

Individually addressed large-scale patterning of conducting polymers by localized electric fields

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A scaleable and site-specific patterning approach with individual addressability is demonstrated via an electropolymerization process within the gap of electrodes. The method can pattern conducting polymer structures by applying a bias between desired electrodes in a monomer vapor. The reaction is proposed to happen in a thin water film condensed inside the electrode gap at ambient environment. It is possible to pattern different conducting polymers on the same substrate by exposing to different monomers. Proof-of-concept experiments on pyrrole and thiophene have shown the generality of this simple and robust method, which enables the real-time monitoring of the resistance and deposition of the conducting polymers. Finally, chemical sensing of the patterned polypyrrole structures to ethanol vapor and ammonia gas are presented. © 2004 American Institute of Physics. [DOI: 10.1063/1.1645323]

Controlled patterning of conducting polymer structures at micro- and nano-meter scale is highly desirable for the fabrication of miniaturized devices, such as light emitting devices, chemical sensors, among many others.¹ These polymers are often synthesized from appropriate monomers by chemical or electrochemical oxidative polymerization in solution, and patterned on substrates by screen-printing,² ink jet printing,³ stamping,⁴ traditional lithographic techniques (photo, electron, and ion beam lithography),^{5,6} and emerging ones (scanning probe lithography,⁷ soft lithography,⁸ electrochemical method,⁹ and others¹⁰). An alternative patterning strategy is to use monomers as building blocks and exploit the polymerization within a spatially restricted volume,¹¹ or at specific locations on a substrate by delivering monomers and passing current through an atomic force microscope tip to induce localized polymerization.¹² Although being successful in satisfying some of the criteria of material patterning, each of the present methods has certain limitations in one or more of aspects regarding, for example, resolution, yield, material multiplicity, and positioning. For the large-scale production of miniaturized complex architectures, an ideal approach should be able to pattern multiple materials at specific locations with high efficiency and resolution, accurate positioning and certainly low cost.

Intuitively, an array of prefabricated electrodes with defined gaps meets practically every need in patterned electronic devices except for the functional material yet to be positioned in the electrode gaps. Filling such gaps with desired functional material helps achieve the goal of working devices. We demonstrate a monomer vapor-based approach capable of large scale patterning of multiple conducting polymers via electric-field-induced polymerization in the gaps of individually addressed electrodes, which subsequently constitute the gateways for electric transport in final devices. The requirement for the precise registry of patterned

structures and electrodes in other methods is not necessary in the present approach. By using different monomer vapors, various conducting polymers can be readily patterned between localized electrode gaps. In principle, the number of patterns that can be produced in one run could be very large provided sufficient electrode gaps and means to address them are available. This simple and robust method is highly compatible with the microelectronics technology and represents a significant progress in the controlled patterning of multiple polymeric materials. Preliminary results of miniaturized gas sensor based on patterned polypyrrole are shown as an illustrative example.

Monomers used in the proof-of-concept experiment (pyrrole and thiophene, Aldrich) are used without purification. The electrode patterns (40 nm thin gold film on 10 nm titanium) are fabricated on silicon (100) substrates covered with 600 nm SiO₂ by photolithography and electron beam deposition. After wiring out via a chip carrier, the setup is put in an environment chamber connected to monomer source and an exhaust pump. A dc voltage is applied between appropriate electrodes in the monomer vapor at room temperature for localized polymerization reaction. The resistance of the electrode gap is measured intermittently by a Keithley 2400 sourcemeter. After the resistance reaches a certain value, the polymerization is stopped by disconnecting the power source and removing the residual vapor. The sensing experiments are performed on a home-built setup as described previously.¹³

Typically, the polymerization of pyrrole occurs between an electrode gap (5 μm) when a 10 V dc voltage is applied in the saturated vapor of pyrrole at 24 °C and the relative humidity of 35%. The occurrence of chemical reaction is signaled by the decreasing gap resistance, with 95% of reduction in the first hour [Fig. 1(a)]. The contrast in scanning electron micrograph (SEM) before and after the reaction shows the presence of new material in the gap [Fig. 1(b)]. Such material is stable during SEM observation (1 h) and is a not physical aggregate of pyrrole that cannot sustain high

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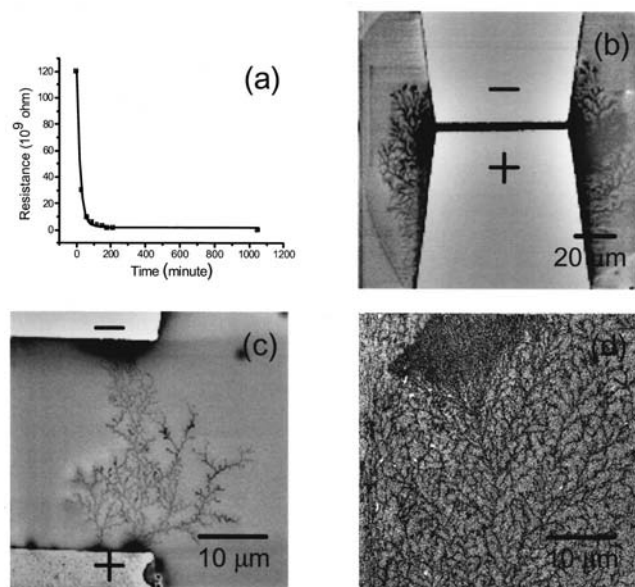


FIG. 1. (a) The resistance changes of a 5 μm electrode gap in pyrrole vapor at the relative humidity of 35%; (b) SEM image of the gap filled with polypyrrole; (c) polypyrrole chains formed in a 30 μm gap at relative humidity of 35%; and (d) polypyrrole chains formed in a 60 μm gap at relative humidity of 83%.

intensity electron bombardment (15 kV) in vacuum. Secondary ion mass spectrometry (SIMS) shows characteristic peaks of polypyrrole in positive and negative ion modes, and its distribution around the gap (figures not shown). In control experiments without any applied voltage, there is no deposition and the resistance does not change when other conditions are kept identical; meanwhile SEM and SIMS images do not show the images and peaks of polypyrrole. When a 30 μm gap is used under the same condition, several fractal shaped chains are visible with preferred growth direction (from positive polarity to negative polarity) [Fig. 1(c)]. This indicates that the electric field in the gap directs and facilitates the growth of polypyrrole. The strength threshold of electric field for the polymerization reaction is about 10^4 V/m at the relative humidity of 35%.

The existence of thin water layers on ionic surfaces in ambient environment is well known.^{14,15} The three-dimensional structure of electrode gaps produces a local environment that may enhance water condensation under ambient condition. When high electric field ($>10^5$ V/m) is generated across the gaps, the polymerization would likely occur within the tiny hydrous environment similar to electrochemical polymerizations in solution. The validity of the proposal is tested by increasing the relative humidity in the chamber. When a 10 V dc voltage is applied across a 60 μm gap in the saturated vapor of pyrrole at 24 $^\circ\text{C}$ and the relative humidity of 83%, no surface discharging was observed and the resistance dropped faster than that at relative humidity of 35%. SEM images show that polymer chains are longer and the density of chains is much higher than those formed between the 30 μm gap at the relative humidity of 35% [Fig. 1(d)]. The probable reason is that the water layer at higher humidity is thicker and more uniform than that at lower humidity; the enhancement of polymerization suggests such water layer can dissolve monomer and provide a channel for the transport of charge carriers, thus forming an electro-

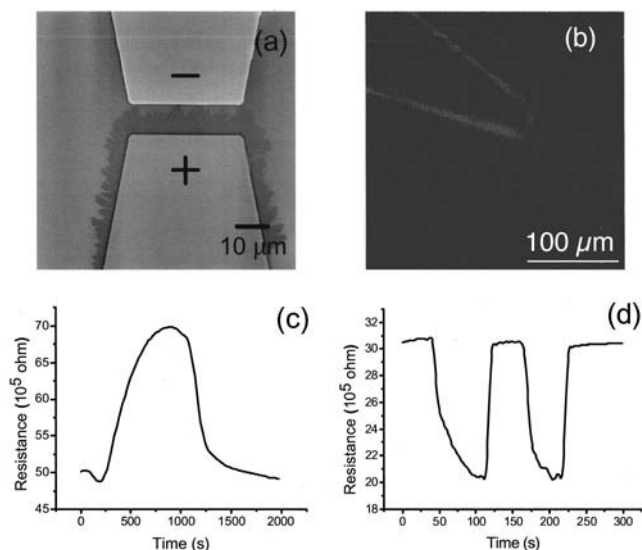


FIG. 2. (a) SEM image of a gap with polythiophene produced by electric field in thiophene vapor; (b) SIMS image of a gap filled with polythiophene, the image is collected using the characteristic peak of the polymer; the response of polypyrrole sensors to ethanol vapor (c) and NH_3 (d), respectively.

chemical cell for the reaction. Note that the polymerization and deposition occurs in-between and surrounding the active electrodes. We believe that electric field polarizes monomers, guides them to higher field regions, and ultimately resulting in the ionization and polymerization within the electrode gap or around active electrode. The mechanism described here is analogous to that of the recently discovered alignment of carbon nanotube by electric fields.¹⁶

The highly localized and enhanced electric field can induce polymerization of other polymers. By applying a 10 V dc voltage across an electric gap in the saturated thiophene vapor for 2 h at room temperature, polythiophene is produced; the localized distribution of polythiophene within the electrode gap is evident in the close-up SEM image [Fig. 2(a)], where polymer chains are shorter and fatter than polypyrrole chains produced under the same condition. In another sample, SIMS image collected using total ions shows uniform contrast of two electrodes (figure not shown), but the images collected using the characteristic peak of sulfur in negative ion mode (32.14) confirm localized distribution and successful patterning of polythiophene [Fig. 2(b)]. The contrast difference of two electrodes suggests thiophene monomers are accumulated and polymerized around or on the positive electrode.

The patterned conducting polymers can be used as miniaturized resistive sensors to detection chemical vapors.¹⁷ The mechanism is based on the changing of interchain transport properties induced by the reversible doping and dedoping of conducting polymer upon exposure to and removing of vapor dopants.^{18,19} The gas sensing experiments are performed at room temperature with pure air as balancing gas at flow rate of 2.5 L/min. Figure 2(c) shows the resistance change of a polypyrrole sensor produced by electrical fields to 8.2% (v/v) ethanol measured at voltage of 5 V. The incorporation of ethanol leads to the swelling of the polymer and the increase in resistance. The resistance recovers to original value after removing ethanol vapor. The sensitivity (defined

as the ratio of resistance change to its original value) of the sensor (0.4) is higher than a typical polypyrrole one, whose sensitivity to 13% (v/v) ethanol is 0.1.¹⁸ Introducing electron-donor molecules (i.e., 1% NH₃) reduces the resistance of a polypyrrole sensor by providing more charge carriers for transport. The resistance measured at voltage of 5 V drops from 3.7 M to 2 M [Fig. 2(d)]. When NH₃ containing air is removed by pure air, the sensor resistance returns to its original value with good sensitivity and response characters.

In addition to its importance in the individually addressed large scale patterning, the method has several other significant implications: (1) the physical properties of thin water film on the substrate have been studied for a long time, this is one demonstration that a polymerization reaction can occur in such environment; (2) the simple and robust method can produce shape-controlled structures by changing the geometry of electrodes according to established theory on the distribution and intensity of electric field; (3) higher electric fields can lower the ionization threshold, enable the patterning of conducting polymer in a sub-100 nm gap, that is beyond the limitations of most current patterning techniques; and (4) concerning the extensive application of electrochemical method in polymerization, the method can be extended to pattern polymer structures, in general, provided volatile monomer is available. Finally, it is noted that in the current method, the substrate is bare silicon dioxide, and it is possible to produce polymer structures only within the gap rather than spread out of the gap by intentionally modifying the surface properties.

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