



## Nano Scale Disruptive Silicon-Plasmonic Platform for Chip-to-Chip Interconnection

### Demonstration of metal-(lithographic) polymer and QD metal-(lithographic) polymer nanocomposites

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### *Executive Summary*

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### *Change Records*

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## 1. Introduction

This milestone report deals with the demonstration of metal-(lithographic) polymer and QD metal-(lithographic) polymer nanocomposite useful for: a) plasmonic nano- and micro-structures for waveguides and b) photodetector based on Plasmonic Patternable Conductive Polymers (PPCPs). We have accomplished:

- In-situ synthesis of conducting polymer into a patternable host matrix.
- In-situ synthesis of Au nanoparticles into a patternable conducting polymer.
- Development of metallic microstructures by a chemical regrowth of metal NPs: towards prepatterned plasmonic nanostructures.

Conducting polymers with patterning capability is one of the routes (or an element) for the fabrication of a plasmonic photodetector in WP4. The first step was the synthesis of a patternable conducting polymer (PCP) based on Polyterthiophene as conducting polymer and Novolak as host matrix. This Novolak-based nanocomposite has shown good electrical properties and patterning capability by means of UV-lithography.

In a second step, a PCP containing Au nanoparticles has been also obtained using a gold salt to polymerize the terthiophene. In this case, the multifunctional material consisted of Au nanoparticles, Polyterthiophene, and PMMA as the host matrix, which can be patterned by means of E-Beam lithography. Preliminary results on the patterning performance of this PMMA-based PCP has been obtained being necessary the optimization of the formulation of the nanocomposite as well as the lithographic process parameters.

Finally, we propose an alternative method for the fabrication of metal micro/nanostructures from metal-polymer (the polymer in this case is dielectric) nanocomposite resists and their subsequent metallization by a novel wet chemistry method. **A patent application on this method has been already presented.**

## 2. Development of a conducting polymer into Novolak-based host matrix

Conducting polymers (CPs) offer a unique combination of electric, electronic and optical properties inherent to semiconductors and metals, with the added value of processability. Polymers with a regular alternation of single and double bonds along the polymer chain ( $\pi$ -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. The generation of charge carriers (polarons and bipolarons) can be achieved by reduction (n-doping), oxidation and protonation (p-doping) of the  $\pi$ -conjugated system, resulting in highly delocalized polycations or polyanions. 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. The successful application of CPs will depend on exploiting their low-cost potential by the innovative design and development of materials for scalable and inexpensive methods to pattern CPs on large-area substrates. Here we report new

multifunctional polymeric materials, which can combine electrical conductivity with other properties, such as UV lithographic capabilities.

A novel material based on Polyterthiophene as CP inside a Novolak-based negative-tone photoresist has been achieved. The nanocomposite is formed by the in-situ polymerization of terthiophene (3T) with  $\text{Cu}(\text{ClO}_4)_2$  (doping agent) inside the host polymer. Conducting films in the order of  $10^{-4}$  to 150 S/cm are obtained depending on the specific nanocomposite composition. References [1] and [2] report the most important results of this research work.

### Synthesis and Optical Characterization

Novolak-based negative-tone photoresist was chosen as host polymer matrix and can be easily processed from several solvents into thin films by spincoating. 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 polymer were dissolved in a common solvent (MPA) and spincoated on a glass substrate. Among other host polymers tested, Novolak and Polystyrene showed the best results in terms of conductivity (Table 1). However, negative-tone Novolak is especially attractive since it is a commercially available photoresist formulated for UV-lithography and hence was the main focus in our study.

**Table 1.** Conducting IPN films prepared from different host polymer under same process conditions.

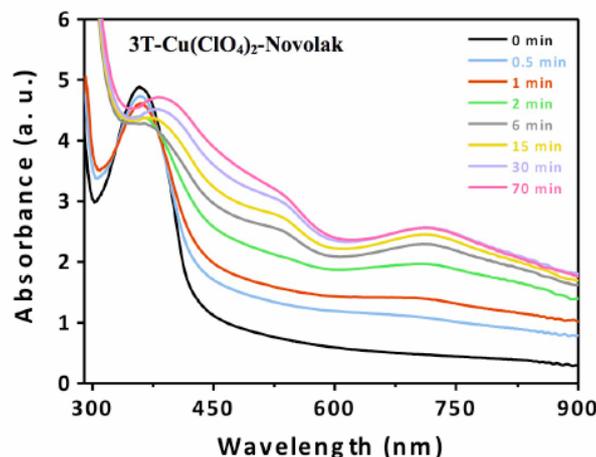
| Host Polymer          | Conductivity<br>(S/cm) | Thickness<br>(nm) |
|-----------------------|------------------------|-------------------|
| PS                    | 80                     | 250               |
| Negative-tone Novolak | 20                     | 260               |
| PMMA                  | 0.8                    | 210               |
| P4VP                  | 0.06                   | 240               |
| P4VP-co-MMA           | 0.003                  | 235               |

The chemical oxidative polymerization of 3T possesses a well-defined autocatalytic character, i.e. a rapid coloration and polymerization proceeds after a definite induction period. The reaction was followed by UV-Vis-NIR spectroscopy (Fig. 1). Initially, Novolak containing 3T exhibits a maximum absorption peak at around 359 nm (black line in Fig. 1). 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 because of the formation of oligomers with a larger  $\pi$ -conjugated system. The two new bands around 535 and 715 nm gain importance during the baking process due to the formation of charge carrier bands (polaron and bipolaron) arising from the oxidation of 3T. Both polymerization and doping (oxidation) of the corresponding conjugated polymer take place simultaneously.

The electrical conductivity of the nanocomposite will be determined by the CP content into the insulating host polymer. The formation of this conductive network is based on the principles of Percolation Theory:

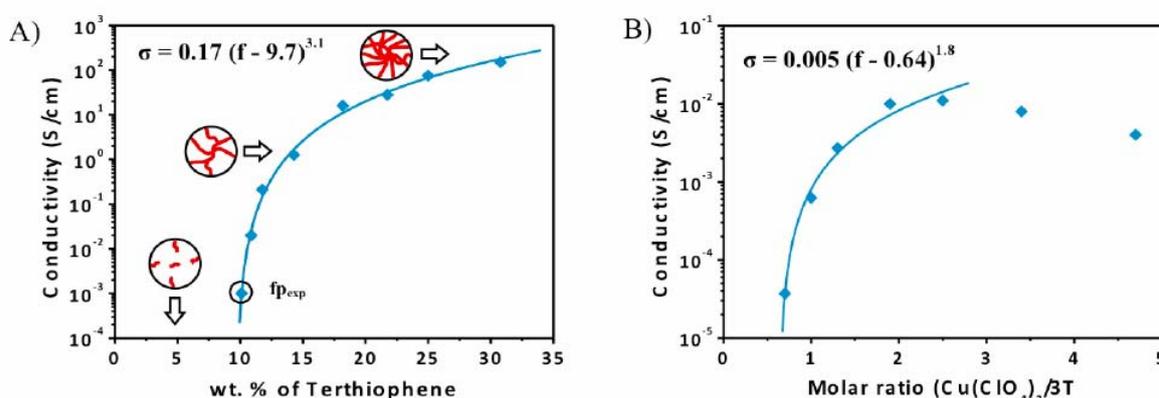
$$\sigma = \sigma_0 (f-f_c)^t \quad (1)$$

where  $\sigma$  is the nanocomposite conductivity,  $f$  the volume fraction of the CP in the film,  $f_c$  the percolation threshold,  $\sigma_0$  a scaling factor and  $t$  the critical exponent representative of the conductive network dimensionality.



**Figure 1.** (a) Time evolution of the absorbance spectrum for a 3T-Cu(ClO<sub>4</sub>)<sub>2</sub>-Novolak film after a baking process at 100 °C.

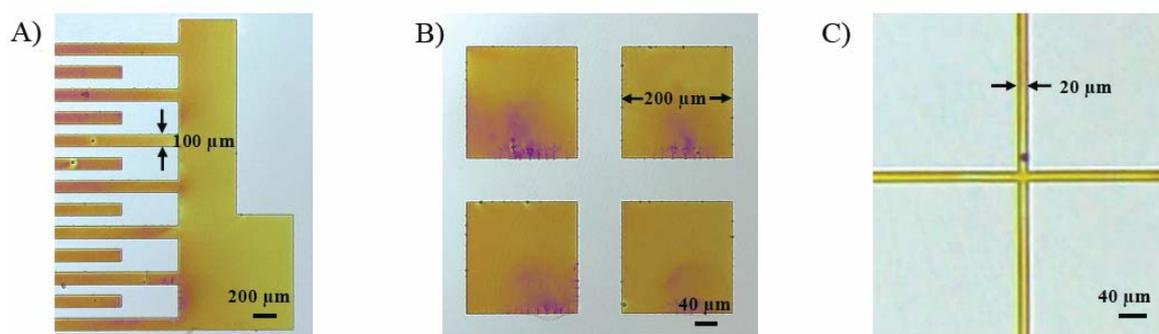
Figure 2a show the electrical response of the nanocomposite for different amounts of 3T and maintaining a molar ratio of Cu(ClO<sub>4</sub>)<sub>2</sub> to 3T equal to 1.8. The percolation threshold and the critical exponent were found to be 9.7 wt. % and 3.1, respectively, by fitting to Eq. 1 (continuous line). Above this value, a significant increase in conductivity is attained with a slight increase in the CP present in the IPN. Films containing 31 wt. % 3T reached conductivities as high as 150 S/cm. Similarly, conductivity versus molar ratio of Cu(ClO<sub>4</sub>)<sub>2</sub> doping also shows a percolating behavior as observed in Fig. 2b (the films were produced using 1 wt. % of 3T). A maximum conductivity is reached for molar ratios around 1.8 and 2.5 with a threshold at 0.64 (after the corresponding fitting to Eq. 1). Above it, conductivity starts decreasing probably due to an over-oxidation of 3T and a subsequent formation of defects in the polymer structure.



**Figure 2.** Dependency of IPN conductivity on a) wt. % of 3T ( $\text{Cu}(\text{ClO}_4)_2:3\text{T} = 1.8$ ) and b) the oxidant/monomer molar ratio (11 wt. % 3T).  $T_B = 140$  °C. Solid lines are conductivities calculated from the fitting of the experimental data to Eq. 2.

The patterning of CPs with conventional UV lithography is a significant technological challenge. Given that the polymerization of 3T into the negative-tone Novolak resist strongly affects its

lithographic performance we carry out the pattern generation (UV-photolithography) and in-situ synthesis of the CP (post-bake at 100-180 °C) in two consecutive steps of the microstructure fabrication process. The optimum formulation of the nanocomposite resist 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. Figure 3 shows optical microscope images of different conducting microstructures with different resolutions generated after the UV lithographic process and a post bake at 130 °C.



**Figure 3.** Optical microscope pictures of different 3T-Novolak conducting patterns on silicon fabricated by UV lithography a) 100 μm-wide interdigitated structure. b) 200 μm-side Squares and c) 20 μm-wide Cross

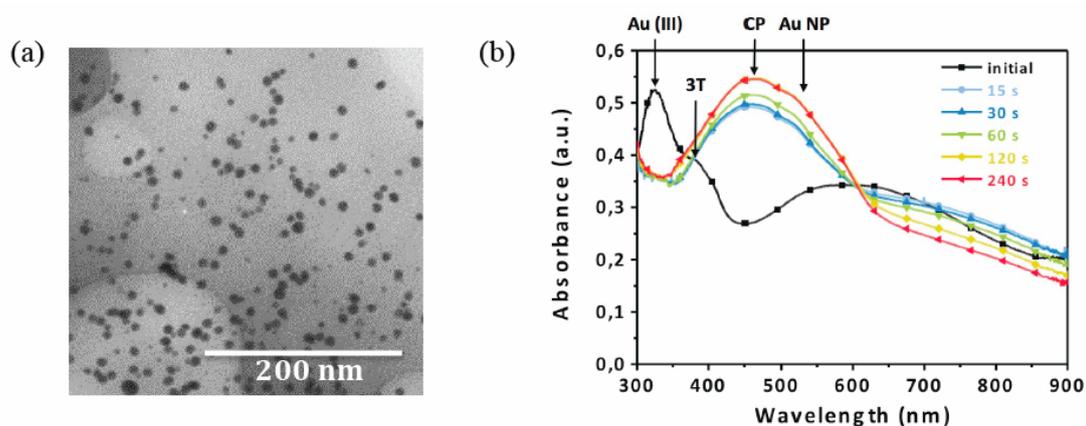
### 3. Development of a plasmonic patternable and conducting polymer nanocomposite

In a second step we have also developed a novel patternable conducting nanocomposite containing gold nanoparticles (NPs) for its application in plasmonic based photodetectors, where light absorbed by these nanoparticles due to their characteristic Localized Surface Plasmon Resonance (LSPR) can be transformed into an electrical current [3]. To synthesize the nanocomposite we use the same procedure as before, but this time the in-situ polymerization of 3T has been carried out using  $\text{HAuCl}_4$  as oxidizing agent inside a matrix of PMMA. Au nanoparticles are in-situ generated from the reduction of Au(III) to Au(0) during the bake step, as observed in Fig. 4a.

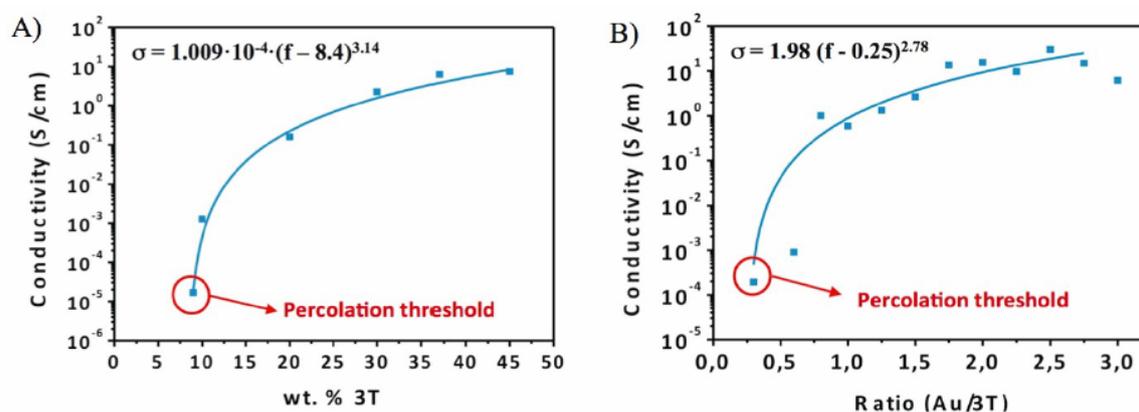
The in-situ synthesis of 3T and Au NPs in PMMA can be also followed by UV-Vis spectroscopy (Fig. 4b). Initially, both 3T and  $[\text{AuCl}_4]^-$  dispersed in PMMA exhibit two narrow absorption contributions at around 380 and 330 nm (black line in Fig. 4b) and a broad absorption band at 600 nm, which is attributed to the polymerization of 3T starting even at room temperature. Any absorption feature from the PMMA matrix is expected between 300 and 900 nm. However, any measurable conductivity was observed at this stage, because of the extent of the polymerization is small. As the polymerization reaction takes place, the peak intensity of the 3T red-band decreases and a new band develops at around 480 nm, which is mixed with the LSPR absorption at 525 nm of the generated Au NPs. This new band gains importance during the baking process and the band of 3T at 600 nm broadens and shifts to longer wavelengths. This is due to the formation of charge carrier (polaron and bipolaron) bands arising from the oxidation (p-doping) of the 3T.

Similar to the Novolak-based nanocomposite, the electrical conductivity of this metal-polymer nanocomposite also exhibits a percolating behaviour (Eq. 1), as shown in Figs. 5a-b. Above the percolation threshold, a significant increase in conductivity is attained up to values of the order

of 10 S/cm. In the oxidative coupling of two 3T by means of the reduction of Au(III) to Au(0), two electrons are involved for every 3T coupling. Theoretically, each 3T-coupling needs 2/3 of the reduction of Au(III) to Au(0), and a certain additional amount of Au(III) is needed to dope the polymer chain synthesized. As a result, the experimental molar ratio Au/3T of the reaction to achieve the highest conductivity values is between 0.5 and 2 (Fig. 5b). These results demonstrate that polymerization and doping take place simultaneously since conducting films can even be obtained with molar ratios of HAuCl<sub>4</sub>/3T as small as 0.7, which is below the stoichiometry of the reaction. After the coupling of two 3T, the resulting oligomer has a lower redox potential than the monomer, and doping will occur before a new coupling takes place. Currently, the lithographic performance of this material is being optimized, but preliminary results are promising. Preliminary measurements of the photoconductivity in these nanocomposites give responsivities of the order of 10<sup>-6</sup> A/W at 1 V.



**Figure 4.** (a) TEM image of a nanocomposite film prepared with a molar ratio of HAuCl<sub>4</sub> to 3T equal to 1, [3T] = 0.08 M at a baking temperature of 140 °C for 60 s; (b) Time evolution of the absorbance spectrum of a 3T–HAuCl<sub>4</sub>–PMMA film during the baking process.

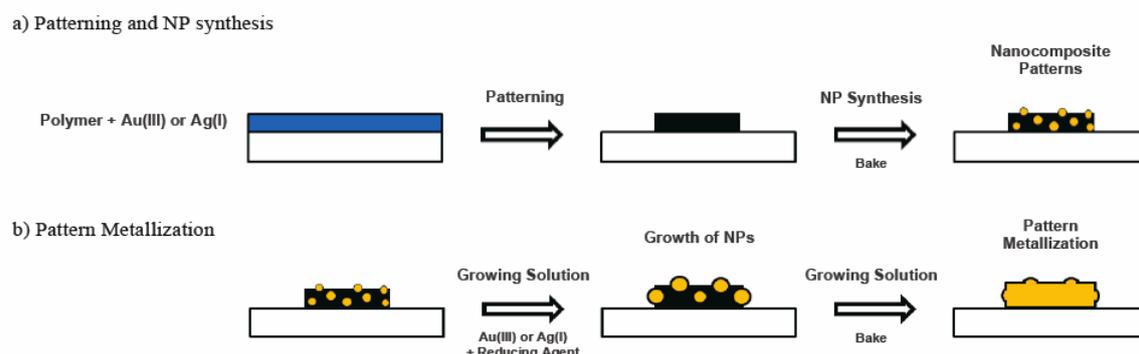


**Figure 5.** (a) Dependency of the nanocomposite conductivity on wt % of 3T using HAuCl<sub>4</sub>: 3T = 2.5; (b) Idem on the oxidant / monomer molar ratio using 33 wt % of 3T with respect to the PMMA). The baking temperature was 140 °C in both cases.

#### 4. Continuous metallization by chemical regrowth of metal nanoparticle seeds: towards prepatterned plasmonic nano- and micro-structures

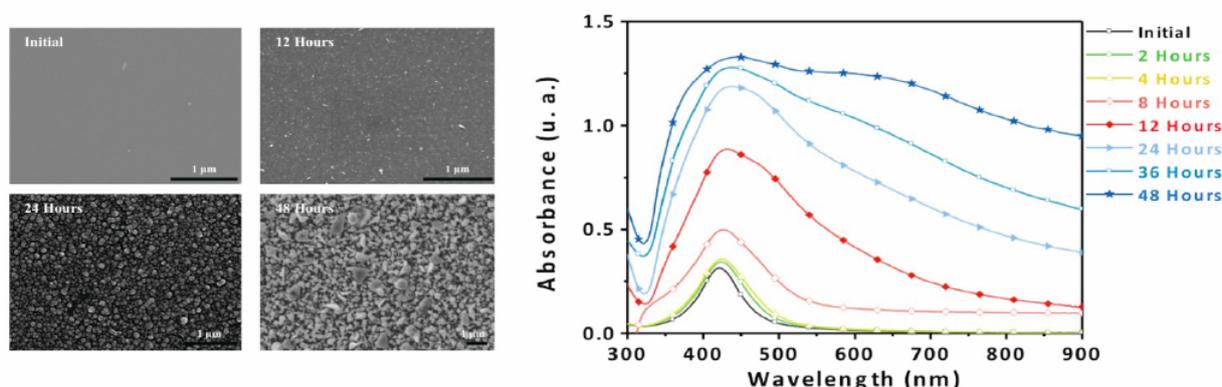
We have developed an alternative method for the fabrication of metal micro- and nano-structures from metal-polymer nanocomposite resists and their subsequent wet chemistry metallization.

The process consists of three simple steps: (1) fabrication of macro-/micro-/nano-patterns by means of lithography or any other direct printing technologies (inkjet, microplotter, ...), (2) in-situ synthesis of metal NPs during a post-bake step and (3) wet chemistry (non-electrochemical) metallization of nanocomposite patterns, as illustrated in Fig. 6. The novelty of our approach is that both metal NPs are embedded into the polymer pattern and act as seeds for the reduction of Ag(I) when immersed into a solution of the corresponding precursor metal salt ( $\text{AgNO}_3$ ) and an appropriate reducing agent. The key point of this procedure is the use of a weak reducing agent so that the metal reduction selectively takes place at the surface of existing previously synthesized NPs. As a result, metal NPs grow significantly into the nanocomposite structure until the pattern is completely metallized.



**Figure 6:** Fabrication process of metallic macro-/micro-/nano-structures: (a) fabrication of patterns by lithography or other patterning methods with in-situ synthesis of metal NPs and (b) non-electrochemical metallization of nanocomposite patterns.

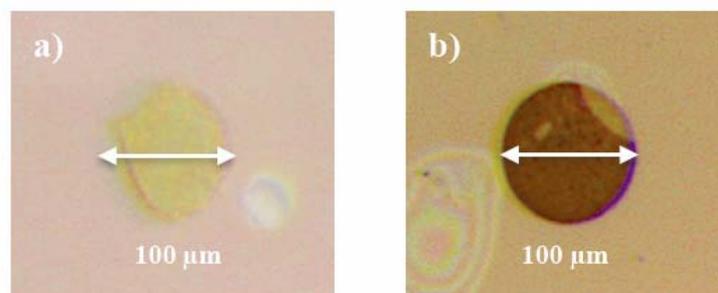
The metallization process was followed by UV-Vis spectroscopy, SEM and TEM for different reaction times (Fig. 7). We also carried out the electrical characterization of the layers and confirmed that bulk conductivities of silver (gold in other experiments) were achieved. Given that the progress of plasmonics is closely related to the advancement of material research and fabrication technology, we believe that this fabrication method may be very useful for the fabrication of future plasmonic (waveguides for Surface Plasmon Polariton) and optoelectronic (electrodes) devices.



**Figure 7.** SEM images for different immersion times of the Ag-PVA nanocomposite (left) and UV-Vis spectra for different immersion times of the Ag-PVA nanocomposite in the growing solution.

Patterning of Ag-PVA was carried out by e-beam lithography. Figure 8a shows an optical microscope image of a 100  $\mu\text{m}$  round pattern of Ag-PVA generated upon exposure to an e-beam at 30 kV at doses of 2  $\text{mC}/\text{cm}^2$ . The formation of Ag NPs in the pattern is confirmed by the

change in colour to yellow after the lithographic process. This can be observed by the naked eye even before the development (NPs created during e-beam exposure). After this, the metallization of the nanocomposite was accomplished, as shown in Fig. 8b, where the same Ag-PVA micro-pattern in Fig. 8a was immersed in the growing solution. As can be seen, the pattern absorption is significantly more intense after the metallization process and any metallic signature is observed outside the pre-patterned Ag-PVA micro-structure.



**Figure 8.** Optical microscope images of an Ag-PVA microstructure fabricated by e-beam lithography before (a) and after (b) the metallization process.

#### 4. Conclusions

PCPs based on Polyterthiophene and a patternable host matrix (Novolak) are synthesized from the oxidative polymerization of terthiophene using an oxidizing salt. This approach allows us to combine the properties of Novolak-based resists with the conducting properties of polyterthiophene. Hence, conductive films on the order of  $10^{-4}$  – 150 S/cm are successfully obtained depending on the specific nanocomposite composition. This multifunctional material shows good pattern capability and conductive micropatterns were generated by means of UV lithography by means of UV- lithography.

Based on this novel approach, a PCP containing gold nanoparticles has been developed. This time the in-situ polymerization of 3T is carried out using  $\text{HAuCl}_4$  as oxidizing agent inside PMMA as the host matrix. As a result, Au nanoparticles are simultaneously generated inside the PMMA-based nanocomposite. This new multifunctional material combines the excellent properties of metal NPs (LSPR effect) and conducting polymers. Conductivities between  $10^{-5}$  to 10 S/cm were measured. Currently, the lithographic performance of this material by means of electron beam is being optimized, but preliminary results are promising.

Finally, an alternative method for the fabrication of metal micro- and nano-structures from metal-polymer nanocomposite resists and their subsequent wet chemistry metallization has been demonstrated. We believe that this fabrication approach may be very useful for the fabrication of future plasmonic (waveguides for Surface Plasmon Polariton) and optoelectronic (electrodes) devices. Based on the novelty of this method, we recently presented a patent application.

## *References*

- [1] R. Abargues, P. J. Rodríguez-Cantó, R. García-Calzada, and J. Martínez-Pastor, “Patterning of conducting polymers using UV lithography: the in-situ polymerization approach,” *J. Phys. Chem. C*, vol. 116, pp. 17547-17553, 2012.
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- [3] S. Mubeen, G. Hernandez-Sosa, D. Moses, J. Lee, and M. Moskovits, “Plasmonic Photosensitization of a Wide Band Gap Semiconductor: Converting Plasmons to Charge Carriers,” *Nano Lett.* **11**, 5548–5552 (2011)