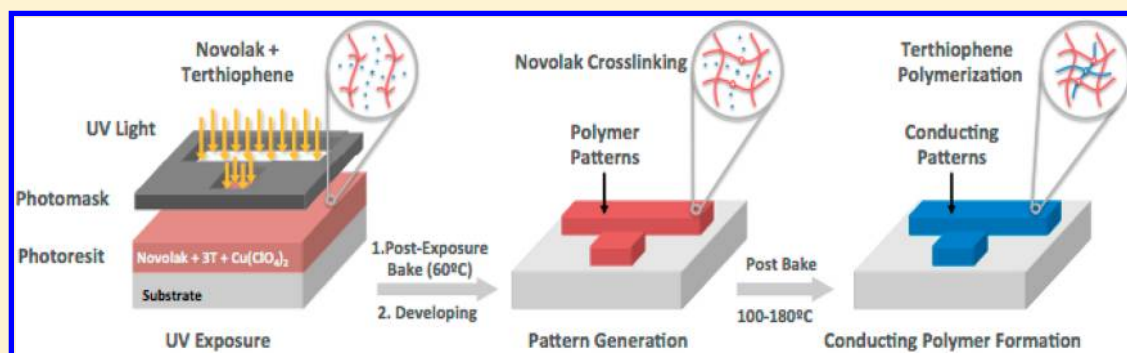


Patterning of Conducting Polymers Using UV Lithography: The in-Situ Polymerization Approach

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ABSTRACT: We report on the in-situ polymerization of 3T with $\text{Cu}(\text{ClO}_4)_2$ inside several host polymers such as Novolak-based negative-tone photoresist, polystyrene (PS), poly(4-vinylphenol) (P4VP), poly(methyl methacrylate) (PMMA), and poly(4-vinylphenol)-*co*-(methyl methacrylate) (P4VP-*co*-MMA) to form an interpenetrating polymer network (IPN). Conducting IPN films in the order of 10^{-4} –150 S/cm are obtained depending on the specific IPN composition. Moreover, the convenience 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 $\text{Cu}(\text{ClO}_4)_2$ to preserve as far as possible the negative lithographic characteristics of Novolak-based photoresist and generate conductive micropatterns by means of UV lithography. The CP is in situ synthesized into the Novolak matrix by a postbake after the lithography process (exposure + development). The electrical conductivity of the patterned film is 10^{-2} S/cm. We accurately patterned three different types of microstructures with different resolutions: interdigitated structures with a width of 100 μm , 200 μm side squares, and a 20 μm wide cross. We believe this synthetic approach is of potential application to modify the conductivity of numerous insulating polymers while preserving their physical and chemical properties.

1. INTRODUCTION

The discovery of conducting polymers (CP)¹ led to a huge impact in important technological emerging applications, from microelectronics^{2,3} and optoelectronics^{4–6} to sensors.^{7,8} Some well-known representatives are polythiophene, polypyrrole, polyaniline, poly(*p*-phenylenevinylene), and their derivatives.¹ These materials offer a unique combination of electric, electronic, magnetic, and optical properties inherent to semiconductors and metals, with the mechanical properties and processability of conventional polymers.

Polymers with a regular alternation of single and double bonds along the polymer chain (π -conjugated polymers) form the basis of the organic CPs. With such an electronic structure, a semiconductor-like band is formed, whose band gap depends on the extension of the conjugation. Conjugated polymers can be only made conducting upon generation of charge carriers (polarons and bipolarons) by reduction (n-doping), oxidation, and protonation (p-doping) of the π -conjugated system, resulting in highly delocalized polycations or polyanions.^{1,9} In this way, the band gap between the filled and empty states can be significantly lowered, giving rise to a dramatic increase in

conductivity by several orders of magnitude. However, achieving a zero-band-gap polymer is difficult because structural defects normally interrupt π -conjugation.¹⁰ The conjugated polymers in their undoped state are semiconductors or insulators and only have a low electrical conductivity of around 10^{-10} – 10^{-8} S/cm. At very low level of doping (<1%), electrical conductivity increases several orders of magnitude up to values of around 0.1 S/cm. Subsequent doping of the CPs will result in a saturation of the conductivity in the range 1– 10^4 S/cm depending on the considered polymer.

CPs are an attractive alternative for certain materials currently used in microelectronics. Some of their potential applications are chemical/biological sensors,¹¹ metallization,¹² antistatic coatings,¹³ anticorrosive coatings,¹⁴ electromagnetic shielding,¹⁵ light-emitting diodes,¹⁶ transistors,¹⁷ photovoltaic cells,¹⁸ electrochromic devices,¹⁹ and micro- and nano-fabrication (conducting resists,³ charge dissipators for e-beam

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lithography²⁰). The successful application of CPs in many of the above given applications will depend on exploiting their low-cost potential by the innovative design and development of materials for scalable and inexpensive methods to pattern these CPs on large-area substrates.^{2,21} Up to now, patterning of CP has mainly focused on inkjet printing,^{22,23} photochemical patterning,²⁴ imprint lithography,²⁵ electron-beam lithography,²⁶ and atomic force microscopy nanoscratching.²⁷ However, continuous efforts are still being directed toward fast and inexpensive methods for patterning conducting polymers over different substrates. The focus of this research is therefore the design of a multifunctional polymeric material, which can combine electrical conductivity with other properties, such as UV lithographic characteristics.

One interesting approach to modify the properties of CPs is by blending with other polymers to combine their properties in a film to more appropriately meet the needs of a given application.^{28–30} Polymer blends can be prepared by spin-coating a mixture of two polymers from a common solvent and provides a simple and effective method to obtain novel materials for optoelectronic applications. However, polymer blends normally leads to highly heterogeneous two phase system films because of the tendency of polymers to phase-separate.^{29,31} In a previous paper, we reported on a novel method to synthesize a conducting polymer in the presence of a host polymer thin film during the bake step after the spin-coating process.²⁰ The resulting synthesized polymer is thus completely embedded into the host polymer, and homogeneous films are generated. This kind of multicomponent materials is called interpenetrating polymer network (IPN).³² The method consisted of the oxidative polymerization of terthiophene (3T) with $\text{Cu}(\text{ClO}_4)_2$ inside a Novolak-based polymer. This approach allowed us to combine the film forming properties of Novolak with the conducting properties of polyterthiophene (P3T). Moreover, we showed that phase separation was considerably reduced because 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.

In this paper we report for the first time on the in-situ polymerization of 3T with $\text{Cu}(\text{ClO}_4)_2$ inside several host polymers: Novolak-based negative-tone photoresist, polystyrene (PS), poly(4-vinylphenol) (P4VP), poly(methyl methacrylate) (PMMA), and poly(4-vinylphenol)-*co*-(methyl methacrylate) (P4VP-*co*-MMA). All these polymers are extensively being used in the formulation of resists for conventional lithography (UV, electron beam, and imprint lithography). Conducting IPN films in the order of 10^{-4} –150 S/cm are obtained depending on the specific IPN composition. Moreover, the convenience 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 $\text{Cu}(\text{ClO}_4)_2$ to preserve as far as possible the negative lithographic characteristics of Novolak-based photoresist and generate conductive micropatterns by means of UV lithography. The CP is in situ synthesized into the Novolak matrix by a postbake after the lithography process (exposure + development). The electrical conductivity of the patterned film is 10^{-2} S/cm. We believe this synthetic approach is of potential application to modify the conductivity of numerous insulating polymers, preserving to some extent their physical and chemical properties.

2. EXPERIMENTAL PROCEDURE

Materials. Terthiophene (3T), $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, poly(4-vinylphenol) (P4VP), polystyrene (PS), poly(4-vinylphenol)-*co*-(methyl methacrylate) (P4VP-MMA), and poly(methyl methacrylate) (PMMA) were purchased from Aldrich. A commercially available negative-tone Novolak photoresist (ma-N 1405) was purchased from Microresist Technology. 1-Methoxy 2-propylacetate (MPA, Aldrich) was used as a solvent.

Interpenetrating Polymer Networks. For the formation of conducting IPN thin films, a solution of 3T and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in MPA is mixed at a 1:1 ratio with a 10 wt % polymer (Novolak, PS, PMMA, P4VP, and P4VP-MMA) solution in MPA. Different amounts of 3T and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ were used. The resulting solution is then spin-coated between 1500 and 3000 rpm onto a glass or Si wafer and baked at 100–140 °C temperature for 120 s, obtaining a film thickness in the range of 210–260 nm.

Lithographic Process. The Novolak-based IPN was first spin-coated at 3000 rpm for 30 s onto a glass wafer and baked at 45 °C for 120 s to remove any trace of solvent. The resulting film was ~250 nm thick. Then, the IPN film was exposed to UV light at 200 mW cm^{-2} for 5 s by using a test mask in a Süss Microtech MJB4 mask aligner for the pattern transfer to the resist. After a postexposure bake at 50 °C for 90 s, the film was developed by immersion in aqueous tetramethylammonium hydroxide (TMAH)-based developer from micro resist technology (ma-D 533/S) for 10 s. Afterward, the sample was rinsed with DI water for 15 s and dried with compressed dry air. A final bake at 140 °C was carried out for the polymerization of 3T.

Interpenetrating Polymer Network Characterization. Conductivity was calculated from *I*–*V* curves registered with a Keithley 236 source-measure unit by using a standard four-point method at room temperature. Contacts were made by sputtering gold dots onto the films. Conducting films exhibited ohmic behavior in most of the cases. The conductivity was taken as the average of six measurements of resistance obtained throughout different places on the sample source by using the relation

$$\sigma = \frac{\ln 2}{\pi t R} \quad (1)$$

where *t* refers to film thickness and *R* is the resistance. Film thickness was measured with a profilometer Dektak 150, from Veeco.

The in-situ polymerization of 3T was followed by UV–vis spectroscopy by means of a Perkin-Elmer Lambda 20 spectrophotometer.

3. RESULTS AND DISCUSSION

Conductive Interpenetrating Polymer Network: Synthesis and Characterization. Novolak-based negative-tone photoresist, poly(4-vinylphenol) (P4VP), polystyrene (PS), poly(4-vinylphenol)-*co*-(methyl methacrylate) (P4VP-*co*-MMA), and poly(methyl methacrylate) (PMMA) were chosen as host polymer matrices. All these polymers can be easily processed from several solvents into thin films by spin-coating. 3T and $\text{Cu}(\text{ClO}_4)_2$ were used as a monomer and oxidant, respectively. Either 3T, $\text{Cu}(\text{ClO}_4)_2$, and the host polymers were dissolved in a common solvent (MPA) and spin-coated on a glass substrate. All these host polymers were formulated with the same amount of monomer and oxidizing salt (18 wt % 3T

and 1.8:1 molar ratio of $\text{Cu}(\text{ClO}_4)_2$ to 3T) and baked at 140 °C. The polymer formulation was diluted before spin-coating in order to obtain the desired film thickness (≈ 250 nm). The in-situ polymerization of 3T inside these host polymers takes place through an oxidative coupling by means of $\text{Cu}(\text{ClO}_4)_2$ during the bake step. Figure 1 shows the I - V characteristics of the conducting IPN films.

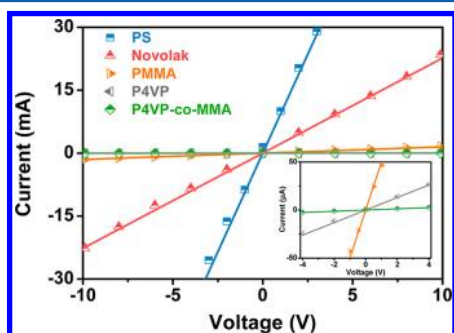


Figure 1. I - V characteristics of conducting IPN films prepared from different host polymer. In the inset a zoom for smaller currents is shown.

All of these IPN films show an ohmic behavior over the experimentally measured range of voltage, as observed from the I - V characteristics of the conducting IPN films in Figure 1 and inset. Table 1 summarizes the conductivities calculated through

Table 1. Conducting IPN Films Prepared from Different Host Polymer^a

host polymer	conductivity (S/cm)	thickness (nm)
PS	80	250
negative-tone Novolak	20	260
PMMA	0.8	210
P4VP	0.06	240
P4VP-co-MMA	0.003	235

^a $T_B = 140$ °C. 3T = 18 wt %. $\text{Cu}(\text{ClO}_4)_2$:3T molar ratio = 1.8.

eq 1 for IPN films based on different host polymers. Films exhibit conductivities in the range from 10^{-3} to 80 S/cm depending on the host polymer. Negative-tone Novolak photoresist and PS show the best results. This synthetic approach is of potential application to modify the conductivity of numerous insulating host polymers. Among these promising host polymers, negative-tone Novolak is especially attractive

since it is a commercially available photoresist formulated for UV lithography and hence will be the main focus in our study.

The chemical oxidative polymerization is followed by visible changes in the color of the film. An initially colorless film turns after few seconds blue and dark blue, indicating that larger oligomers have been formed. This chemical polymerization possesses a well-defined autocatalytic character; i.e., a rapid coloration and polymerization proceed after a definite induction period. The in-situ polymerization of 3T in Novolak was followed by UV-vis-NIR spectroscopy (Figure 2A). The 3T- $\text{Cu}(\text{ClO}_4)_2$ -Novolak films were baked at a mild temperature (100 °C) to slow down the reaction rate and observe better the extent of the reaction.

Initially, Novolak containing 3T exhibits a maximum absorption peak around 359 nm (black line in Figure 2A). This is explained by the convolution of the absorption spectra corresponding to 3T monomers (in hexane solution) and the pure Novolak film that exhibits absorption bands at 355 and 365 nm, respectively, as shown in Figure 2B (black and blue lines). Absorption spectra of 3T corresponds to π - π^* interband transition. As the polymerization reaction takes place, the peak intensity of the 3T band gradually decreases, and new optical absorption bands appear at the red side (Figure 2A) because of the formation of oligomers with a larger π -conjugated system. This is partially masked by the absorption of the host polymer at 365 nm that also shifts to red up to 382 nm when Novolak is baked for different times (Figure 2B). The two new bands around 535 and 715 nm gain importance during the baking process due to the formation of charge carrier (polaron and bipolaron) bands arising from the oxidation of the polythiophene.^{9,33,34} It is well-known that during the oxidative polymerization of thiophene-based monomers both polymerization and doping (oxidation) of the corresponding conjugated polymer take place simultaneously.^{35,36} The synthesized polymer was doped simultaneously during the reaction with ClO_4^- . A possible byproduct of the in-situ polymerization reaction may be Cu nanoparticles. However, it is well-known the relative difficulty of Cu(II) reduction to Cu(0) in mild reaction conditions as well as the easy oxidation of zerovalent Cu nanoparticles in air under ambient atmosphere conditions.³⁷ After inspection with transmission electron microscopy (TEM), we did not observe the formation of Cu nanoparticles. Most probably, in case of formation of Cu nanoparticles, these may be immediately oxidized to either Cu(I) or Cu(II) during the bake step.

The electrical conductivity of an IPN is characterized by the CP content into the insulating host polymer. As the CP amount

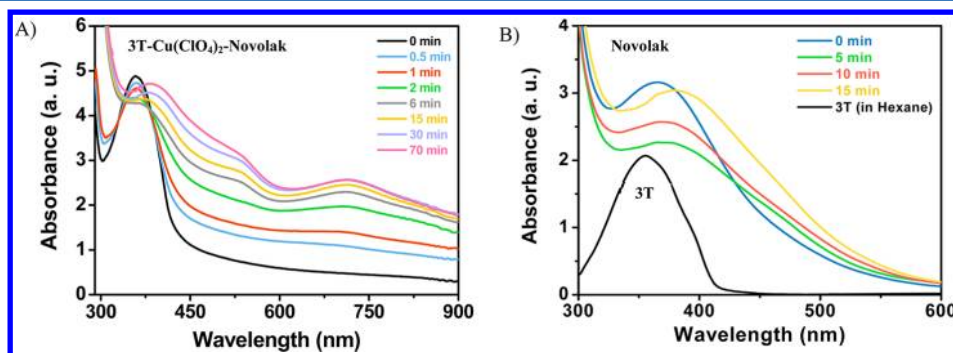


Figure 2. (A) Time evolution of the absorbance spectrum for a 3T- $\text{Cu}(\text{ClO}_4)_2$ -Novolak film after a baking process at 100 °C. (B) Absorbance spectrum of 3T monomers in hexane solution and time evolution of the absorbance spectrum for a Novolak films during after baking at 100 °C.

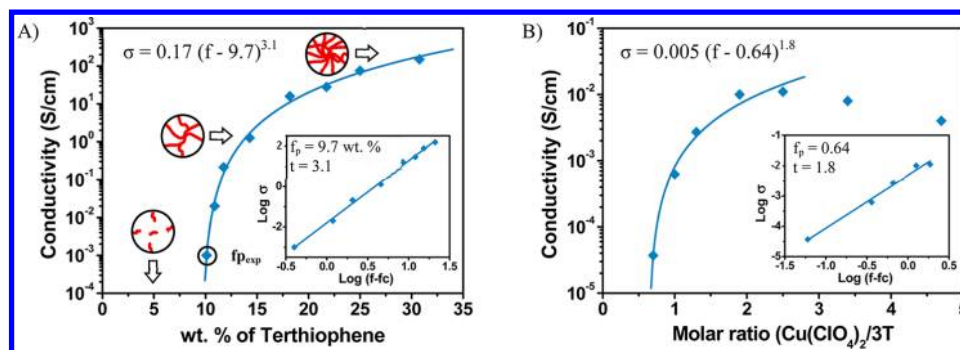


Figure 3. Dependency of IPN conductivity on (A) wt % of 3T ($\text{Cu}(\text{ClO}_4)_2\text{:}3\text{T} = 1.8$) and (B) the oxidant/monomer molar ratio (11 wt % 3T). $T_B = 140^\circ\text{C}$. Solid lines are conductivities calculated from the fitting of the experimental data to eq 2. Insets show log–log plots according to the best fits for f_p and the critical exponent t of eq 2.

in the blend is increased, their chains begin to contact each other, and a continuous path is formed through the volume of the sample for the electrons to move. The formation of this conductive network is based on the principles of percolation theory³⁸ given by

$$\sigma = \sigma_0(f - f_c)^t \quad (2)$$

where σ is the IPN conductivity, f is the volume of the CP in the IPN film, f_c is the percolation threshold, σ_0 is a scaling factor, and t is the critical exponent. For single percolation, the exponent t is a parameter that depends on the dimensionality of the conductive network.

Parameters that affect the conducting polymer content in the IPN should also follow this scaling law. Both the 3T monomer load and the $\text{Cu}(\text{ClO}_4)_2\text{:}3\text{T}$ molar ratio play a key role in the synthesis of the CP into the host polymer. Figure 3A shows the electrical response of the IPN for different amounts of 3T and maintaining a molar ratio of $\text{Cu}(\text{ClO}_4)_2$ to 3T equal to 1.8. We observe that conductivity increases considerably above a 10 wt % of 3T. This is a characteristic property of each IPN system and depends on the shape, the size, and the distribution of conductive domains in polymer matrices. Below this concentration, resistance was too high to be measured. To determine the percolation threshold, we fitted the experimental data using log-to-log scales of eq 2 (inset of Figure 3A). The percolation threshold and the critical exponent were found to be 9.7 wt % and 3.1, respectively. A conducting IPN reaches its percolation threshold when enough CP is synthesized so that CP's chains begin to form for the first time a conductive pathway through the host polymer. Above this value, a significant increase in conductivity is attained with a slight increase in the CP present in the IPN. An increase of the 3T load in Novolak from 10 to 14 wt % leads to an enhancement of conductivity from 10^{-3} to 1 S/cm, respectively. After this region of drastic increase the conductivity reaches the values of the pure CP. This occurs since the conductive network in the sample is complete: the charge carriers follow the pathway created by the connected CP's chains. Films containing 31 wt % 3T reached conductivities as high as 150 S/cm.

The critical exponent was found to be $t = 3.1$, which is higher than the theoretical value $t = 2$ predicted by the classical single percolation theory for three dimensions.³⁸ A similar t -value has been reported in a similar conducting IPN.³⁹ Levon et al.⁴⁰ proposed an explanation for such a large critical exponent in terms of the existence of multiple percolation paths. Apart from the formation of CP domains interconnected through the sample, tunneling conduction among the formed CP domains

may contribute to raise the t -value. This has already been observed in other kinds of percolating systems.^{41,42}

Similarly, conductivity versus molar ratio of $\text{Cu}(\text{ClO}_4)_2$ to 3T also shows a percolating behavior as observed in Figure 3B. This study was carried out with films containing 11 wt % of 3T; this is near the percolation threshold. In the oxidative coupling of two 3T by means of the reduction of $\text{Cu}(\text{II})$ to $\text{Cu}(\text{I})$, two electrons are involved for every 3T coupling. Moreover, polymerization and doping take place simultaneously. Therefore, the stoichiometry of the reaction is between 1 and 2. As expected, conductivity is negligible for a low molar ratio. An increase in the $\text{Cu}(\text{ClO}_4)_2\text{:}3\text{T}$ molar ratio from 0.7 to 1.2 results in a dramatic increase in conductivity from 3×10^{-5} to 3×10^{-3} S/cm, respectively. Conductivity increased strongly up to values in the order of 10^{-2} S/cm. A maximum conductivity is reached for molar ratios around 1.8 and 2.5. Above it, conductivity starts decreasing probably due to an overoxidation of the polythiophene. Monomers polymerized with a high amount of oxidant are more susceptible to the introduction of defects in the polymer structure, which could interrupt the extended conjugation.⁴³ One must be aware of the fact that oxidative doping produces the polymer in its semioxidized state. Further increase of oxidation can result in irreversible oxidation of the conjugated backbone (overoxidation), which in turn renders the polymer insulating.⁴⁴

For the estimation of the percolation threshold of $\text{Cu}(\text{ClO}_4)_2\text{:}3\text{T}$ molar ratio, experimental data were also fitted to eq 2 (inset of Figure 3B). It is worth mentioning that molar ratio data above 2.5 were not taken into account for the fitting because for these values P3T has already experienced overoxidation. Percolation threshold and critical exponent were determined to be 0.64 and 1.8, respectively. These results demonstrate that polymerization and doping take place simultaneously since conducting films can even be obtained with molar ratios of $\text{Cu}(\text{ClO}_4)_2\text{:}6\text{H}_2\text{O}\text{:}3\text{T}$ as small as 0.7; this is below the stoichiometry of the reaction. After the coupling of two 3T, the resulting oligomer has a lower redox potential than the monomer. Therefore, doping will occur before a new coupling takes place.

The critical exponent associated with percolation conductivity with the $\text{Cu}(\text{ClO}_4)_2\text{:}3\text{T}$ molar ratio is now $t = 1.8$, which corresponds to the single percolation limit for three dimensions. This t value is lower than that found for percolation studies using the wt % of 3T. As stated above, the critical exponent is associated with different conduction mechanisms involved in the charge carrier transport phenomena. The evolution of conductivity with the $\text{Cu}(\text{ClO}_4)_2\text{:}3\text{T}$

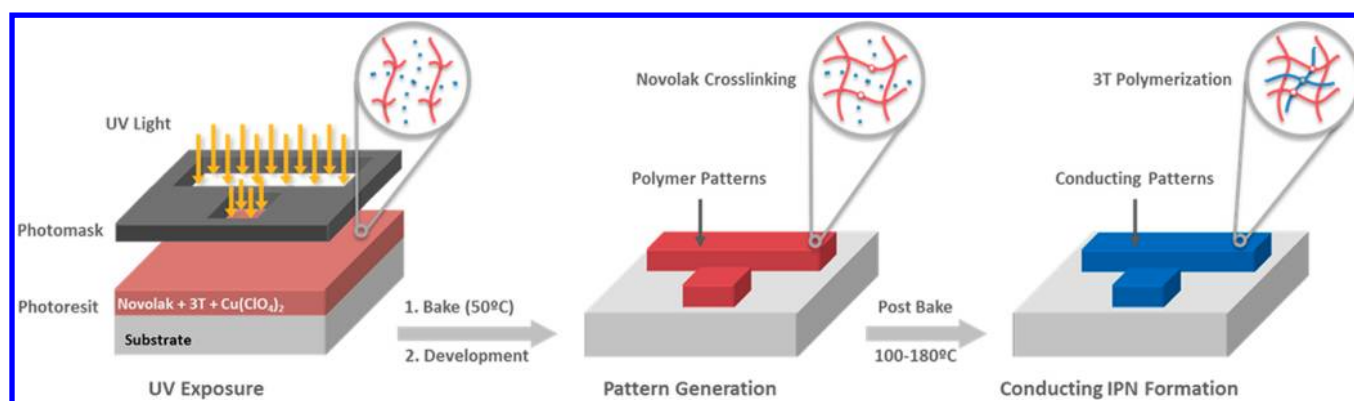


Figure 4. Scheme of the fabrication of the conducting IPN patterns: first, a spin-coated UV-patternable polymer containing 3T and $\text{Cu}(\text{ClO}_4)_2$ is exposed to UV light, baked, and developed. After the pattern generation, the resulting structures are postbaked and CP is synthesized.

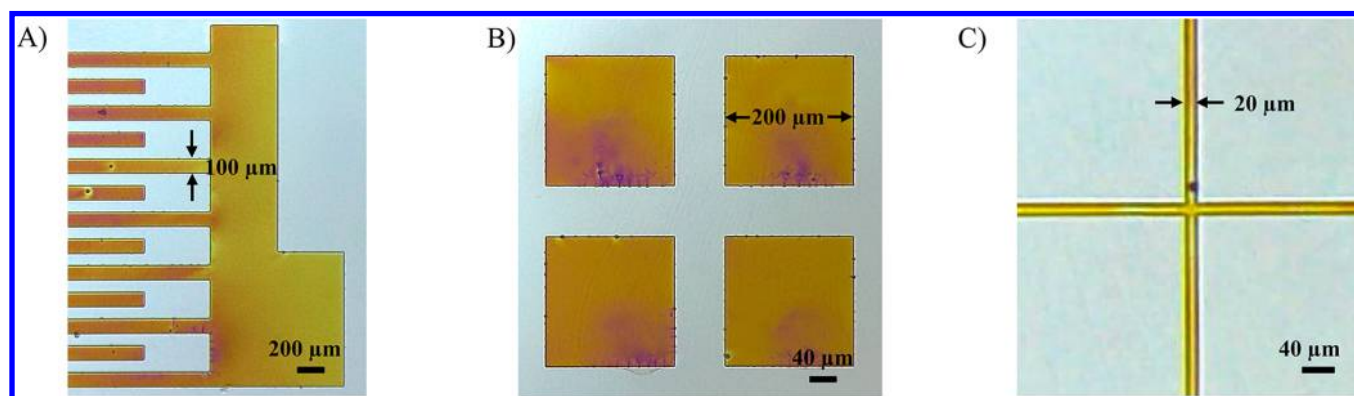


Figure 5. Optical microscope pictures of different conducting IPN patterns on silicon fabricated by UV lithography: (A) 100 μm wide interdigitated structure, (B) 200 μm side squares, and (C) 20 μm wide cross.

molar ratio was performed with a fixed concentration of 3T close to its percolation threshold (11 wt %). Thus, the amount of CP into the resulting IPN film is low, and therefore the spacing among CP domains will be larger than in the case of higher 3T contents. As a result, the tunneling current will be strongly reduced or even negligible because these samples are probably below the percolation threshold needed for this kind of conduction mechanism. This has been reported in the literature for different percolating systems.^{41,45} This could explain why the t -value of the percolation conductivity is now in agreement with the single percolation limit for three dimensions.

Patterning of Conducting IPN. The patterning of CPs with conventional UV lithography is a significant technological challenge. As we demonstrated above, IPNs of two polymers show properties between those of the two unblended materials depending on their relative amounts. This allows the optimization of the IPN according to the target characteristics. However, we did not observe lithographic properties when we tried to pattern Novolak-based conducting IPN films by UV lithography. Novolak negative photoresist system consists of a phenolic resin, a photoacid generator (2-diazo-2H-naphthalen-1-one, DNQ), and a cross-linker (*N*-methoxymethylated melamine). Upon UV exposure, the DNQ photolyzes and carboxylic acid is released.⁴⁶ During a postexposure bake, the acid generated catalyzes the cross-linking reaction between Novolak and the methoxymethylated melamine. As a result, the exposed areas of the film remain insoluble in the aqueous base developer, while the unexposed areas are dissolved away,

generating a negative-tone relief image. The polymerization of 3T into the negative-tone Novolak resist strongly affects its lithographic performance, and unexposed areas cannot be developed. Since the CP is synthesized inside Novolak, the networking degree of the resulting IPN is high enough to achieve annealed films. As a result, both exposed and unexposed areas are completely insoluble in the developer. We observed this effect at any percolation level, even very close to the percolation threshold. To circumvent this problem, we propose to carry out the pattern generation and in-situ synthesis of CP in two separate steps of the microstructure fabrication process, as illustrated in Figure 4.

Initially, Novolak photoresist, 3T, and $\text{Cu}(\text{ClO}_4)_2$ are spin-coated from a common solution in MPA and prebaked at 45 °C for 2 min. Then the sample is exposed to UV light and baked at 50 °C for 1 min. Consequently, the cross-linking reaction of Novolak takes place, and the exposed areas of the film remain insoluble in the aqueous base developer, while the unexposed areas are dissolved away, generating a negative-tone relief image. The polymerization of 3T does not take place under the pre- and postexposure bake conditions since mild temperatures are used. The resulting microstructures are then baked at 100–150 °C, and 3T polymerizes to the corresponding polythiophene generating conductive micropatterns.

We observed that lithographic performance of Novolak photoresist is strongly affected by the conducting component loading. As a result, Novolak photoresist needs to be properly formulated with 3T and $\text{Cu}(\text{ClO}_4)_2$ to preserve the negative lithographic characteristics of Novolak-based photoresist and

generate conductive micropatterns. IPN films with high concentration of CP (20 wt % 3T, $\text{Cu}(\text{ClO}_4)_2/3\text{T}$ molar ratio = 1.8) exhibited very poor lithographic properties probably because the large concentration of $\text{Cu}(\text{ClO}_4)_2$ can affect the photoacid generation as well as the cross-linking reaction between Novolak and the cross-linker. Upon exposure to light, DNQ undergoes a series of reactions where radical species are involved to form carboxylic acid, which is responsible for the imaging properties of Novolak. $\text{Cu}(\text{ClO}_4)_2$ is an oxidant agent that can easily react with radical intermediates generated during the photolysis of DNQ. This can certainly disturb the photogeneration of carboxylic acid and hence the lithographic process. We observed a similar effect in a recent work where we formulated positive tone Novolak with KAuCl_4 to form Au nanoparticles embedded into polymer patterns.⁴⁷ As long as the wt % of 3T and $\text{Cu}(\text{ClO}_4)_2$ decreases, the lithographic performance of the IPN improves. Only near the percolation threshold of 3T (Figure 3a) does the conducting IPN exhibit adequate lithographic properties.

The optimum formulation was found to be 11 wt % 3T and $\text{Cu}(\text{ClO}_4)_2/3\text{T}$ molar ratio = 1.5. The electrical conductivity obtained with this formulation is 10^{-2} S/cm. We found that pre- and postexposure bake at low temperature is compulsory to inhibit the oxidative polymerization of 3T before the development step. As a result, only the exposed areas of the resists are cross-linked and completely insoluble in the developer after the postexposure bake, indicating the negative tone characteristics of these resists. Figure 5 shows optical microscope images of different conducting IPN microstructures generated after the UV lithographic process and a postbake at 130 °C. We accurately patterned three different types of microstructures with different resolutions: interdigitated structures with a width of 100 μm , 200 μm side squares, and a 20 μm wide cross. We achieve a maximum resolution of 20 μm , which corresponds to that of the photomask used. With this IPN formulation and process conditions, the lithographic performance of negative-tone Novolak is not disturbed.

4. CONCLUSIONS

The focus of this research is the design of a multifunctional polymeric material, which can combine electrical conductivity with lithographic characteristics. We report on a novel approach to modify the conductivity of numerous insulating host polymers such as negative-tone Novolak, poly(methyl methacrylate) (PMMA), polystyrene (PS), poly(4-vinylphenol) (P4VP), and poly(4-vinylphenol)-*co*-(methylmethacrylate) (P4VP-*co*-MMA). The synthetic approach consists of the in-situ polymerization of terthiophene with $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ into these host polymer thin films during the bake step after spin-coating to form an interpenetrating polymer network (IPN). Conductive films on the order of 10^{-4} –150 S/cm were successfully obtained depending on the specific IPN composition. Among the host polymers proposed, we focused on Novolak since it is a commercially available negative photoresist formulated for UV-lithography. Polymerization of 3T in Novolak was followed by UV-vis spectroscopy. The conducting properties of these materials can be easily tuned changing the CP content. We show that the electrical response of the IPN for different amounts of 3T and $\text{Cu}(\text{ClO}_4)_2$ ratio follows a clear percolation tendency. Their percolation thresholds were found to be 9.7 wt % and 0.7, respectively.

For the fabrication of conducting micropatterns, we proposed to carry out the pattern generation and in-situ

synthesis of poly(terthiophene) in two separate steps of the microstructure fabrication process. For such a purpose, we found that pre- and postexposure bake at low temperature is compulsory to inhibit the oxidative polymerization of 3T before the development step of the lithographic process. After the lithographic process, $\text{Cu}(\text{ClO}_4)_2$ initiates simultaneously the oxidative polymerization of the 3T and the subsequent doping of the in situ synthesized poly(terthiophene) inside the Novolak micropatterns during a postbake step at 130 °C. From the percolation curves, Novolak photoresist was properly formulated with 3T and $\text{Cu}(\text{ClO}_4)_2$ to preserve the lithographic performance of Novolak-based negative photoresist and generate conductive micropatterns by means of UV lithography. The optimum formulation was found to be 11 wt % 3T and $\text{Cu}(\text{ClO}_4)_2/3\text{T}$ molar ratio = 1.5. The electrical conductivity obtained with this formulation is 10^{-2} S/cm. As a result, we accurately patterned three different types of microstructures with different resolutions: interdigitated structures with a width of 100 μm , 200 μm side squares, and a 20 μm wide cross. We believe this synthetic approach is of potential application to modify the conductivity of numerous insulating polymers preserving to some extent their physical and chemical properties.

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Notes

The authors declare no competing financial interest.

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