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Citation: Appl. Phys. Lett. **91**, 243104 (2007); doi: 10.1063/1.2816401
View online: http://dx.doi.org/10.1063/1.2816401
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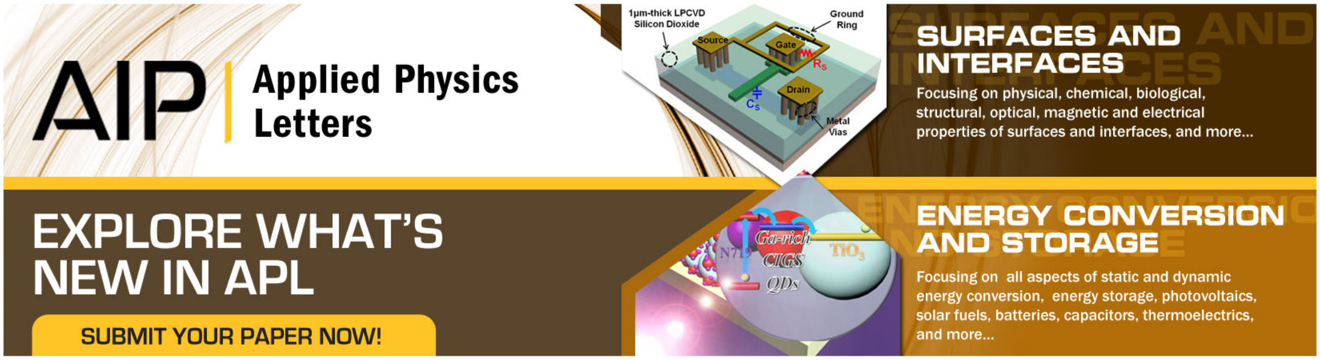

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APPLIED PHYSICS LETTERS **91**, 243104 (2007)

Local wettability modification by thermochemical nanolithography with write-read-overwrite capability

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(Received 17 September 2007; accepted 1 November 2007; published online 11 December 2007)

The wettability of a thin polymer film was modified twice by thermochemical nanolithography. By means of a first local chemical modification induced by an atomic force microscope tip heated to 110±20 °C, hydrophilic patterns are written over an originally hydrophobic polymer surface. By further heating to 190±20 °C, a second chemical modification reverses the local wettability change introduced by the first chemical modification. This write-read-overwrite capability can be particularly useful in the design of complex nanofluidic devices. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2816401]

In the past decade, the need to introduce local chemical modifications on a variety of substrates, particularly useful for the immobilization of biomolecules, has motivated the development of scanning probe-based nanopatterning techniques.[1,2] Dip-pen nanolithography enabled the deposition of a wide variety of inorganic, organic, and biological inks with a resolution of tens of nanometers[3] and an overwriting capability.[4] However, only some substrates are suitable for this technique and the overwriting process requires a probe change and the use of elaborate alignment marks. Combined write-read-erase-rewrite or write-read-overwrite capabilities are not only important for data storage applications but they also give the flexibility required by complex multiple-step manufacturing processes. Previous attempts to develop these rewriting/overwriting capabilities relied on reversible light-induced chemical reactions,[5] oxidation/reduction reaction,[6] and electrochemical deposition/removal of metallic particles.[7] Each of these methods has its disadvantages such as the low resolution, the slow writing speed, the need for a conductive substrate, and the lack of control over the water meniscus in electrochemical processes. Recently, we reported on thermochemical nanolithography (TCNL), a versatile technique that allows for simultaneous control of the local chemistry and topography of thin polymer films.[8] This technique can pattern sub-15 nm features by inducing thermally activated chemical reactions using a heated atomic force microscope (AFM) tip at a speed above 1 mm/s. TCNL can be performed in different environments and can be easily adapted to a variety of substrates and chemical functionalities.

In this letter, we demonstrate that it is possible to use TCNL to write-read-overwrite chemical patterns on thin polymer films *in situ* and with no need of probe change. The polymer used in this study is originally functionalized with tetrahydropyranyl (THP) groups that lead to a hydrophobic surface. Macroscopic scale heating at about 130 °C cleaves the THP side groups creating carboxylic acid groups (as confirmed by infrared spectroscopy) and leading to a hydrophilic surface (vide infra). Further heating at 180 °C results in dehydration of the carboxylic acid groups forming anhydrides. The resultant surface becomes increasingly hydrophobic (vide infra). This hydrophobic-hydrophilic-hydrophobic change of the polymer surface has been reproduced at the microscopic scale by heating the polymer surface with an AFM tip. A first local tip-induced chemical modification at 110±20°C is accompanied by a dramatic increase in friction, consistent with the hydrophobic-hydrophilic local change. By further local heating to 190±20 °C, a second chemical modification makes the friction return to its original value, in agreement with a full reversal of the wettability change. This write-read-overwrite capability facilitates the design of complex nanopatterns with tunable wettability, particularly desirable for the immobilization of inorganic nanostructures or biomolecules, and for the design of nanofluidic devices.[9]

The polymer used in this study was a poly(tetrahydro-2*H*-pyran-2-yl methacrylate)$_{80}$ poly(3-{4-[(*E*)-3-methoxy-3-oxoprop-1-enyl]phenoxy}propyl-2-methacrylate)$_{20}$ copolymer [p(THP-MA)$_{80}$p(PMC-MA)$_{20}$]. Films of bulk copolymer were heated entirely to selected temperatures between 24 and 210 °C using a hot plate (PC-200, Corning). Chemical modifications in the *macroscopically* heat-treated samples were characterized in ambient conditions by Fourier transform infrared (FTIR) spectroscopy (UMA-600, Digilab) (Fig. 1), static water contact angle measurements (Phoenix 150, SEO), and AFM friction measurements (CPII, Veeco) [Fig. 2]. The FTIR spectrum collected on the untreated, e.g., not heated, sample [Fig. 1(a)] is characterized by the presence of the carbonyl band corresponding to the stretching vibration of the C=O bond in esters around 1730 cm^{-1}.[10] The FTIR spectrum of the sample heated to 70 °C shows no significant shift of the ester band

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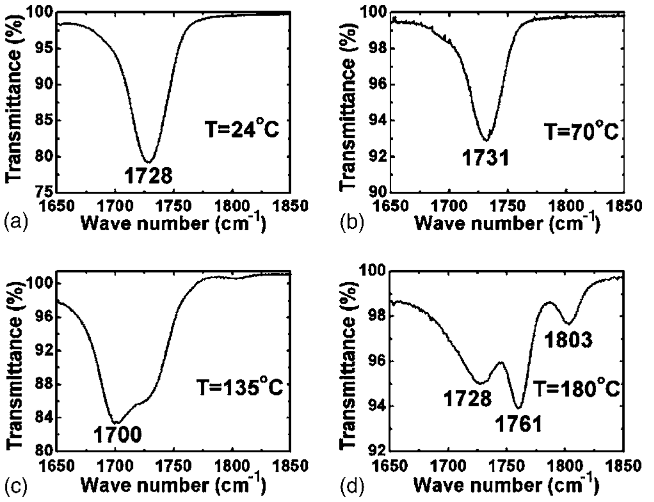

FIG. 1. FTIR spectra of a p(THP-MA)$_{80}$ p(PMC-MA)$_{20}$ copolymer (a) without chemical modifications heated to (b) 70 °C, (c) 135 °C, and (d) 180 °C.

[Fig. 1(b)]. The static water contact angle is 77° for temperatures at 70 °C, where no chemical modification is expected. A thermogravimetric analysis indicates that the removal of THP groups starts around 110 °C (data not shown) and the FTIR spectrum of the sample heated to 130 °C shows that the carbonyl band shifts from 1730 to 1700 cm^{-1}, consistent with the THP removal and formation of carboxylic acids [Fig. 1(c)]. The friction force, measured by AFM (Ref. 11) at a normal load F_N=70±2 nN, increases by 48±7% upon heating to 135 °C. The friction force increase in the chemically modified area is consistent with a local change of the wettability, i.e., the originally hydrophobic surface becomes hydrophilic.[12] This is confirmed by the static water contact angle that decreases from 79±0.2° to 62±1.0° as the temperature increases from 70 to 135 °C. After further heating above 180 °C, the appearance of two additional peaks at 1760 and 1802 cm^{-1} on the FTIR spectrum confirms the conversion of carboxylic acids into anhydrides [Fig. 1(d)]. This second chemical modification is accompanied by a water contact angle increase to 84±0.7°. Consistently, the friction force (at F_N=70±2 nN) decreases to a value almost equal to that of the untreated sample. The wettability change introduced by the first chemical modification (THP to carboxylic acid) is fully reversed by the second chemical modification (carboxylic acid to anhydride).

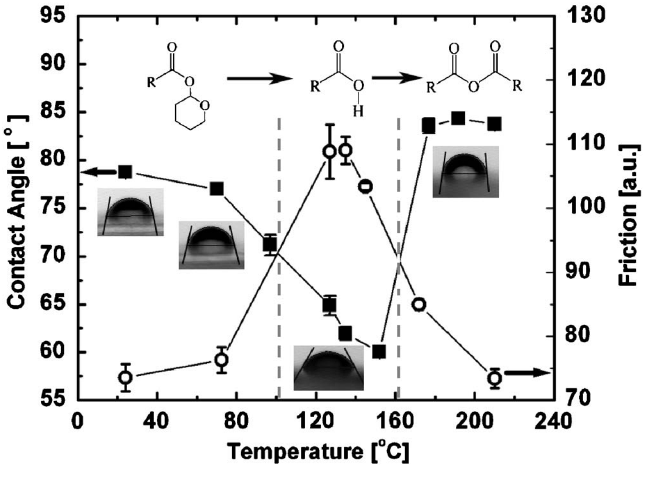

FIG. 2. Static water contact angle (solid squares) and friction force (open circles) as a function of the temperature used to macroscopically heat a p(THP-MA)$_{80}$ p(PMC-MA)$_{20}$ copolymer. Contact angle images of the samples without heating treatment, heated to 70, 135, and 180 °C, are shown as insets. The error bars represent the standard deviations.

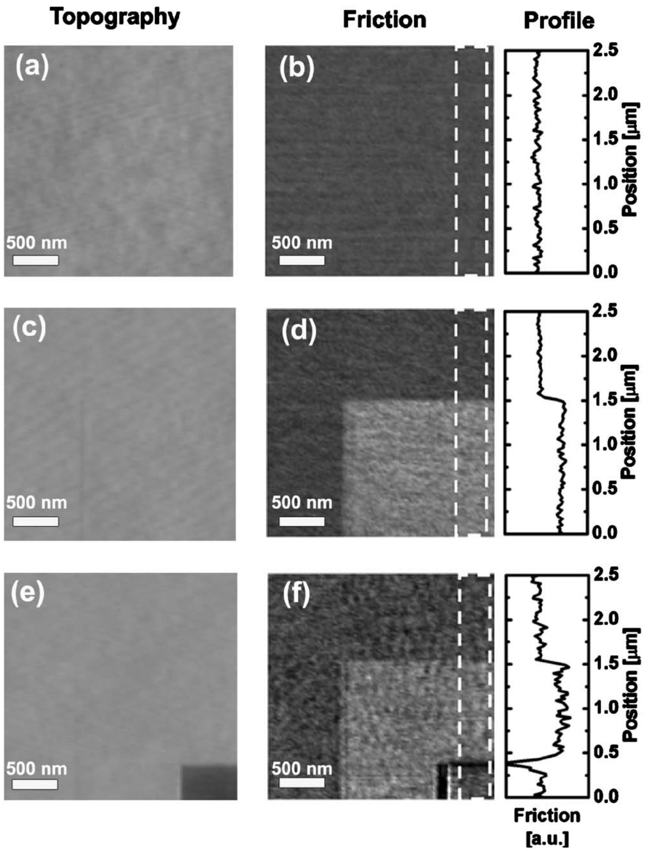

FIG. 3. Topography and friction images of a p(PMC-MA)$_{80}$ p(PMC-MA)$_{20}$ copolymer surface before [(a) and (b)] and after modification by TCNL at 110±20 °C over an area of 1.5×1.5 μm^2 [(c) and (d)] and at 190±20 °C over an area of 0.65×0.4 μm^2 [(e) and (f)]. The friction profiles are averages over the areas delimited by the dashed lines. The scale bars are 500 nm long.

Local heating, imaging, and friction measurements were all carried out with the same AFM (Nanoscope Multimode IV, Veeco) and the same resistively heated cantilever.[8,11,13] Local chemical modifications were performed by scanning the sample with an AFM tip heated to a selected temperature in the contact mode with 29±5.8 nN of applied normal force, a speed of 6 μm/s, and a 41±1.3% humidity environment. Topographic and friction images of the sample were collected before and after the local thermochemical modification under the same conditions at room temperature. The temperature calibration of the thermal cantilevers has been done by means of Raman spectroscopy and resistance versus voltage measurements across the resistively heated cantilevers.[13] A ratio of 0.4 between the polymer surface temperature and the calibrated cantilever temperature was determined by measuring the temperature dependence of the wavelength of heat-induced ripples on bulk polymers of well-known glass transition temperatures.[14,15] This value is consistent with the 0.4–0.6 values obtained from the temperature-dependent depth of indents made by thermomechanical lithography with similar cantilevers.[16]

The p(THP-MA)$_{80}$p(PMC-MA)$_{20}$ copolymer surface was first heated to 70±20 °C, below the THP deprotection

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temperature, by means of a thermal cantilever. No change in topography or friction was detected on the heated area [Figs. 3(a) and 3(b)]. After heating a $1.5 \times 1.5\ \mu m^2$ square to $110 \pm 20\ ^\circ C$ a corresponding pattern in the friction image is observed [Fig. 3(d)]; the topography shows no depletion inside the square [Fig. 3(c)]. The friction increase in the written pattern suggests that the THP groups were deprotected, leaving the area covered with hydrophilic carboxylic acid groups. A second smaller $0.65 \times 0.4\ \mu m^2$ square pattern was overwritten inside the hydrophilic pattern by further heating to $190 \pm 20\ ^\circ C$ [Figs. 3(e) and 3(f)]. The friction image [Fig. 3(f)] shows that after a second local chemical modification at $190 \pm 20\ ^\circ C$ the surface becomes again hydrophobic (lower friction). The corresponding topography depletion is 6 nm deep [Fig. 3(e)]. This change is consistent with the anhydride formation observed for macroscopic heating.

In summary, a thin polymer film was locally chemically modified twice by TCNL. A hydrophilic pattern was written on the originally hydrophobic surface by scanning an AFM tip heated to $110 \pm 20\ ^\circ C$. The wettability change introduced by the first local chemical modification can be reversed by a second chemical modification with further local heat treatment to $190 \pm 20\ ^\circ C$. This additional overwriting capability can facilitate the design of complex nanopatterns, with tunable wettability, particularly desirable in the fabrication of chemical/biological sensors and nanofluidic devices.

This work was supported in part by the STC program of the National Science Foundation under Grant No. DMR-0120967, the COE Cutting Edge Research Award, the DOE (DE-FG02-06ER46293 and PECASE), Georgia Institute of Technology Research Foundation, and ONR Nanoelectronics. We would like to thank Dr. Joseph Perry and Vincent Chen for FTIR measurements.

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