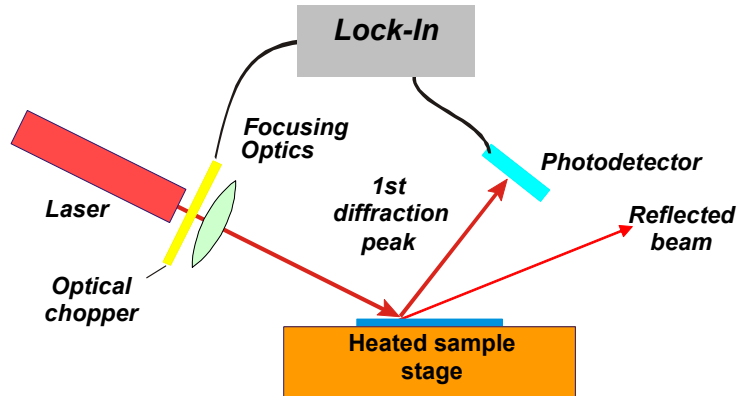


Figure 5: Schematic of experimental setup for polymer relaxation measurement.

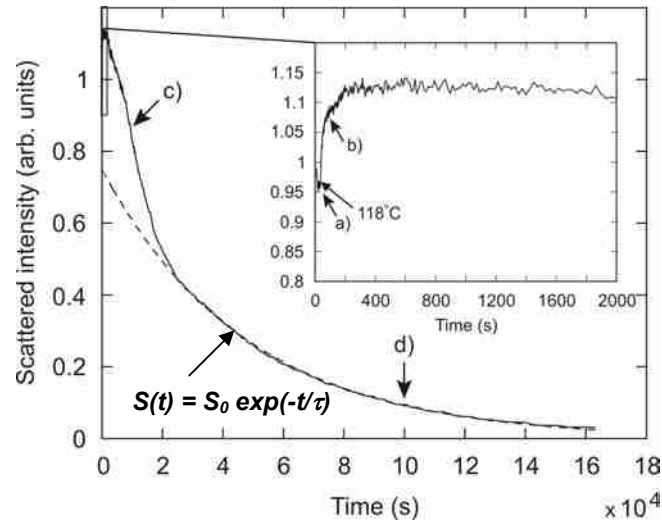


Figure 6: Typical optical signal time trace for the decay of a polymer corrugation structure [58]. This data is for 50 nm wide lines in 70 nm of PMMA.

Figure 6 shows a typical example of an intensity signal evolution for a polymer grating structure. The heater is turned on at $t = 0$ sec and the temperature is ramped to the final temperature, 125 °C within 50 seconds. The time-trace characteristics common to all of the samples measured are: (a) a lack of change until the polymer is heated to its glass transition temperature T_g , (b) an almost instantaneous increase in the scattering signal at T_g , (c) a phase with an almost constant intensity, a transition regime with a rapid drop of the intensity

by 30% to 50%, and then eventually (d) an exponential decay. For each of the samples measured, the relaxation (b) was extremely fast and always corresponded to a scattering signal increase of 10-15% over the initial intensity. An exponential decay $S(t) = S_0 \exp(-t/\tau)$ well represents the long time scale decay (d), also shown in Fig. 6.

Assisting interpretation of the intensity data, AFM snap shot images of the grating topography are recorded, shown in Fig. 7. For these, heat is applied to a fresh sample for a fixed time interval and then rapidly quenched to room temperature. Figure 7a shows the topography of an example grating (60 nm wide lines in 130 nm PMMA) before heating. The sharp edges of the etched trenches exhibit perfectly vertical side walls. Panel 7b shows the same type of grating that was quenched after 100 seconds of heating to 120 °C, visualized shortly after the sudden increase of the scattered intensity had been observed. A drastic initial relaxation can be observed as evidenced in the rounded edges. Also, the PMMA surface is smoother than in 7a and one can discern a slight upward bow of the originally flat terraces. This overall rounding effect induces a redistribution of the Fourier components of the grating - high spatial frequency harmonics are convoluted onto the fundamental grating period as a result of total volume conservation - which corresponds to the initial rise in the scattered intensity. The polymer sample retains this overall shape for longer times in images 7c and 7d, with the exponential decay of the scattering signal corresponding to the polymer structure being most sinusoidal in shape.

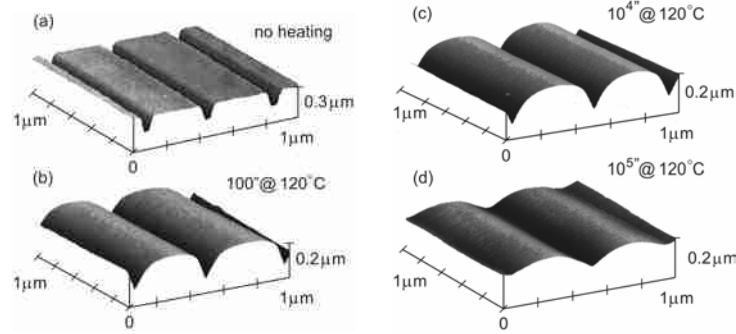


Figure 7: AFM 'snapshot' images of the melting polymer corrugation structures a) before heating, b) after 10^2 sec at 120 °C, c) after 10^4 sec at 120 °C, and d) after 10^5 sec at 120 °C [58].

The initial relaxation shown in 7b and by the difference is 7a and 7b can be interpreted in terms of a surface force-driven elastic response. The average initial stress acting on the PMMA film due to the sharp rectangular edges of the grating is of the order of $\sigma = \gamma/l \approx 0.1$ MPa where $\gamma \approx 0.03$ N / m is the surface tension of PMMA at T_g [60] and l is a relaxation length of the order of the grating period. Below T_g the shear modulus is of the order of 1 GPa and therefore relative elastic strains are below 10^{-4} . At T_g , the PMMA softens

dramatically as evidenced by a drop of the shear modulus by three orders of magnitude to values of typically 0.5 to 1 MPa in the rubbery regime [61]. Accordingly, substantial elastic strains of the order of 10^{-1} must develop in order to balance out surface tension forces. This relaxation effect can in fact be used to determine the glass transition temperature in thin film samples in general.

The AFM images of Fig. 7 show that the surface of the polymer is much smoother after a short heating time. Scanning probe studies of the decay of the surface roughness of polystyrene and PMMA films at elevated temperatures found increased molecular diffusivity for roughness features of size less than the polymer radius of gyration [62,63,64]. The observed sharp temperature transition of surface wave morphology in Fig. 7 is markedly different from the measurement of Kerle [64], who observed in thick polystyrene films a broad temperature transition in the decay of roughness features of similar size to our corrugation trenches. It is possible that confinement effects in the thin films contribute to a sharper transition.

Viscous flow, which is also surface tension-driven, provides a second much slower relaxation mechanism which lets the PMMA film recover a completely stress-free final state. The measured relaxation time τ can then be related to the decay rate Γ [65]

$$\Gamma = \frac{1}{2\tau} = \beta \Gamma_{\text{inf}} = \beta \frac{\gamma k}{2\eta} \quad (1)$$

The parameter β accounts for the impact of the nearby substrate on the polymer flow. For an infinitely thick film $\beta = 1$ and $\Gamma_{\text{inf}} = \Gamma$. The influence of the nearby surface must be considered in order to describe the relaxation of the thin film samples. Imposing a no-slip boundary condition at the polymer-substrate yields $\beta = 2/3 (kh)^3$. Imposing a slip boundary condition at the polymer-substrate interface yields $\beta = 1/2 kh$.

A line-shape analysis of the polymer surface further aids in interpreting the optical measurement data. According to Eq. 1, the relaxation constant Γ_{inf} is proportional to the polymer sample corrugation wave number k . Thus, correct selection of the parameter β yields a linear relationship between Γ and k . Comparing a spatial Fourier transform of the snapshot images of Fig. 7 with measured Γ yields the expected relationship between Γ and k for a slip polymer-substrate boundary condition for the 35 nm thick samples, and for a no-slip polymer-substrate boundary condition for all of the other samples. It is possible that the change from no-slip to slip boundary conditions for the thinnest samples is due to molecular orientation in the thinnest films. Molecular-level simulations [66,67] show that the polymer chains are substantially more oriented near a surface compared to polymer chains in the bulk. Furthermore, the density of chain segments near the wall is substantially reduced in the presence of a weakly attractive surface compared to a strongly attractive surface. This can be explained by chain packing and confinement effects that prohibit chain segments from approaching the wall to within a distance of R_g unless there is an additional driving force.

Figure 8 shows calculated polymer viscosity, based on relaxation time measurements and appropriate selection of the rescaling parameter β . For constant viscosity and surface tension at a given temperature, the data should collapse onto a single master curve. Time-temperature superposition [68] can be used to predict the temperature-dependence of polymer viscosity. The temperature-dependence of the polymer viscosity is given by

$$\log\left(\frac{\eta}{\eta_g}\right) = -\frac{-17.44(T - T_g)}{51.6(T - T_g)} \quad (2)$$

Where η_g is the viscosity at the glass transition temperature, T_g is the glass transition temperature and T is measurement temperature. Within experimental scatter, the calculated fit compares well with the data for the thickest films. However, for the thinnest polymer films there is more than one order of magnitude increase in the relaxation time of the grating, suggesting that the relaxation dynamics are substantially different in these very thin films.

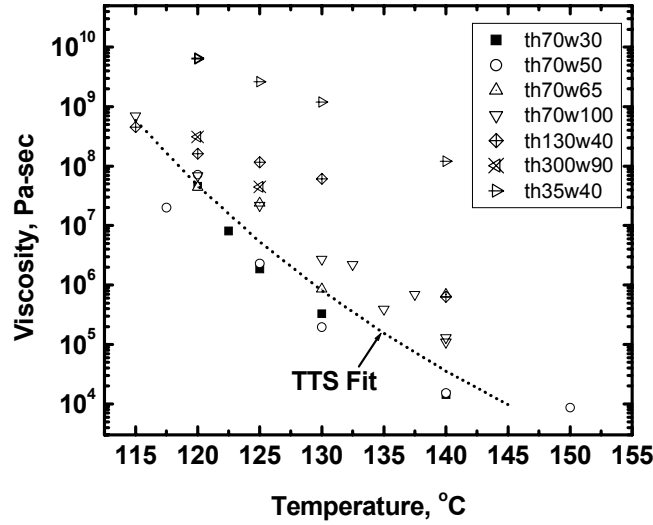


Figure 8: Polymer film viscosity as a function of temperature [58]. Data are rescaled with β chosen for the polymer-substrate interface condition measured with AFM. Solution of Equation 2 yields the time-temperature superposition (TTS) fit. The nomenclature thXwY refers to a polymer film thickness of X nm and a corrugation line width of Y nm. A time-temperature superposition fit is shown to the th70w100 data.

In general, the macromolecular kinetics of polymers at interfaces and in confined geometry depends upon chemical interaction with the surface,

macromolecular confinement, and details of the chemistry of the polymer such as tacticity. The lack of a strong chemical interaction at the PMMA-SU8 interface for the above indicate that the results of Fig. 8 can be largely attributed to the impact of macromolecular confinement.

The slip effect at the polymer-substrate interface is not necessarily a function of the mechanical confinement, as it has been observed in bulk polymer flows [69]. However, molecular orientation and slip are linked through polymer-substrate interfacial chemistry. For a confined polymer film on a weakly adsorbing substrate such as SU8, modelling predicts a slip boundary condition [70], compared to a no-slip boundary condition for a confined polymer film on a strongly adsorbing substrate [71]. This modelling also predicts a linear relation between viscosity η and polymer thickness h for values of h comparable to and less than the radius of gyration R_g [70]. While Eq. 1 reports a substantially larger viscosity thickness-dependence of h^3 , the modelling of Refs. [70] and [71] are for sandwiched polymer layers, as opposed to the uncapped films of the present study.

The possibility of increased polymer viscosity of Fig. 8 can be viewed in light of highly local measurement of polymer diffusion. Measurement of interdiffusion of PMMA in layers of thickness near R_g shows a two order of magnitude increase in polymer interdiffusion, comparing well with the results of this chapter [72]. In general, for polymer films of thickness comparable to R_g , the overall polymer chain mobility is reduced [73,74] while the polymer chain mobility can be increased within R_g of the surface [74], thus motivating a two-fluid model of thin-film polymer flow [74,73]. The two-fluid model assumes a given molecular mobility within R_g of the substrate, and a second molecular mobility farther away from the substrate. One recent experiment [75] measured the shear modulus of the polystyrene films and found that the shear modulus was increased by near a factor of 30% for films of thickness R_g compared to the bulk polymer. However these authors made one measurement at $0.3 R_g$ and found the shear modulus *decreased* by approximately 15% compared with the bulk polymer.

Scanning probe measurements of temperature-dependant mechanical properties provide contradictory reports with some reporting thickness and substrate dependence [76,77], and others reporting a lack of thickness or substrate dependence [78,79,80]. These studies in general leave open questions as to tip-polymer interaction, and it is possible that these studies probed the polymer properties only at the polymer surface. For example, one study reported a T_g depression measured with a controlled-temperature AFM stage on *bulk* polymer samples [81].

3 Modelling and Simulation of Nanometer-Scale Thermomechanical Data Bit Formation

Two recent developments in the operation of AFM cantilevers for thermomechanical data storage have significantly advanced its viability as a commercial technology. The first is the ability of the cantilever to thermally detect the presence of previously written data bits via conduction across the air

gap [3,82]. The second recent development in the operation of AFM cantilevers for thermomechanical data storage is the use of ultrathin polymer films as the data substrate to produce extremely small data bits [3,10]. While these data bits were extremely small at 10-50 nm in diameter, a detailed engineering understanding of these developments had not been made, thus prohibiting optimization.

Thermomechanical data storage technology yields a spatial resolution and maximum writing rate that are governed by heat transfer from the cantilever. Past work [20] investigated thermal conduction within the cantilever with the goal of minimizing the time required for temperature changes near the tip region. Chui [20] used finite element simulations to predict transient temperature fields along the cantilever legs during Joule-heating pulses of duration near one microsecond. Electro-thermal simulations and measurements were also made to characterize cantilever operation. Ashegi [83] found that the decreased thermal conductivity of the thin, heavily-doped silicon cantilever legs, compared with bulk, pure silicon, decreased the thermal time constant of the cantilever cooling. Research on high-resolution thermal microscopy motivated several studies of thermal and thermoelectric transport at the contact of a probe tip and a surface [84,85,86]. A recent study [87] reports detailed simulations of heat transfer within the AFM cantilever tip and polymer data layer during thermomechanical data bit formation.

Published work on thermomechanical data storage noted the temperature, time, and loading force required to form a data bit [3,30], but until recently [10] did not examine the process of data bit writing in detail and instead studied system-level figures of merit. Binnig [3] and Lutwyche [29] wrote data bits with loading forces in the range of 100 nN to 1 μ N and heating pulses near 20 μ s. These studies did not have optical access to the cantilever and could not make a direct measurement of the cantilever deflection required to determine loading force. It was possible, however, to estimate loading force from the motion of the cantilever mounting package after tip-polymer contact. The temperature of the cantilever heater region can be found by measuring the electrical resistance of the cantilever, which is a function of temperature. The two studies above [3,29] found the minimum temperature in the cantilever heater region required to induce thermomechanical bit writing in thin layers of PMMA was 350 $^{\circ}$ C, and that below this temperature bit writing was not possible. This threshold writing temperature of 350 $^{\circ}$ C is significantly higher than the glass transition temperature of PMMA, which is 105 $^{\circ}$ C in the bulk. The large temperature difference between the glass transition temperature of bulk PMMA and the cantilever heater could be in part due to an elevated glass transition temperature in the thin polymer layer [32,33,34]. However, any shift from the bulk value is likely no more than 10 to 15 $^{\circ}$ C for PMMA, even in the presence of a strong polymer layer-substrate surface interaction [88]. Other possible explanations are that there exists a temperature drop across the length of the cantilever tip, or that the local temperature gradient in the polymer near the cantilever tip is sufficiently steep that not enough polymer is heated to melting temperatures in order to allow tip motion. One goal of thermomechanical data storage system development is to decrease device power consumption in data bit writing [92],

and it is therefore important to identify the lowest temperature at which data bits could be written.

One study [90] used a modelling and simulation approach to predict the modes of heat transfer during data bit writing and reading, and finds that significantly more heat travels across the cantilever-substrate air gap than travels through the length of the cantilever tip [83,89,90]. Thus, it is the thermal impedance of the cantilever-substrate air gap, not the thermal impedance at the cantilever tip-polymer interface, which governs thermal data reading. This metrology approach, while thermal in nature, is distinct from scanning thermal microscopy [27], where the thermopower measured in small thermocouple scans over a heated, structured surface to measure both temperature and feature size. The differences between scanning thermal microscopy and the thermal impedance imaging technique of this paper emerged after the first demonstration of the present thermal data reading approach. Modeling of heat transfer in the cantilever [91] and cantilever tip and measurement validated the designs [82]. This modeling approach has since been used to design cantilevers for improved thermal data reading performance [92].

An important feature of an accurate model of bit formation is the ability to predict the spread of heat in the polymer data layer, and to predict the corresponding polymer temperature-dependant mechanical properties. Softening of the heated polymer in the neighborhood of the tip is a function of the cantilever tip temperature, the tip-polymer thermal contact resistance, and the thermophysical properties of the polymer. The polymer glass transition temperature [32,33], thermal conductivity anisotropy [35], surface tension [59], and viscosity [93] are all expected to have values for thin polymer layers different than the values for bulk polymer. The relationships between mechanical relaxation time, temperature, and mechanical properties are likely different as well for thin layers. Theoretical treatments exist for the prediction of polymer properties at small scales [93], but progress yet to be made in the fundamental understanding of the physics of polymers at small scales does not justify their application here, particularly for a complicated geometry with time and temperature dependence. Because of the lack of accurate mechanical property values, the present work employs property values for bulk PMMA, and modifies them with the best information available for size effects. The lack of accurate property values will induce inaccuracies in bit formation simulation. Therefore, the modeling and simulation approach follows an approach that preserves the qualitative link between model and experiment, in order to understand the relative impact of the many parameters on bit writing.

This section presents the analysis of heat and mass transfer during data bit formation through a steady-state analysis of temperature in the cantilever tip, a prediction of the onset of bit writing, and prediction of bit formation time and bit size.

3.1 Thermal Analysis of the Cantilever Tip and Polymer Layer

The total heat generated in the highly resistive heater region of the cantilever is transported along the cantilever, into the environment, and across the cantilever-

substrate gap. The total power conducted down the tip is very small compared to the power transferred along other transport paths. The power density in the cantilever tip is substantially higher than the power density along any other heat transfer path from the cantilever heater, and provides several hundred degrees of heating at the tip-substrate interface. Thus, it is the presence of the cantilever heater region that performs the thermal data reading, and the presence of the heated cantilever tip that performs the data bit indentation. The temperature at the tip-polymer interface is a key parameter in engineering the bit-writing process.

Phonon-boundary scattering in the silicon cantilever tip reduces heat transfer along the length of the cantilever tip below the value predicted using bulk properties. Several approaches exist for estimating temperatures with constrictions of size comparable to or smaller than the phonon mean free path. Previous work on phonon-boundary scattering in single-crystal silicon layers solved the Boltzman transport equation with a frequency-dependant phonon mean free path and specularly-reflecting film boundaries [94], and found good agreement with experimental data. One study of heat transport in silicon films of thickness near 100 nm [95] found that thermal conductivity data fit very well to a model that assumes only longitudinal acoustic phonons (LAP) carry heat. This study predicted an average mean free path for the LAP was approximately 300 nm. A study of heat transport in a more complicated geometry [96] separated phonons into heat-carrying LAP and reservoir transverse acoustic and optical phonon modes. This study found substantial reduction in heat transport near a heated source in a crystalline film, both having critical dimensions small compared to the LAP mean free path.

The most rigorous study of heat conduction in the cantilever tip would provide a detailed account for phonon dispersion, and scattering on the tip walls and other phonons. Several unknown parameters reduce the usefulness of the most rigorous possible approach. As silicon is self-passivating, a thin layer of silicon dioxide certainly covers the tip. We speculate that the thickness of this oxide layer depends upon the overall time at which the tip is heated. There may also be contamination on the tip due to long scanning times on an organic substrate. The degree of thermal conductivity anisotropy in the polymer layer is not known, and the surface tension and viscoelastic properties at length scales comparable near the polymer radius of gyration have not been measured, nor do good physical models exist for their prediction. And finally, while there is good tip shape uniformity over an entire cantilever array [29], reports of tip shape between arrays or after long scanning times have not been published, and it is possible that tip wear could be important in thermomechanical data storage. Thus, the modelling of thermomechanical data bit formation employs a more approximate model of phonon transport in the cantilever tip that leverages the physical insights derived from measurements made on thin silicon layers [95] while accepting a larger overall modelling error closer to experimental uncertainties.

Predictions of the temperature distribution along the cantilever tip are made with an analysis that divides the tip into many finite volume elements. Models calculate thermal conduction between adjacent volume elements in the tip,

conduction to the nearby air, and radiation to the nearby surfaces. When the diameter of the cantilever tip is locally comparable to or smaller than the mean free path of the heat carriers in the tip, thermal conductivity is reduced as phonons scatter against the tip walls. The silicon thermal conductivity is therefore calculated using Matthiessen's rule [97]

$$k = \frac{1}{3} C v \left(\frac{1}{\Lambda^{-1} + d^{-1}} \right) \quad (3)$$

Where d is the local tip diameter, k is the local thermal conductivity of the tip, C is volumetric heat capacity, v is the average phonon speed, and Λ is the phonon mean free path in the bulk material [97]. A value of $1.8 \times 10^9 \text{ W / m}^2\text{K}$ is used for the product Cv [98]. The model assumes constant Cv over the range of temperatures considered, which will produce an error of less than 15% [98]. Equation 3 is a modified exact solution for ballistic transport in radially symmetric media [99]. The temperature dependence of the bulk thermal conductivity of silicon is modelled using a fit to room temperature data for bulk samples [100].

Heat is transferred away from the side of the tip through radiative exchange with the heater and the substrate and conduction to the surrounding air. This steady-state model assumes that conduction across the cantilever-polymer air gap produces a constant, linear temperature gradient across the gap. Typical heating times are $1 - 100 \mu\text{s}$ [3,10,29,82] which are much longer than the time of 100 ns for heat to diffuse across a typical cantilever-substrate air gap of thickness $0.3 - 1 \mu\text{m}$. Thus the air between the cantilever and substrate is at thermal steady-state. Even at the smallest gap thickness of 300 nm, the gap is large compared to the mean free path of air molecules at room temperature, which is approximately 60 nm [101]. Thus the temperature gradient across the cantilever-substrate air gap is nearly constant. The resistance to thermal conduction between the tip and the air depends only on the Knudsen slip resistance, which accounts for the diameter of the tip being smaller than the mean free path of the air molecules [102].

For typical loading forces, the tip-substrate contact diameter is near 10 nm. For a perfectly crystalline silicon-silicon point contact, phonon transport across the tip-substrate would be fully ballistic. However, the silicon tip is in contact with a highly disordered polymer medium. Thus the model enforces a scattering site at the end of the tip. The total thermal impedance between the tip and the polymer is given as this phonon scattering site at the end of the tip and a spreading resistance into the polymer. The total thermal impedance, R_{contact} , into the polymer is given as

$$R_{\text{contact}} = \frac{12}{C v \pi d_{\text{contact}}^2} + R_{\text{spread}} \quad (4)$$

Where d_{contact} is the diameter of the tip-polymer contact area, k_{polymer} is the thermal conductivity of the polymer layer, and R_{spread} is the thermal resistance

due to the spread of heat in the polymer layer. The first term in Eq. 4 enforces a phonon scattering site at the tip-polymer interface [103]. The second term is extracted from solution of the heat conduction equation in the polymer layer.

It is clear from Eq. 4 that the diameter of tip-polymer contact strongly affects the top-polymer thermal impedance, and will therefore impact the temperature at the tip-polymer interface. Typically, contact between an AFM tip and a surface is approximated by a Hertzian model, sometimes including terms that account for adhesion forces or viscoelasticity [104]. This typical approach is most appropriate for tip load forces comparable to or less than ~ 5 nN, where adhesion is important; and for hard materials where there is a nearly flat tip-substrate interface [105]. While the PMMA polymer data layer is relatively hard with a Young's Modulus of 3.0×10^9 Pa [106], it is much softer than the silicon tip, and complies with the shape of end of the silicon cantilever tip, thus violating the criteria for a simple Hertzian contact. There exists an exact solution [107] for the indentation of a half sphere into a compliant surface, which relates the loading force, F_{load} , to the contact diameter, $d_{contact}$. The relation is given as

$$F_{load} = \frac{G}{1-\chi} \left\{ \left(r_{contact}^2 + r_{tip}^2 \right) \cdot \log \left(\frac{r_{tip} + r_{contact}}{r_{tip} - r_{contact}} \right) - r_{tip} r_{contact} \right\} \quad (5)$$

Where G is shear modulus, $r_{contact}$ is the radius of contact and half the value of $d_{contact}$, and r_{tip} is the tip radius of curvature. The Poisson's ratio, χ , is 0.5 for an incompressible material.

Typical tip loading forces are in the range of 5 nN – 300 nN [10] and the typical tip radius of curvature is near 20 nm [21]. However, the thickness of the cantilevers will vary with variations in the fabrication process and will also vary across an array or cantilever array, thus inducing a variation in the loading force. The cantilever spring constant varies as a function of the cube of the cantilever thickness [108]. Furthermore, while there is anecdotal evidence that tip wear is minimal for thermomechanical data writing [109], it is possible for tips to wear as they are in contact with and scan over a substrate for a long time [110]. Therefore, the cantilever tip radius of curvature varies from 10 nm to 50 nm in the present work to cover the range of possible practical values.

A range of tip loading forces has been reported to successfully write data bits. While some experimental bit writing data [10] has been reported for tip loading forces near 5 nN, the present contact model does not accurately predict tip-contact diameter below several times the lattice constant of silicon, or in the range of 1 nm, corresponding to loading forces near 30 nN. The maximum tip loading force will be approximately governed by the spring constant of the cantilever, which can be as stiff as 1.0 N / m [3], or as low as 0.02 N / m [10]. Experimentally, the tip loading force can be calculated as the product of the cantilever spring constant and the displacement of the base of the cantilever after the tip has first made contact with the polymer. As sharper tips have a larger dependence of contact diameter on loading force than rounder tips, so too will there be a stronger variation of tip-polymer interface temperature.

The tip is discretized into 1000 volume elements and the temperature distribution is found using Gauss-Seidel iteration. Temperature predictions are validated by an energy balance on each volume element and on the entire tip, and compare well with solutions made with twice the number of volume elements. The calculated value of R_{spread} compares well with a shape factor for a disk source on an infinite half space [111]. For the transient analysis uses time steps equal to 0.01 of the total simulation time. The numerical solution yields of heat transfer in the polymer layer agrees to within 2% of the analytical solution for the transient temperature field induced by constant temperature boundary conditions in both the radial and normal directions.

3.2 Bit Writing Analysis

The conditions required to initiate bit formation include the time, temperature, and force with which the tip presses into the polymer data layer. Transport phenomena in both the cantilever and in the polymer govern the thermomechanical data bit writing process. Heat is generated in the cantilever, and cantilever motion is required for bit formation. The electrical and mechanical design of the cantilever impacts both the thermal and mechanical time constants of bit formation. The tip couples the cantilever beam to the polymer layer both mechanically and thermally. As mentioned above, for times longer than 20 ns, the tip is in thermal equilibrium with the cantilever heater region and acts as a simple thermal resistance. Analogously, the cantilever tip is rigid and therefore has no impact on the mechanical time constants. The polymer layer has a thermal time constant governed by the polymer layer thickness, and a mechanical time constant governed by the temperature field in the polymer near the tip. For a bit to be fully formed, the cantilever must be hot long enough for heat to spread from the tip into the polymer, the cantilever must have sufficient time to move into the bit, and the temperature of the tip must be sufficiently high for the polymer to be soft enough to move away from the tip in this time.

By coupling the mechanical and thermal analysis of bit formation, it is possible to predict the onset of data bit formation and the ultimate data bit size for a given heater temperature, heating time, and loading force. For cantilever heating times that are comparable to cantilever mechanical time constant or the polymer mechanical relaxation time, equations of motion describe the forces acting on data bit formation, allowing an estimate for the threshold temperature for bit formation. For heating times that are very large compared to the cantilever heater temperature and the cantilever mechanical time constant, a quasi-steady model based on the contact model above allows estimate of the same.

In the measurements of Gotsmann [112] and Cross [113], the cantilever has a tip of height 300 nm, tip radius of curvature of 20 nm, spring constant of 0.055 N/m, and a mechanical resonance frequency of 100 kHz, or a mechanical time constant of 10 μ s. The polymer data substrate is a bilayer consisting of 35 nm of PMMA on 80 nm of SU8 epoxy. The polymer bilayer resides on a silicon substrate. The purpose of the SU8 layer is to stop the tip from penetrating to the

silicon, and for thermal insulation [3]. In the experimental analysis of data bit writing [10], a cold cantilever tip is brought into contact with a cold polymer surface. After tip-polymer contact, the base of the cantilever is brought closer to the substrate such that the cantilever tip is pressed into the substrate. The cantilever tip loading force, F_{load} , is the product of this displacement and the cantilever spring constant, k . The cantilever heats at a fixed voltage for a fixed time. Several measurements are made for varying heating voltages and heating times. The cantilever is then calibrated for the cantilever heating temperature produced for each heating time and voltage, as in [91,92].

The temperature-dependant mechanical shear modulus of the polymer is calculated as a function of temperature, pressure, and time. The shear modulus has time, pressure, and temperature-dependant properties. The temperature dependence takes the form of the WLF shift parameter [114], which is used to extract polymer properties from tabulated bulk values [61]. The Reynolds number of tip motion through the polymer is always less than 0.01, and therefore inertial forces inside the polymer can be neglected.

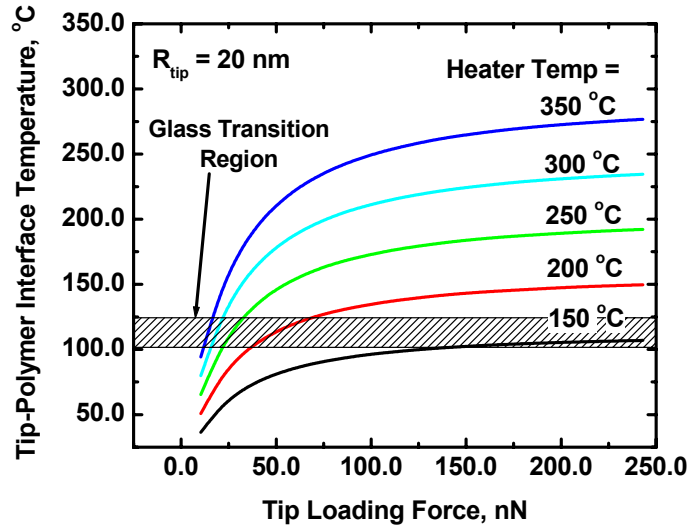


Figure 9: Predicted steady-state tip-polymer interface temperature as a function of loading force for a range of heater temperatures and a tip radius of curvature of 20 nm [87]. The shaded region represents the glass transition region, above which a bit will be written for long heating pulses.

For times comparable to and longer than 10 ms, the cantilever is in thermal and mechanical equilibrium with the polymer data layer. A simple calculation of the mechanical restoring force of the polymer as a function of temperature and time shows that for the longest heating pulses, a temperature of ~ 120 °C in the

polymer layer is required to induce data bit formation. Figure 9 shows predictions for the tip-polymer interface temperature as a function of loading force for various heater temperatures. This model predicts that the lowest heater temperature at which a bit could be written is near 200 °C for a loading force above approximately 75 nN.

It is possible to predict the motion of the cantilever tip through the equation of motion of the cantilever, which is

$$m_{cant}\ddot{x} + kx = F_{load} - F_{pl} \quad (6)$$

Where m_{cant} is the mass of the cantilever, x is the vertical position of the cantilever tip and F_{pl} is the force with which the polymer resists tip motion. The force with which the polymer resists tip motion is a function of the temperature field in the polymer near the tip.

Simulations of heat transfer from the cantilever tip for loading forces less than 500 nN and cantilever heater temperatures less than 700 °C show that the thickness of the softened polymer near the cantilever tip is always less than the cantilever tip radius of curvature. The thickness of the softened polymer is very thin because of the superposition of two steep gradients: the temperature gradient near the cantilever tip is very large since the polymer thermal conductivity is very low at 0.2 W / mK, and the temperature-dependence of the shear modulus is logarithmic. Thus, the very thin region of melted polymer near the cantilever tip allows for modeling of the tip penetration into the polymer as a lubrication problem.

An analytical solution to the force required to displace the lubrication layer links the tip motion to polymer relaxation. At every time step the simulation tests whether the tip loading force is sufficient to move the tip one finite volume element thickness into the polymer layer, according to Eq. 6. The force with which the polymer resists tip penetration F_{pl} can be divided into the viscous resistance of the polymer, $F_{pl,viscous}$ [115] and the elastic resistance of the polymer, $F_{pl,elastic}$ [116]

$$F_{pl} = F_{pl,viscous} + F_{pl,elastic} = 3\pi \frac{\eta_{pl} r_{tip}^4}{t_{pl}^3} \dot{x} + 3\pi G' r_{tip}^2 \varepsilon \quad (7)$$

Where η_{pl} is the polymer viscosity, t_{pl} is the average thickness of the softened polymer near the tip, r_{tip} is the effective radius of the tip-polymer contact, or half of $d_{contact}$, x is the vertical position of the tip, G' is the elastic part of the shear modulus and ε is the strain in the melted polymer. If the criteria for tip motion are met, then the tip moves one element into the polymer. The new position of the tip serves as a position of the constant-temperature boundary in the solution of the heat equation. The polymer from the elements replaced by the tip are

thrown away as they are assumed to have flowed away from the tip. The simulation stops when the tip has penetrated to a depth of 10 nm, which corresponds to the threshold for experimental bit writing.

Figure 10 shows measurement and prediction results. The measurement results are for loading forces of 30 nN, 90 nN, and 100 nN, and the prediction results for 30 nN and 100 nN. The measurements are from Gotsmann [117] and Cross [118]. Both measurements and predictions are for a cantilever tip radius of curvature of 20 nm. Predictions from the modeling of the present study are shown for both a moving tip and for steady-state thermal conditions. To within experimental error and measurement scatter, the modeling and simulation of the present work compares well with measurements.

The drop in threshold writing temperature for longer writing times is due to three factors: the inertia of the cantilever which must be overcome for tip motion, heat diffusion into the polymer, and the viscoelastic response of the polymer to tip penetration. First, the cantilever mechanical time constant of 100 kHz prohibits a data bit from being written much faster than approximately 1 μ s, so due only to the cantilever mechanical time constant, we expect an asymptotic increase in threshold writing temperature as heating times decrease to near 1 μ s. The steep increase in temperature required to write a data bit for short times also corresponds to the time required for heat to diffuse into the polymer layer away from the tip, and the time- and temperature-dependence of the polymer properties away from the tip. As shown in Eq. 7, the force with which the polymer resists tip penetration has a cubic dependence on the thickness of the soft polymer near the penetrating tip. The long time behavior of tip penetration, which asymptotically approaches a threshold bit-writing temperature of approximately 200 $^{\circ}$ C, is a function of only the polymer temperature-dependant shear modulus.

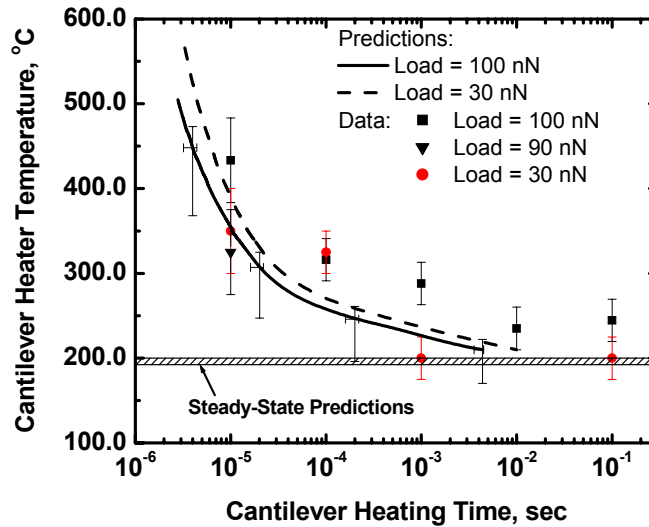


Figure 10: Measurement [112,113] and prediction [87] of the threshold conditions of time, temperature, and tip loading force required to produce a data bit for a 20 nm tip radius of curvature. The grey area shows predictions for equilibrium conditions, bounded by loading forces of 30 nN and 100 nN.

The two loading forces of 30 nN and 100 nN for which predictions are made in Fig. 10 bound the reasonable practical loading window of the present thermomechanical data storage cantilever [3,10,29,117,118]. Measurements are shown for these two loading forces, plus a single measurement at a loading force of 90 nN. The 30 nN and 90 nN measurements were made as a group [118] and the 100 nN measurements were made at a separate time [117]. The large experimental scatter can be attributed to the difficulty of calibrating the cantilever heating temperature and loading force, as well as the difficulty of accurately measuring features of size near 10 nm. In practice, the data storage is extremely robust and the tip usually penetrates through the polymer layer. The predictions show a 20 – 50 °C difference in threshold writing temperature between the 30 nN and 100 nN loading forces at a given heating time. This is consistent with the difference between the measurements made at 30 nN and 90 nN, which were made at the same time with the same cantilever. However, the scatter between the two sets of data cannot further support this prediction. The predictions of Fig. 10 also show that for a constant heating temperature, the difference in loading force between 100 nN and 30 nN will yield a 50 – 100 % difference in heating time required to produce a data bit.

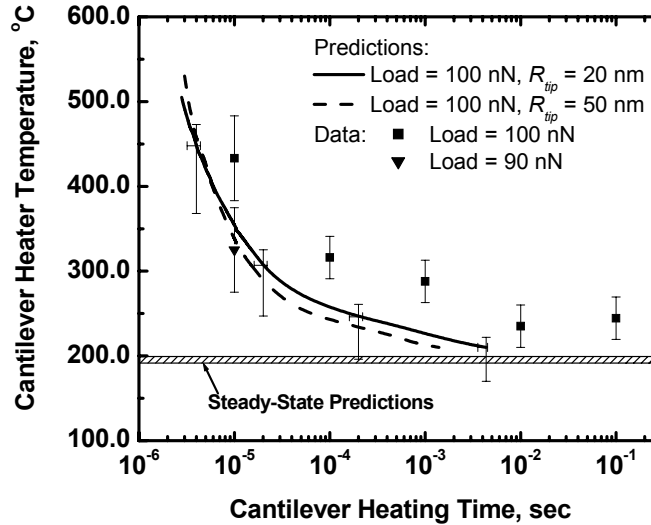


Figure 11: Measurement [112,113] and prediction [87] of the threshold conditions of time, temperature, and tip loading force required to

produce a data bit. The data is for a measured 20 nm tip radius of curvature. The predictions are for two values of tip radius of curvature, at 20 nm and 50 nm. The grey area shows predictions for equilibrium conditions, bounded by loading forces of 30 nN and 100 nN.

Figures 10 and 11 provide insight into the previously published experimental results that a threshold temperature of 350 °C writes a data bit [3,29]. One possible explanation is that, as shown in Fig. 9, 350 °C is the temperature at which a bit is *always* written, regardless of loading force. Another important parameter is that these reports always wrote bits at 10 – 20 μ s, for which the predictions of Fig. 5.3 show that the threshold writing temperature is 300 – 350 °C.

The shape of the cantilever tip can impact the onset writing conditions. Previous work has investigated the wear of cantilever tips during AFM data storage [18,110,119]. These studies have focused on AFM reading of features much larger than the present thermomechanical data storage bits at 100 nm or more. It was possible for these authors to fabricate AFM cantilever tips with a radius of curvature of 4 nm [18]. Long-term experiments with the tip scanning large distances over polymer media, in one case as high as 16 km of tip travel [110], found that the tip wears to a radius of curvature of 100 nm [110,119]. The limits of data density in a thermomechanical data storage system depend upon the sharpness of the cantilever tip, and thus it is desirable to reduce the wear of the tip as much as possible. The tip shape affects not only the size of the ultimate bit, but also the time and temperature required for bit formation. Figure 11 displays the 100 nN and 90 nN measurements shown in Fig. 10, as well as predictions for bit writing with cantilevers with tip curvature radii of 20 nm and 50 nm. The measurements were made with cantilever tips of 20 nm radius. The predictions show that a less sharp tip will have a higher threshold writing temperature at short times, but at long times the less sharp tip can penetrate the polymer with a lower heating temperature. These predictions are reasonable consequences of the model of heat transfer between the cantilever tip and the polymer substrate. The less sharp tip reduces the thermal impedance between the cantilever tip and the substrate, reducing the tip-polymer contact temperature for a given cantilever heater temperature. Thus, a higher heater temperature is required in order to form a data bit. For long heating times, the contact area between the tip and the sample is increased for the less sharp tip over the contact area of the sharp tip, and increasing the spread of heat into the polymer substrate. Because more polymer is heated underneath the less sharp cantilever tip at long times, the temperature required to write a data bit is reduced.

Errors in the analysis of bit writing originate from three sources: differences between tabulated properties for bulk PMMA and the actual properties of PMMA in an ultrathin film, errors in modelling the value of F_{pl} , and numerical errors. The largest of these are modelling errors for F_{pl} and the errors originating from unknown property values. The sum of the property errors, numerical errors, and modelling errors induce a total error of +7% / -

22% in time and +6% / -23% in temperature [87]. Figures 10 and 11 display the overall error of the present modelling approach through error bars on the smooth prediction curves in several places.

The modelling and simulation approach and results could be used to improve writing rate and data density of thermomechanical data storage device. The two most easily modified cantilever design parameters are the tip shape and the cantilever resonance frequency/loading force. One possible improvement in the tip shape would be to flatten the tip-polymer interface, or even to create cylindrical rather than conical tips, in order to reduce the tip-polymer interface temperature. One possible improvement in the cantilever design would be to increase the cantilever resonance frequency while preserving the cantilever spring constant, which would allow high loading forces and improved cantilever mechanical response time.

4 Thermal data reading and topography mapping

A major consequence of the model of data bit writing described in Section 3 is its aid in understanding the mechanism of thermal data bit writing versus thermal data reading. The first report of thermal data reading [3] noted the change in thermal impedance between the cantilever and the polymer data substrate as the mechanism that allowed measurement of the nanostructured polymer surface. However, it was unclear whether the change in thermal impedance was due to thermal conduction through the cantilever tip or due to conduction across the air gap. It was further unclear as to whether the softening of the polymer required for data bit formation was due to heating from the cantilever tip alone or heat delivered from the cantilever heater across the air gap. A comparison of the modified continuum model of conduction through the cantilever tip represented by Eqs. 3-5 to a one-dimensional model of heat transfer across the air gap shows that the temperature rise at the tip-polymer interface is much higher than the temperature rise in the polymer layer due to conduction and radiation across the cantilever-polymer gap. Predicted typical values for the temperature of the tip-polymer interface are several hundred degrees Celcius, and the predicted temperature rise in the polymer due to heating from the cantilever alone is less than 20 °C. Therefore, it is the presence of the cantilever tip that induces polymer melting and the resulting data bit formation. Comparison of the quantity of heat that is transferred through the cantilever tip with the quantity of heat that is transferred across the air gap shows that a factor of approximately 10^3 more heat goes across the air gap than through the cantilever tip. It is therefore the change in thermal impedance between the cantilever and substrate that allows thermal data reading. The realization that separate heat transfer mechanisms facilitate data bit writing and thermal data reading allowed simultaneous improvement of cantilevers for thermal data reading and writing [82] and also for cantilever array operation [92].

The thermal detection of data bits could be expanded as a general topography mapping technique. Typically, AFM cantilevers designed for topographic sensing employ optical detection of cantilever deflection [1], or a piezoresistive cantilever that acts as a strain gauge [2]. The advantage of the

piezoresistive cantilever is that optical access is not required, thus allowing the operation of cantilever arrays. This section ^[120] compares the theoretical sensitivity and resolution limits of piezoresistive and thermal cantilevers for topographic mapping.

The thermal conductance from the cantilever governs thermal reading sensitivity. Through operation in a Wheatstone bridge where each leg of the bridge has an electrical resistance equal to the electrical resistance of the cantilever, the voltage displacement sensitivity of the thermal cantilever is **[Error! Bookmark not defined.]**

$$\frac{\partial V}{\partial z} = -\alpha \frac{V_b^3}{8C(z)^2 R} (\partial C(z) / \partial z) \quad (8)$$

Where V is the voltage read from the bridge, z is the distance between the cantilever and the substrate, α is the temperature coefficient of electrical resistivity, V_b is the bridge bias voltage, C is the thermal conductance from the cantilever, and R is the temperature-dependant cantilever electrical resistance.

The ability to detect small displacements is limited by several factors, including amplifier noise, Johnson noise, thermomechanical noise, and 1/f noise. It is possible to provide analytical expressions for all of these noise sources, and carry out a quantitative analysis of their relative importance. While there are several proposed mechanisms behind 1/f noise, it has been shown that a model for this noise offered by Hooge provides an excellent empirical fit to data [2], and that it competes with Johnson and amplifier noise only for very lightly-doped piezoresistors in very thin cantilevers, or at low frequencies. For the purposes of this analysis, it is neglected. Amplifier noise is also neglected, although it will be an important practical consideration for both the piezoresistive and thermal cantilevers. The total thermal and Johnson noise in the cantilevers will have a magnitude

$$V_{noise} = \sqrt{(\alpha V_b T)^2 \frac{k_B}{C(z)} + 4k_B T R} \quad (9)$$

The first part of Eq. 10 refers to the thermal noise, and the second part accounts for Johnson noise. The minimum detectable feature size is then

$$z_{min} = \frac{Noise}{Sensitivity} = \frac{V_{noise}}{\frac{\partial V}{\partial z}} \quad (10)$$

The thermal conductivity of the thin, doped silicon cantilever is less than the thermal conductivity of pure, bulk silicon due to phonon-impurity and phonon-boundary scattering. While the thermal conductivity of doped, thin silicon layers does not exist for a wide range of temperature, thickness and doping concentration, a nominal value of $k_{cant} = 50 \text{ W / mK}$ can be taken from the

available literature [121] for a cantilever doped to its saturation point near room temperature and of thickness 300 nm. The thermal conductivity of the air is $k_{air} = 0.03 \text{ W/mK}$ at room temperature. At $z = 300 \text{ nm}$ $k_{air} = k_{air,bulk}$. However, the mean free path of air molecules at standard temperature and pressure is approximately $\lambda_{air} = 60 \text{ nm}$ [101] and thus for values of z comparable to and less than λ_{air} the thermal conductivity will be reduced from its bulk value

In practice, the design space for thermal cantilever is large and extends considerably beyond the sizes and shapes of thermal cantilevers suggested previously. For convenience, the dimensions for both the thermal cantilever and the piezoresistive cantilever are selected such that the cantilever length, width, and thickness are the same as the Millipede cantilever.

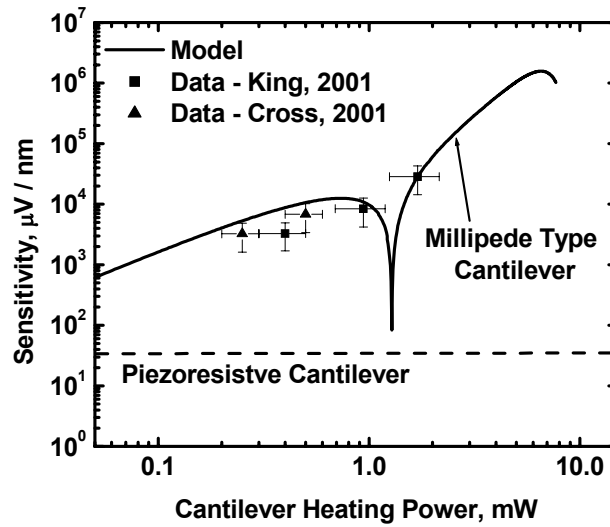


Figure 12: Voltage displacement sensitivity for the Millipede cantilever in thermal operation and for an identically-sized piezoresistive cantilever [120]. Data is from Refs. [10,82]. The piezoresistive cantilever operates at a constant bias voltage.

Figure 12 shows predicted sensitivity for the thermal cantilever over a range of operating power, which corresponds to a range of operating voltage and temperature. The sensitivity increases with decreasing cantilever thickness. The sensitivity shown is the absolute value: temperatures near room temperature, the temperature coefficient of resistivity is negative. The sharp decrease and subsequent rise of sensitivity near 1 W is the point where the temperature coefficient of resistance changes numerical sign. The measurements in Fig. 12 were not explicitly made for differential sensitivity, but rather a step change in cantilever height [92]. However, the trend and order of magnitude in the model compares very well with the data, thus building confidence in the analysis.

Figure 4 also shows the predicted operation of the piezoresistive cantilever at a constant bridge voltage of 2 V. The piezoresistive coefficient of doped silicon decreases with increasing temperature, and it is therefore desirable to operate the piezoresistive cantilever as close to room temperature as possible. The models for the behavior of piezoresistive cantilevers are well established and while no data is provided for the piezoresistive cantilever sensitivity, matching measurements and models has been demonstrated elsewhere [2]. Overall, the thermal cantilever is between two and four orders of magnitude more sensitive than the piezoresistive cantilever.

Figure 13 shows predictions for the minimum detectable resolution of the thermal cantilever and piezoresistive cantilever. The model for the behaviour of the piezoresistive sensor is taken from established measurements and models [2]. While sensitivity is important, it is the overall cantilever resolution that is most important for measuring small features. The lowest possible resolution is desired, which corresponds to thinner cantilevers and higher heating powers. While more experimental work remains to more fully understand the thermal topography sensing, the remarkable improvement of thermal sensing over piezoresistive sensing offers great potential for metrology with heater-cantilevers.

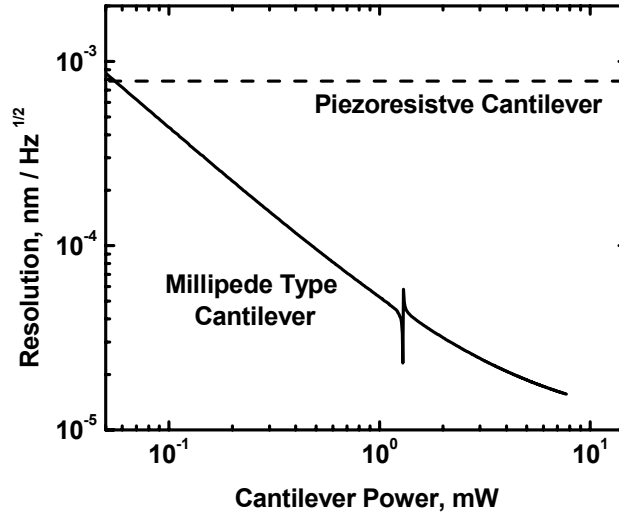


Figure 23: Predicted minimum detectable feature size for the Millipede cantilever in thermal operation and for an identically-sized piezoresistive cantilever [120]. The piezoresistive cantilever operates at a constant bias voltage.

5 Summary and Conclusions

This chapter reviews fundamental and applied work that aids in understating the basic physical processes in the thermomechanical formation of polymer nanostructures, and improves the designs of devices for their formation and detection. Significant open scientific questions address the physics of soft materials at length scales comparable to molecular size, described in a review of fundamentals of sub-continuum mass transport in soft materials. A fundamental investigation of mechanical relaxation in ultrathin nanostructured polymer films shows the thickness-dependence of polymer mechanical properties at dimensions comparable to the polymer radius of gyration. The nanostructures show remarkably fast local relaxation compared to the relaxation of the whole polymer. Analysis of thermomechanical data bit formation shows the temporal and spatial limits of thermomechanical features formed in polymer, and the dependence of the processing on cantilever tip geometry. The large temperature drop across the cantilever tip accounts for the high temperatures required in the cantilever heater region in order to induce onset bit writing. Predictions show that future tips could be optimized such that the tip cone is very sharp but the tip-polymer interface would be broadened. Thermal analysis of the cantilever and cantilever tip improves understanding of the heat transfer paths in thermomechanical writing and reading. Cantilevers are optimized simultaneously for thermomechanical data bit writing and thermal data reading, allowing design improvements for cantilevers, cantilever arrays, and data storage systems. Finally, an analysis of the thermal cantilever for topographic sensing shows that the thermal cantilever has one-four orders of magnitude more sensitivity and one-two orders of magnitude higher resolution than piezoresistive sensors of comparable size and shape.

Technical challenges remain in the development of a thermomechanical data storage system. While the basic mechanisms of thermomechanical data bit write, read, and erase are understood, a detailed relationship between tip shape, bit shape, and operating parameters remains has not been established, either theoretically or experimentally. The sub-continuum models of heat and mass transport in the cantilever tip and in the polymer layer should be improved with detailed numerical studies supported by measurements. Mechanical wear of the tip and of written bits has not been investigated in detail, nor has possible chemical wear in the polymer. The overall accuracy of the manufacturing process will also affect the window of cantilever operation.

The thermomechanical formation of polymer nanostructures offers an inexpensive technique for the controlled formation of mechanical structures with dimensions near 1 nm. The thermomechanical manufacturing platform consists of a heated AFM cantilever, which can form polymer nanostructures as well as thermally map the modified polymer surface. Additionally, micromachined imprinting masters mold large areas with nanometer-sized features [122]. This manufacturing technique allows the formation of small mechanical features for MEMS and micro-mechanical devices. Engineering a polymer nanostructure will not only address the thermomechanical process by which it is formed, but also the chemical nature of the polymer and the imprinting device, to produce mechanical structures which interact with biological and chemical systems. The growth of the organic electronics market offers opportunities for direct

mechanical formation of nanometer-scaled quantities of bandgap-engineered polymers for organic light emitting diodes and other organic electronics [123]. Another example is compliant fluidic MEMS fabricated from elastomeric materials [124]. Finally, MEMS structures could be produced where the polymer mechanical elements are also optically [123] or biochemically [125] active.

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