In-situ synthesis of conducting polymers into patternable polymer matrices

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The discovery of conducting polymers opened up many new possibilities in microelectronics. These materials offer a unique combination of optical, electrical, and mechanical properties (they can be processed into thin films) that make them attractive alternatives for certain materials currently used in microelectronics. Some of the potential applications of CP in microelectronics are e.g. in metalization, electrostatic discharge protection, electromagnetic interference shielding, interconnection technologies/wiring, devices (diodes, transistors, photovoltaic cells), corrosion protection of metals, lithography (charge dissipators, conducting resists). [1]
Polymers with a regular alternation of single and double bonds (conjugated bounds) along the polymer chain, form the basis of the organic conducting polymers. With such an electronic structure, a semiconductor-like band is formed, which band gap depends on the extension of the conjugation. However, conjugation is not enough to achieve conducting properties in polymers since normally structural defects interrupt conjugation and make a zero band gap impossible. [2] These polymers are made conducting, or "doped," by reacting the conjugated semiconducting polymer with an oxidizing agent, a reducing agent, or a protonic acid resulting in highly delocalized polycations or polyanions. The band gap between the filled and empty states is thus lowered, giving rise to a dramatic increase in conductivity of several orders of magnitude. The conductivity of these materials can be tuned by chemical manipulation of the polymer backbone, by the nature of the dopant, and by the degree of doping. In addition, polymeric materials are low-cost, lightweight, easily processed, and flexible.

In a previous paper, we reported on a novel method to synthesize a conducting polymer in the presence of a host polymer during the bake step of the spincoating process. [3] The method consisted of the oxidative polymerization of terthiophene (3T) with $Cu(ClO_4)_2$ inside a phenolic-based polymer to form an interpenetrating polymer network (IPN). The major advantage of IPN compared to polymer blends is that the phase separation is controlled since monomers are completely dispersed at the molecular level into the host polymer. The IPN was successfully formulated to be used as charge-dissipator bottom layer for e-beam lithography. Here we report for the first time on the in-situ polymerization of 3T with $Cu(ClO_4)_2$ inside several polymers such as polymethylmethacrylate (PMMA), Novolak, polystyrene (PS), poly4vinylphenol (P4VP), and poly(4-vinylphenol)-co-(methylmetacrylate) P4VP-co-MMA, which have been extensively used in the formulation of resists for conventional lithography (UV, electron beam and imprint lithography). IPNs conducting films in the order of 10^{-3} to 100 S/cm were successfully obtained with different film morphologies depending on the specific resist composition. Figure 1 shows the I-V Characteristics of conducting IPN films prepared from different host polymer. The potential of this synthetic approach has been demonstrated using a commercially available negative-tone photoresist based on novolak as a host polymer. Novolak photoresist was properly formulated with 3T and $Cu(ClO_4)_2$ to preserve the lithographic performance of novolak-based negative photoresist and generate conductive micropatterns by means of UV lithography. The pattern generation and the in situ synthesis of polyterthiophene are carried

out in two separate steps. After the lithographic process (exposure + development), $Cu(ClO_4)_2$ initiates simultaneously the oxidative polymerization of the 3T and the subsequent doping of the in-situ synthesized poly(terthiophene) (P3T) inside the Novolak micropatterns during a post-bake step. As a result IPNs conducting micropatterns in the order of 10^{-2} S/cm were successfully obtained (Figure 2).

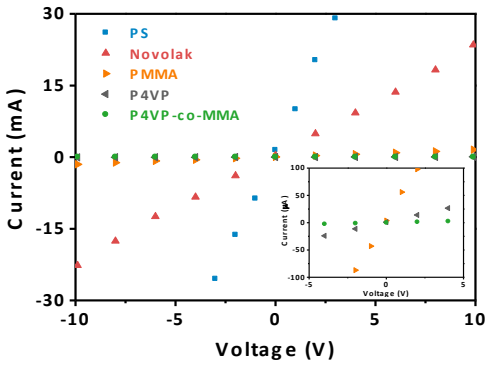

Figure 2: I-V Characteristics of conducting IPN films prepared from different host polymer.

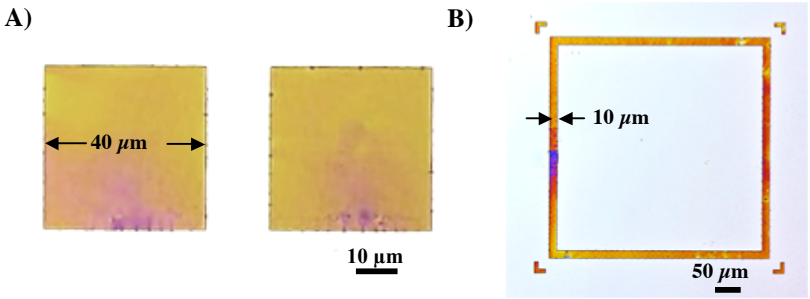

Figure 1: Examples of micropatterns of novolak-based conducting polymer fabricated by means of photolithography

References

[1] M. Angelopoulos, *IBM J. Res. & Dev.*, **45**, No. 1, (2001).
[2] J. Roncali, *Macromol. Rapid Commun.* **28**, 1761 (2007).
[3] R. Abargues, U. Nickel, P. Rodríguez-Cantó, *Nanotechnology*, **19**, 125302 (2008).