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Exploiting Chemical Switching in a Diels–Alder Polymer for Nanoscale Probe Lithography and Data Storage**

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Reversibly crosslinked polymer films have properties that are beneficial to scanned-probe data storage and lithographic applications that use thermomechanical nanoindentation as a write or expose mechanism. The novel polymer under study contains linkages based on thermally reversible Diels–Alder crosslinking. Thermomechanical properties on the nanometer scale are analyzed by indentation experiments on polymer thin films using heated tips. The underlying indentation mechanism is studied at varying tip temperatures and indentation times, revealing Arrhenius kinetics. This is in contrast to the Williams–Landau–Ferry kinetics usually observed for polymer systems. The discrepancy is explained by the reversible crosslinking incorporated into the structure of the polymer that allows switching between two different states: a rigid, highly crosslinked, low-temperature state, and a deformable, fragmented, high-temperature state. An individual indentation volume of less than 10^{-20} L (10 000 molecule pairs) is estimated. These kinetics experiments demonstrate that a chemical reaction of only a few thousand molecules can be transduced into a mechanically measurable action. The ability to cycle between two sets of properties in these materials opens up new perspectives in lithography and data storage. Examples of data storage with densities up to 1 Tb in.^{-2} and mask-less lithography with resolution below 20 nm are demonstrated at writing times of 10 μs per bit/pixel.

1. Introduction

The small tip dimensions and high lateral resolution of scanning-probe devices constitute a strong driving force for probe-based lithographic and data-storage applications.^[1–8] In an AFM-based (AFM: atomic force microscopy) device currently under development,^[6] a nanometer-sized tip in mechanical contact with a surface makes indentations at predefined positions. The existence (absence) of an indent then represents written information: a “1” (“0”) in a data-storage context or “exposed” (“unexposed”) resist in the context of lithography. Concomitant trade-offs, such as speed and price, are being addressed by batch fabrication and parallelization. For example, the relatively low writing speeds of 1–10 μs per indent (0.1–1 MHz) can be increased by a factor of 100–1000 by using arrays of probes.^[6]

These scribing strategies impose significant mechanical and physical requirements on the recording medium ranging from i) homogeneity on the nanometer scale, to ii) resistance against wear of the sliding tip, to iii) facile deformability during the write/expose step. One concept that satisfies these demanding material requirements is to switch the mechanical properties of the material between two states: 1) a compliant state for writing (indentation), and 2) a tough state for reading the written pattern. Polymers are good candidates because of their thermal behavior and their homogeneous composition of repeat units down to the nanometer scale. This has been demonstrated in schemes for thermomechanical writing that use a combination of heat and force to press a heated, sharp tip into a polymer surface, creating a plastic deformation.^[2,6,9,10] The heated tip causes very local heating of the polymer material above its softening temperature, which effectively acts as the switch to turn on the writing process.^[11]

Although linear polymers exhibit such switching behavior above and below the glass-transition temperature (T_g),^[6] they do not satisfy the other device requirements, especially stability to the repeated motion of surface scanning during imaging (e.g., reading).^[12] To optimize the long-term stability of the polymer in its low-temperature rest state, crosslinking is proposed to increase the barrier of polymer-network disentanglement. Crosslinking improves wear resistance while conserving homogeneity in the polymeric thin film that serves as a resist or recording medium. However, the increases in hardness and T_g that accompany crosslinking cause increased wear on the scribing element. Hence, the two sets of requirements for the passive rest state and the active indentation state appear to be mutually exclusive.

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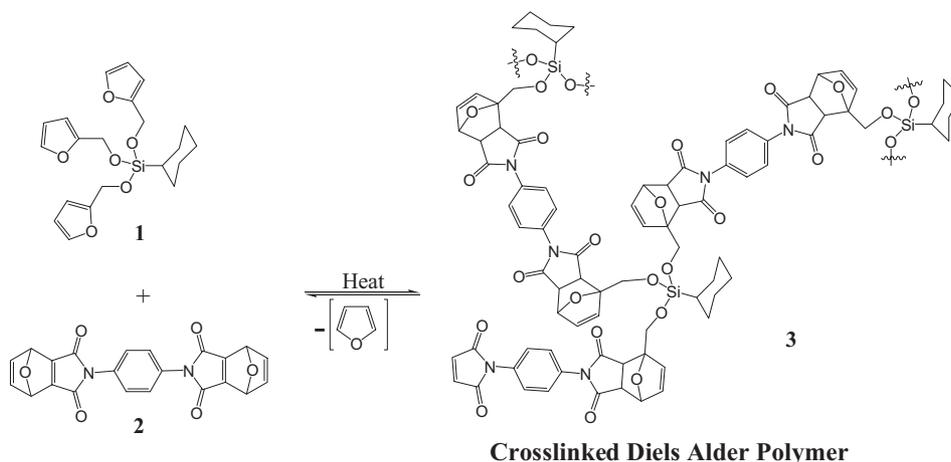
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To overcome the divergence between the two sets of requirements, a scheme of reversible crosslinking is proposed that allows the thin film to exist in two different chemical states: a low-temperature state of high-molecular-weight material and a high-temperature state of low-molecular-weight molecules (see Scheme 1). Reversibility is critical to the success of such a switchable thermally responsive medium; the switching between the two states occurs via an associative/dissociative mechanism. The dissociation of molecules replaces the glass transition in normal polymers as a switch. A transition temperature, T_r , between the two states in the range of technical interest (75–150 °C) can be found in thermoreversible Diels–Alder (DA) reactions.

Thermally reversible DA reactions, particularly the cycloaddition reaction between maleimides and furans, have been used in the preparation of crosslinked polymers.^[13–20] In this report, we demonstrate the feasibility of this reversible crosslinking approach in the study of reaction dynamics during thermomechanical indentation.

2. Results and Discussion

Key to the use of DA materials^[21] in this study is an initial coupling reaction between the tris(furan), **1**, and the protected bis(maleimide), **2** (Scheme 2). The novel use of furan-protected bis(maleimide) derivatives such as **2** was dictated by the inability to obtain high-quality, reproducible thin films from

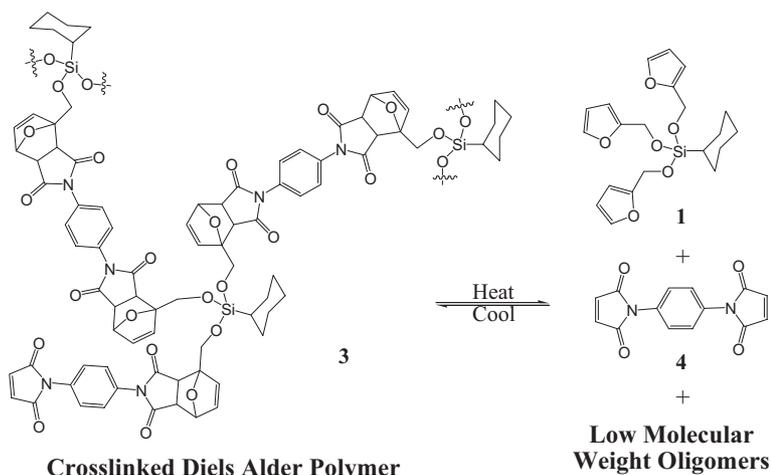


Scheme 2. Facile formation of crosslinked DA thin films, **3**, by a novel, protected-monomer approach.

unprotected bis(maleimide), **4**, due to uncontrolled crosslinking which occurs even at room temperature with **4**. The use of the protected derivative, **2**, allowed significant improvement in the processability of these materials and permitted the reproducible formation of defect-free thin films of the DA thermoset, **3**. On heating, these films underwent a retroreaction to give a soluble film that was shown by chromatographic analysis to contain the tris(furan), **1**, bis(maleimide), **4**, and low-molecular-weight oligomers (number-average molecular weight, $M_n < 2000$ amu) (Scheme 1).

In the course of our studies on the suitability of DA polymers for lithography and storage, we have exploited the thermomechanical response of our local-probe technique to address the kinetics of thermal transitions in the thin-film sample. We uncovered critical differences between the indentation dynamics of standard polymers and the DA polymers. Dynamics were addressed in writing threshold experiments by varying the duration of the heat pulse. The time–temperature inter-relationship is known to be universal and does not depend on the particular quantity measured in the mechanics of polymers.^[6] In particular, it should not depend on pressure, contact size, thermal conductivity, or transient interaction field.

The measurements were performed under ambient conditions using a home-built atomic force microscope and cantilevers with heatable tips for local heating of the polymer under the tip. In all the experiments reported here the tip was initially brought into contact with the sample using a low loading force of less than 10 nN. Indentation was performed by simultaneously applying a force and a heat pulse to the tip using electrostatic means and a resistive heater element, respectively.^[11,22] The heater is integrated into the cantilever. Since the heat has to be transported from the heater through the tip into the polymer media, there is some thermal loss between the heater and polymer. The temperature of the polymer surface, T_{polymer} , can be expressed as



Scheme 1. Reversible Diels–Alder (DA) reaction for depolymerization of crosslinked thin films on heating and recrosslinking of the low-molecular-weight products on cooling.

$$T_{\text{polymer}} = RT + c(T_{\text{heater}} - RT) \quad (1)$$

where RT denotes room temperature and T_{heater} denotes the heater temperature. For most polymer–tip combinations, the heating-efficiency coefficient, c , is on the order of 0.4–0.6.^[11]

The conditions required to create (write) and characterize (read) an indentation in the DA polymer film are determined in a “read–write” operation, shown in Figure 1. The indentations in Figure 1a and b were written by applying heat pulses of 10 μs duration at final heater temperatures of 350 °C (Fig. 1a) and 260 °C (Fig. 1b). With each heat pulse, force pulses of 390 nN (Fig. 1a) and 340 nN (Fig. 1b) were simultaneously applied. The densities of the written indentations correspond to storage densities of 600 Gbit in.⁻² (Fig. 1a) and 1.1 Tbit in.⁻² (Fig. 1b).

The nanoindentations written in the DA polymer material are surrounded by rims, similar to nanoindentations written in standard polymer materials.^[6,11] The rims result from a pile-up of the material displaced from the indented volume, and their formation is a characteristic of plastic deformation. To further elucidate the indentation process, the indentation size was examined as a function of the writing conditions. Figure 1c shows the influence of load and temperature for a fixed write time of

10 μs . A minimum temperature for any given load is required to form a permanent indent. On increasing the temperature or load the indents increase in size until neighboring indents begin to overlap, constituting conditions for erasure.^[6,11]

The minimum heater temperature required to produce an indentation of 0.5 nm depth is called the writing threshold. We chose this well-defined criterion for the characterization of the indentation process as the limiting case of nearly zero-depth indentation, thereby avoiding the more complex indentation dynamics of greater depths. The writing-threshold temperature depends linearly on the applied load, as shown in Figure 1d. In this case, the threshold obeys a linear relationship given by an intercept value of 566 °C for the heater temperature at zero force and a slope of 0.6 °C nN⁻¹. Hence, we conclude that the writing threshold is governed by a softening transition whose temperature strongly depends on the applied load. The same generic behavior is also observed for standard polymers.

Combining writing threshold measurements with a heating efficiency of $c = 0.4$ (see Experimental section, Eq. 4.), the DA material is found to have an effective polymer temperature at the writing threshold as a function of the load force, F , given by:

$$T_{\text{polymer}} = T_0 - bF \quad (2)$$

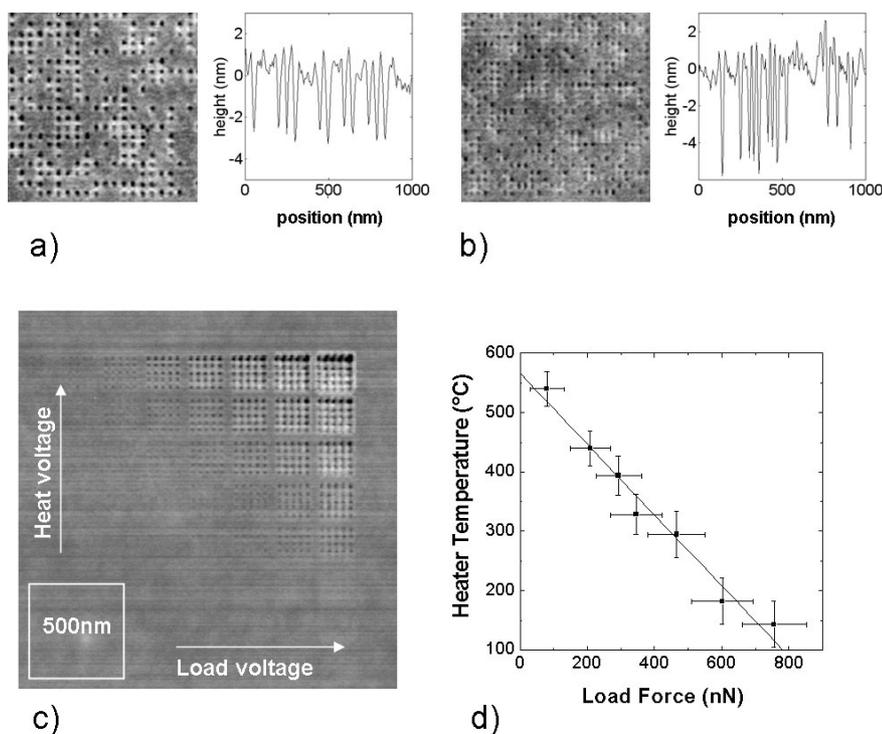


Figure 1. Indentation conditions and quality of DA polymer films (130 nm thick). a,b) AFM images and line traces of two random patterns of indentations recorded at indentation pitches of 36.6 and 27.5 nm, respectively. See text for writing conditions. Using appropriate coding the resulting signal-to-noise would support a storage density of more than 1Tb in.⁻² at sufficiently low error rates [22]. c) AFM image of indentations (“bits” or “pixels”) for varying heater and load voltages. The load and temperature ranges are, respectively, from 50 to 750 nN and from room temperature to 550 °C. An array of five-by-five indentations is written for each set of write parameters. The indentation pitch is 36.6 nm and the write time per indentation is 10 μs . d) Writing threshold deduced from (c). The threshold is defined as the minimum heater temperature required for the formation of an indent of at least 0.5 nm depth at a given load force.

with two empirical parameters: $T_0 = (230 \pm 30) \text{ }^\circ\text{C}$, describing the polymer threshold temperature in the limit of zero load, and $b = (0.25 \pm 0.1) \text{ }^\circ\text{C nN}^{-1}$, describing the dependence of the threshold temperature on load.^[11] The given value of b is valid for a tip radius of 10–20 nm and will be lower for blunter tips.

Equation 2 holds for polymeric systems in general,^[11] regardless of their chemical nature. We compared writing parameters of threshold and indentation depth as a function of heater temperature for linear polymers of similar T_g (T_g of polymer $\sim T_r$ of DA system) and for permanently cross-linked polymers (of similar crosslink density to our DA materials). The observed differences^[23] in T_0 and b do not allow definite conclusions on the indentation mechanism to be drawn. In particular, we cannot distinguish whether thermomechanical indentation of the DA material is governed by the reversible crosslink reaction or by polymer-chain dynamics, as in standard polymers. For that we must proceed to an examination of the indentation kinetics.

A plot of the writing threshold temperature versus the heating time, τ , is shown in Figure 2. Three polymers are compared: the DA polymer at a load of 100 nN, a linear poly (methyl methacrylate) (PMMA)

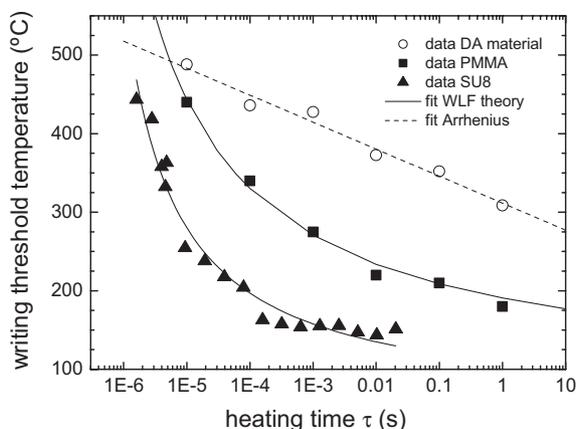


Figure 2. Writing threshold heater temperature as a function of heating time at a fixed load for the DA material (○), linear polymer PMMA (■) and irreversibly crosslinked SU8 (▲). The dashed and solid lines are fits using Arrhenius and Williams–Landau–Ferry (WLF) kinetics, respectively (for which it is taken into account that the actual temperature of the polymer is significantly lower than the heater temperature).

sample^[6] at very low loads (< 10 nN), and a highly crosslinked epoxy, SU8^[11] at 200 nN. For linear polymers such as PMMA, extensive studies of chain dynamics have established that their main mechanical properties follow the so-called time–temperature superposition^[25] and their kinetics are well described by the Williams–Landau–Ferry (WLF) equation. We found good correlation between our PMMA data and literature values for WLF fit parameters of bulk PMMA.^[26] We obtain the WLF parameters $T_{\infty} = 59^{\circ}\text{C}$, $c_1 = 10$, $c_2 = 61^{\circ}$ (T_{∞} , c_1 , and c_2 are defined in the literature^[25]) for a reference temperature of 120°C using a heating-efficiency coefficient, $c = 0.5$. It is noteworthy that these kinetics measurements are made on a sampling size in a confined region of 20 nm laterally on films of 130 nm thickness.

SU8 is a second complementary reference material where crosslinking occurs at a similar density as in the DA material, but in a permanent, irreversible manner. Thin films of SU8 also demonstrate WLF indentation kinetics when measured with our heated probe ($T_{\infty} = 33^{\circ}\text{C}$, $c_1 = 3.13$, for a reference temperature of 120°C). It is important to note that the lower writing threshold temperatures for SU8 in Figure 2 do not indicate superior performance as a medium in applications. On the contrary, its high T_g ($\sim 220^{\circ}\text{C}$) and crosslink-induced hardness require a high load force (200 nN) in order to perform in the same writing temperature range as the other polymers.

Note that the heater temperature is not sufficient to raise SU8 above its T_g . Macroscopically, plastic deformation below T_g is described as “yielding” and follows Arrhenius-type kinetics.^[27] It has been argued, however, that the glass transition is lowered for materials under high deformation and stress, giving rise to WLF kinetics even below the tabulated T_g .^[28] Our data on SU8, in fact, strongly support the latter explanation of T_g lowering under high forces. The sensitivity of our heated-probe setup has allowed the demonstration that thin films of conventional linear and permanently crosslinked poly-

mers exhibit indentation kinetics controlled by standard polymer-chain mobility, well described by WLF theory.

Notably different behavior is observed for making indentations in the DA material, best characterized by Arrhenius kinetics:

$$1/\tau = A \exp(-E_a/kT_{\text{polymer}}') \quad (3)$$

where k is the Boltzmann constant, $T_{\text{polymer}}' = 273 \text{ K} + T_{\text{polymer}}$ is the absolute writing temperature in the polymer (according to Eq. 1), τ the heating time, and A is a constant. Using a c value of 0.4 (see temperature calibration in the Experimental section) we can determine the activation energy, E_a , albeit subject to a large systematic error given the uncertainty associated with the value of c . The activation energy $E_a = 2.8 \text{ eV}$ (64 kcal mol^{-1}) $\pm 50\%$ ^[29] obtained in this way is consistent with the activation energy for the dissociation reaction of a DA crosslinked matrix (see previous publications^[20,30] and references therein). Hence, we conclude that the primary mechanism for indentation formation in the DA polymer is dissociative uncrosslinking and *not* polymer-chain mobility.

A simple estimate^[31] of the indentation volume of less than 10^{-20} L in a writing-threshold experiment corresponds to less than 10 000 DA molecule pairs. The kinetics experiment therefore demonstrates that a chemical reaction of only a few thousand molecules can be transduced into a mechanically measurable action.

There are distinct advantages for the development of future technologies in having a polymeric medium that conforms to Arrhenius reaction kinetics. For example, in extending writing operations toward the nanosecond timescale, WLF kinetics predict prohibitively high heater temperatures in excess of 1000°C . On the other hand, the thermal requirements of materials that follow Arrhenius kinetics increase logarithmically, typically 50°C per order of magnitude of timescale (see Fig. 2), and, thus, nanosecond timescales can potentially be achieved with manageable operating temperatures.

A previously unresolved issue of using nanoindentation for lithography has been caused by volume conservation of the polymer material. Each pixel (indentation) and line is surrounded by a pile-up area,^[4] making line-crossing difficult at very high densities. Our DA polymer has the distinct advantage that, above the critical temperature T_r , the medium contains small molecular entities, that, in principle, can be removed locally by evaporation before recombination. This is illustrated in the following example in which the scanning probe is used for thermolysis.

Demonstration that the DA material can be controllably and locally removed by a thermal probe has been termed “nano thermal gravimetric analysis”. While the tip temperature is continuously increased along the slow-scan axis, low loading forces are maintained between the tip and polymer surface. A real-space image of thermal degradation (a “wear track”) is generated, in which each fast-scan line corresponds to a certain tip temperature. In the example given in Figure 3 no change in the surface is seen in areas scanned with heater temperatures up to 320°C . (The difference in writing parameters, i.e., tem-

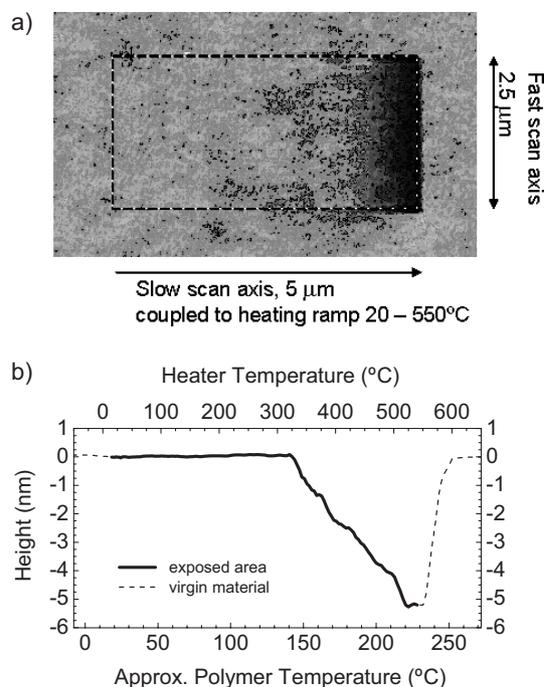


Figure 3. “Nano thermal gravimetric analysis” with a scanning thermal probe. a) AFM image of the surface of the DA film after exposing the center region (dashed) to ramped heater temperatures from room temperature to 550 °C while scanning with 512 lines at $50 \mu\text{m s}^{-1}$ along the fast scan axis. The exposure was repeated ten times. The loading force was $<10 \text{ nN}$. The grey scale spans 5 nm in height. b) Height profile of (a) averaged over the exposed region. The x-axis (0– $5 \mu\text{m}$) is replaced by the heater temperature (room temperature–550 °C). The change in height is directly proportional to the amount of material volatilized. The approximate polymer temperature under the tip is calculated from the known dissociation temperature of the DA material at the given timescale (see text).

perature and force, that modifies the DA surfaces shown in Figures 1d and 4 is caused by the different indentation time-scales used in the two experiments.) On further increasing the temperature, the depth of the wear track increases linearly up to 550 °C. Notable is the lack of debris. In addressing the mech-

anism of track formation, compression is ruled out based on the observation that measured wear is cumulative: repeating the experiment in a given area yields a proportional increase of the wear depth. Hence, we conclude that the material is lost by evaporation or diffusion onto the tip.

The amount of material loss at each temperature can be determined from the dimensions of the void volume created in the wear track: dimensions of depth and width are readily provided by the topography image. Coupling the volume with density yields thermogravimetric analysis results, obtained in situ and on remarkably small amounts of material.

The wear behavior induced by the mechanical scanning action of the tip on linear polymers such as PMMA and polystyrene^[32] is characterized by rippling of the polymer surface. Since ripple wear is suppressed in highly crosslinked polymers,^[33] we take the lack of rippling in unheated DA films as evidence that they, too, are in a highly crosslinked state.

Conventional polymers do not show significant material loss above T_g (up to the maximum experimentally accessible temperature of 550 °C), irrespective of the degree of crosslinking. The DA polymer’s capacity for switching into a volatilizable state, in contrast, offers a novel control option over volume conservation in nanoindentation via the choice of the writing conditions. Low tip temperatures and correspondingly high indenting forces constitute volume-preserving indentation conditions, whereas high writing temperatures and correspondingly low loading forces assist indentation by polymer volatilization.

In the process of quantifying the volatilization rate, we have demonstrated that this localized removal of material effectively reduces the pile-up region around inscribed sites (Fig. 4a). For writing temperatures greater than 450 °C complete removal of pile-up residuals can be achieved (Fig. 4b and c). The imaged area was inscribed using pixels spaced at 3.0 nm within a line, and at a line spacing of 107 nm. Each pixel was written using heat pulses of 20 μs duration and a loading force of 40 nN. The DA polymers are shown to be capable of producing repeatable lithographic feature sizes of 12–15 nm (full width at half maximum) by sequential inscription. This ability allows overlaying

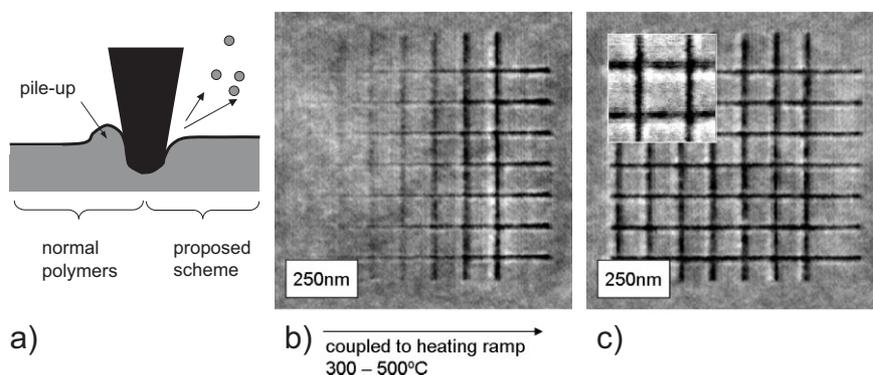


Figure 4. a) Indentation scheme: In normal polymers an indentation is surrounded by a pile-up region. With the DA polymer, low-molecular-weight fragments are able to escape from the surface, thereby reducing pile-up and facilitating line-crossing. b,c) AFM images of DA material after being inscribed using scanned probe indentation. In (b) heating was ramped along the slow-scan axis between 300 and 500 °C. The load force was around 40 nN. These conditions are similar to those of Figure 3. In (c) a fixed heating temperature of $\sim 500 \text{ }^\circ\text{C}$ was used. The image and a magnified region demonstrate superior line-crossing capabilities. The line (trench) width (full width at half maximum) is 12–15 nm.

of line patterns and faithful reproduction of line crossings, features sought in lithography.

The creation of sub-50 nm indentations as pixels of lithographically formed structures is very appealing as the feature sizes of existing technologies decrease. In contrast to traditional photoresists with separate exposure and development steps, the thermal probes create the desired topological features in a single step. This allows direct verification of the written structure by topographical imaging and, if required, allows for immediate mask repair. More importantly, this allows in situ inspection and direct compensation for stitching errors, a fundamental problem inherent to scanned-probe techniques and to electron-beam exposure. Hybrid approaches combining the local probe technique with conventional lithography readily can be envisioned.

3. Conclusion

We have shown that Diels–Alder crosslinked polymers feature thermally reversible switching between different compositions. The transformation is controlled by heat, which can be confined to small volumes using local probe techniques. The switching between two chemical states offers distinct advantages for data-storage and lithographic applications. In a high-temperature state, the polymer exists as dissociated fragments forming an easily deformable medium. In the low-temperature state, the fragments associate to give a crosslinked, macromolecular network that persists as a stable solid, freezing in written structures and resisting mechanical wear. We have shown that the kinetics of the switching transformation follows Arrhenius behavior, which is distinctively different from the WLF kinetics observed for amorphous linear and irreversibly crosslinked polymers in their deformable rubbery state. Of particular note are the length and timescales of our applications of the Diels–Alder mechanism: nanometer and microsecond scales, respectively. The demonstrated control over localized thermal, chemical, and mechanical properties in multifunctional switches constitutes an asset in the development of nanotechnology.

4. Experimental

4.1. Sample Preparation

The Diels–Alder polymer was made using a prepolymer consisting of 1,1-(methylene-di-1,4-phenylene)bismaleimide, tris(furfuryloxy)cyclohexylsilane, and furan dissolved in dry propylene glycol monomethyl ether acetate (PGMEA) (10.0 wt % solution) [21]. The solution was filtered through a 0.1 μm filter and spin-coated onto silicon wafers at 2500 rpm. The wafers were heated at 120 °C for 5 h to achieve full deprotection of the maleimide groups with associated loss of the furan-protecting group and subsequent crosslinking on cooling. The resulting thin films, the thicknesses of which could be controlled by the spin speed and solution concentration, were fully crosslinked and defect-free, suitable for lithography and data-storage applications using scanning-probe techniques. The films used in this study were \sim 120 nm thick with a root-mean-square roughness $<$ 1 nm (measured by AFM over 1 μm^2).

4.2. Instrumentation

The cantilevers have a spring constant of 0.05–0.15 N m^{-1} (as calculated from the dimensions) and a tip radius between 10 and 20 nm (as measured by scanning electron microscopy). The cantilever design is similar to the one shown in the literature [6,11]. A resistive heater is included in the cantilever directly under the integrated silicon cantilever/tip. The relatively low-doped region ($5 \times 10^{17} \text{ cm}^{-3}$ As doping) of the heater exhibits a strong dependence of resistivity on temperature.

4.3. Temperature Calibration

The known temperature dependence of the resistivity of doped silicon was used to calibrate the temperature of the resistive heater [6,11]. However, the temperature of the polymer surface under the tip, T_{polymer} , does not reach that of the heater, T_{heater} . A heating-efficiency coefficient, c , relates the two temperatures by Equation 1. For most polymer–tip combinations, c is on the order of 0.4–0.6 [11]. The exact value of c , however, has to be determined empirically in a calibration experiment.

The origin of the low heat efficiency ($c < 1$) stems from a temperature drop due to the thermal resistances of the tip [34] and the tip–polymer interface that are comparable to the spreading resistance in the polymer film (a detailed discussion of the generic issues is provided in the literature [35]). A systematic error of 30 % (due to differences between individual cantilevers and measurement error) was taken into account in calibrating our heater temperature. Relative temperature measurements, however, are reproducible by better than 10 % deviation in multiple uses of the same cantilever/tip.

The DA polymer's thermal dissociation temperature (T_r) of 130 °C (determined in separate studies [21]) is detected at a T_{heater} value of 320 °C in the dataset shown in Figure 3b. From these temperatures, we calculate c in Equation 1, to be

$$c = (T_r - RT)/(T_{\text{heater}} - RT) \\ = (130^\circ\text{C} - RT)/(320^\circ\text{C} - RT) = 0.4 \quad (4)$$

as expected for the given tip shape [11].

At timescales down to 10 μs the heat transfer process is equilibrated. Below that, the thermal time constant of the heating elements has to be taken into account [11].

4.4. Indentation Procedure

The experiments were performed under ambient conditions. The procedure involved scanning the heated tips with a given contact load of less than 10 nN across the polymer surface. For writing, the tip was stopped at a predefined lateral position, and heat and load pulses of 10 μs length were simultaneously applied. The heat pulses were generated using a resistive heater platform that supported the tip and that was integrated into a cantilever-style force sensor [22]. The temperature was measured by exploiting the thermoresistive effect of the heater element which was made of lightly (10^{16} – $5 \times 10^{17} \text{ cm}^{-3}$) p-doped Si. The load was applied to the tip by biasing the sample substrate, resulting in a corresponding electrostatic force. This force was calibrated in a separate experiment in which a DC bias was applied and the corresponding pull-off force was measured. Within a small error of a few nN the pull-off force is identical to the loading force during writing for any given value of the bias voltage. The indentations resulting from writing events were subsequently imaged using the same tip in a standard AFM contact-imaging mode.

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