Selective dewetting of polymers on metal/silicon micro-patterns

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Modification of electrode surfaces plays an important role for electronics. Most often, lithography techniques are used, but they suffer from high fabrication cost, material restrictions and size limitations. Here we investigate if dewetting can be used to selectively coat a micron-sized gold stripe electrode on a silicon substrate.

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I. INTRODUCTION

Modification of inorganic or semiconductor surface patterns with functional organic materials is the basis of many organic devices, e.g. sensors, organic light emitting displays, organic field effect transistors, just to name a few. Methods for this functionalization include photolithography, printing, vacuum deposition through a shadow mask, and thus are methods in which a pre-designed pattern is reproduced. Another methodology to selectively deposit a material on top of a pattern uses differences in surface characteristics, e.g. surface energy, surface tension, hydrophilicity, surface charge, and so on. This selective deposition on a micro-patterned substrate was demonstrated elegantly by Whitesides, et al. in the case of hydrophilic/hydrophobic pattern on gold [1]. Sirringhaus, et al. recently produced a narrow gap of conducting polymers by combining ink-jet printing, which produces droplets of tens of microns in diameter, with dewetting [2]. We have already reported the formation of two-dimensionally ordered patterns of sub-micrometer droplets, or ‘domes’ of polymers and low molar mass compounds on non-patterned substrates by using dewetting from dilute solution [3]. Here we show that the same dewetting process can be used to prepare dewetted microstructures on gold/silicon surface patterns.

II. EXPERIMENTAL

The patterned substrates were received from Matsushita Electric Co., and consisted of gold stripes with a width of 40 µm and a height of 500 nm on silicon. Polystyrene (Aldrich, \( M_w = 280,000 \) g/mol), regiorandom poly(hexylthiophene) (Aldrich), and regioregular poly(hexylthiophene) (Aldrich) [4] were used as purchased. Chloroform solutions containing 1-10 mg/ml polymer for dewetting were prepared and kept for one day to ensure complete solution. A 2 mg/ml solution containing 1.8 mg/ml Au colloids (Tanaka Kikinzoku Kogyo KK) and 0.2 mg/ml regiorandom poly(hexylthiophene) was prepared by using aliquots of polystyrene and Au colloid solutions. A home-built roller apparatus [5] was used to cast each of the solutions at a constant speed of a few mm/min onto the substrate. Optical and fluorescence microscopy (Olympus BX-50) was used to image the polymer patterns.

III. RESULTS

A. Dewetting of polystyrene

The use of the roller apparatus enables us to form a straight three-phase-line (the contact line of the solution with the substrate) and control the receding speed and direction of the contact line. In this setup, the receding is always perpendicular to the extension of the contact line. The roller speed was a few mm/min. Figure 1 shows the reflection micrograph of a patterned substrate after the dewetting of a 1 mg/ml polystyrene solution. The Au stripe is bright yellow, and the silicon substrate greyish-blue. The receding direction was from top to bottom. The deposited polystyrene microdroplets can be seen as dark spots. They usually cover the substrate randomly with a narrow size distribution and a mean density with an inter-dome distance of approximately 3-5 times the di-
ameter [6], which is around the diffraction limit of light at this receding speed and solution concentration. Close to the Au stripe, though, one can see a single row of domes with a diameter of 2-3 \( \mu \text{m} \) at a distance of ca 60 \( \mu \text{m} \) parallel to the Au stripe. In the vicinity of this row, there are no polymer domes visible, because they have a size below the diffraction limit [7]. Closer to the Au stripe, the domes become gradually larger until they reach a diameter of just below 1 \( \mu \text{m} \). On the gold stripe, close to the front edge, a single row of large polystyrene domes with a diameter of 6 \( \mu \text{m} \) is deposited. The contact angle is shallow, as indicated by the weak contrast between Au substrate and the polymer domes, and thus neighboring domes are joined at some places. The trailing edge is covered with a line of polymer. The space in between is seemingly void of polymer droplets. After the gold-edge, there is a 30 \( \mu \text{m} \) wide stripe without discernible polymer deposits, followed by a single row of larger polymer domes, which mirrors the situation before the gold stripe. Au has much higher surface energy (estimated to be 2000 mN/m at room temperature) than silicon that is covered by a natural oxide layer and thus hydrophilic. Hence the polystyrene will tend to spread on gold and dewet from silicon. This information, together with the lack of good contrast of the polymer domes in the reflection micrograph allows us to propose that there is a thin, continuous polymer film on the Au stripe that shows height undulations at both edges. The undulation at the front edge stems from the regular fingering instability at the contact line of the evaporating solution [3]. The height of the undulations can be estimated from the interference pattern. The lack of dark rings in a prove that their height is less than half of the wavelength of the reflected light, that is 300 nm at most. Since the polymer spreads on the gold surface, the fingering instability disappears over the width of the Au strip.

The formation of this particular superstructure, domes spaced at 60 \( \mu \text{m} \) from the Au stripe, and height undulations at the front and rear edges of the Au stripe can be explained by the effect of the Au edges on the receding of the polymer solution, as shown schematically in Fig. 2. The vertical profile of the receding polymer solution has not been probed in situ. Nevertheless, from microscopic investigation of an evaporating polymer solution, as well as by atomic force microscopic investigations of deposited polymer domes [3, 7], we can assume a contact angle of the solution of around 5 degrees. When a solution with such a low contact angle approaches a protrusion from the substrate, one can anticipate that it will affect the deposition of the polymer by introducing a capillary dewetting. The point of capillary action is indicated by the arrow in Fig 2a. In other words, the contact line of the solution will abruptly change its velocity and position. Such a 'jumping' then will lead to a single row of polymer in front of the edge (Fig. 2b). Similarly, a 'pinning' of the contact line at the rear edge of the Au stripe would lead to a deformation of the profile (arrow in Fig. 2c) of the evaporating solution until the strain would overcome the adhesion of the pinning, leading to sudden jump in the position of the contact line (arrow in Fig. 2d). The final pattern (Fig. 2e) thus well reproduces the experimental findings.

B. Dewetting of poly(hexylthiophene)s

A logical extension of the dewetting of common, that is insulating, polymers on a silicon/metal micro-pattern is the dewetting of conducting polymers, because of the obvious applications in the field of electronics. Depositing conducting polymers on or in between a metal pattern on an insulating substrate by dewetting will greatly reduce the cost and time required to produce electrical circuits and interconnections.

Thus we applied the dewetting technique to conducting poly(hexylthiophene)s (PHTs). The hexyl sidegroups can be attached at a regular position at each thiophene monomer along the polymer chain (head-to-tail, or regioregular), or randomly (regiorandom) (Fig. 3). The regularity of the hexyl sidegroups has profound effects on the electronic structure of the conjugated backbone and the side-by-side packing of the polymer chains. Regiorandom PHT behaves very much like any other semi-flexible polymer and adopts a random coil structure.
The regioregular polymer can adopt a straightened polymer chain conformation due to the interlocking of alkyl chains from neighboring polymer chains. Thus regioregular poly(alkylthiophene)s have a liquid-crystalline nature [8]. This difference between random and regular polymer architecture should also influence the dewetting patterns, since the crystallinity of the polymer during solvent evaporation will affect the fingering instability and thus the size and distribution of the polymer domes.

Figure 4 shows the reflection and fluorescence micrographs of a 2 mg/ml chloroform solution of regiorandom PHT on an electrode pattern that consists of 40 µm wide zigzag stripes. PHT fluoresces red during excitation with green or yellow light and this fluorescence be used to monitor the spatial polymer distribution. The receding direction of the three phase line is from top to bottom for all pictures. The orientation of the zigzag pattern is such that the straight elements of the electrode stripes are either parallel or perpendicular to the receding direction of the three-phase-line. We found that PHT is deposited in a similar fashion as polystyrene. Along areas with parallel orientation of the electrode stripe, the PHT is deposited as a row of droplets on the front edge of the electrode and a thin line on the trailing edge (Fig. 4a). Interestingly, the PHT fluorescence is stronger on Au than on silicon, even though a quenching of fluorescence by the metal could have been expected. But since the polymer deposits are larger, and thus higher, on the gold, quenching only affects the polymer chains close to the gold surface, hence the large aggregates at both electrode edges are less affected by metal quenching and thus visible in the fluorescence image (Fig. 4b). Electrode stripes that are oriented perpendicular to the receding direction exhibit a totally different deposition pattern. Since the three-phase-line does not pass over steps while receding, there are no discontinuities in the polymer deposition and small polymer aggregates are distributed on the silicon surface. The metal stripe seems to be covered with polymer (Fig. 4c), but since the polymer film is thin (at most a few ten nm), it cannot be seen in the fluorescence micrograph (Fig. 4d), because of the metal quenching. There is a little fluorescence that originates from areas very close to the edges of the metal stripe. PHT is deposited in the corners because of capillary action due to the height difference of silicon substrate and metal electrode. Note that the shutter speed is the same for all pictures. The contrast in Fig. 4d had to be raised to 90% (from standard 50% in Fig. 4b) and the brightness to 95% to visualize these very faintly fluorescing features. The knees of the zigzag electrode pattern show the transition between these two deposition patterns (Figs. 4e and f). One can see that the three-phase-line was pinned at the front electrode edge. The polymer deposits are bigger the further away from the knee, because the jumping of the three-phase-line is initiated at the corner. Roughly, the bend in the deposition pattern of PHT on the metal stripe is the result of the shape of the three-phase-line of the PHT solution at that position on the sample. Also here, in order to show smaller polymer aggregates, the contrast and brightness had to be adjusted.

The ordered arrangement of the hexyl sidegroups in regioregular PHT gives rise to a different packing (liquid crystalline versus the amorphous regiorandom polymer) of the polymer chains on the nanometer scale. Since the packing of the alkyl chains occurs not only in the condensed phase, but also in concentrated solution, there should be an effect of side chain packing on the dewetting of the polymer on a metal pattern. Since the previous experiments with regiorandom PHT showed that a metal stripe oriented perpendicular to the three-phase-line does not drastically influence the dewetting, we only show the result of a metal stripe parallel to the three-phase-line of a solution of regioregular PHT. Figure 5 shows the fluorescence micrograph of this sample after dewetting. The only detectable fluorescence is found on the metal stripe. Based on the average grayscale and the noise level of camera pixels on silicon and gold, respectively, we estimate that the amount of regioregular PHT is at least 50 times larger on gold than on silicon. The amount of PHT is large enough to give a strong violet color in the
reflection micrograph. Similar to regiorandom PHT, most polymer is deposited along the edges of the metal stripe, even though no height undulation at the front edge can be seen. That means that the fingering instability is suppressed and a stick-slip motion during the pinning of the three-phase-line is the main mechanism for polymer deposition. Furthermore, the central area of the metal surface is covered with small fluorescent PHT particles and not a thin, featureless film, as in the case of the regiorandom polymer. It is not clear if the aggregation into these sub-micrometer particles occurs already in solution or after the solvent evaporation.

Poly(hexylthiophene)s are conjugated polymers and thus intrinsically conducting, but significant conductivity can only be achieved by doping with Lewis acids or iodine. We investigated the local conductivity of native regiorandom PHT on Au micro-stripes by conducting atomic force microscopy (AFM), and found a resistivity of at least 1 MΩ. Thus doping would be necessary to yield high conductivity. Another method to increase conductivity is the incorporation of metal particles in a film of polymer in a sufficiently high concentration to allow for a percolation-type of electrical conduction.

C. Conductivity of PHT/Au nano-particle aggregates

Here we demonstrate that a polymer/metal nano-composite can be selectively dewetted and that electrical conducting domes can be realized. Regiorandom PHT and Au nanoparticles were mixed in a 1:9 weight ratio in chloroform and the solution was adjusted to contain 2 mg/ml of composite material. The atomic force microscopy (AFM) images of the micro-domes (see Fig. 6) show a rugged surface structure that is most likely due to aggregates of the metal nanoparticles. The diameter of the dome is a few µm and it has a height of 200-300 nm. The numbered cross-marks indicate the places where local conductivity was measured by the gold-coated AFM tip. Positions 4 and 5 are on the bare Au substrate to check the ohmic contact of the AFM tip. The I-V curve characteristics in Fig. 7 are taken at a spot on top of the micro-dome. It shows a deviation from linearity at low voltages, but is more or less linear above 0.2 V and shows the expected bipolarity, that is, no rectification. The leveling off at 20 nA is due to the current restrictions of the amplifying electronics.

IV. SUMMARY

We could show that hydrophobic polymers like polystyrene and poly(hexylthiophene) form dewetted patterns on micro-structured substrates. Sample preparation consisted of solution casting by using a roller apparatus. The dewetting patterns are influenced by the orientation of gold stripes in respect to the roller direction. By using regioregular poly(hexylthiophene) a selective adsorption solely on the gold stripes was observed. Doping with gold nanoparticles led to conducting polymer micro-domes. This work is an extension of the previously reported dewetting of polymers on non-structured substrates and will hopefully open a new strategy of polymer patterning for applications in photonics and electronics.

Acknowledgments

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