

MICRO-PATTERNING OF FLUOROPOLYMER SURFACES FOR ELECTRONIC AND BIOMATERIALS APPLICATIONS

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INTRODUCTION: Micro-contact printing (μ CP) is a soft lithography process that offers an alternative route for the formation of conducting polymer structures on a variety of substrates for application in polymer-based sensor and electronic devices. The present study is focused on creating polypyrrole-based sensor structures on a flexible, bio-compatible substrate (poly(tetrafluoroethylene), PTFE). The key requirements are to optimize polypyrrole (PPy) growth on an active metal (copper)¹, to form an adherent multi-layer film with appropriate interlayer grafting² that incorporates PPy and copper layers³, and to pattern this structure using μ CP to create sensor arrays.

METHODS: PPy films doped with a surfactant (dodecylbenzene sulfonic acid), PPy(DBSA), were deposited on mechanically polished and electropolished copper substrates in an aqueous solution of 0.05 M pyrrole and 0.05 M DBSA at a constant potential in the range 1.0 – 3.5 V.

Multi-layer films were deposited on poly(tetrafluoroethylene) (PTFE) film. The film was cleaned ultrasonically in acetone (5 min.), Ar plasma-treated for 0 to 300 s (Harrick Scientific PDC-32G, Ar pressure 5×10^{-2} mbar; power 18 W), air exposed for 10 min., then immersed N-[3(trimethoxysilyl) propyl] diethylene triamine (TMS) (1 wt% solution in 1,4 dioxane). The film was washed in 1,4 dioxane to remove excess TMS and dried in nitrogen. The film was activated in an aqueous solution of 0.1 wt% PdCl₂ and 1.0 wt% HCl for 10 min. and rinsed in deionised water. Electroless copper was deposited in a CuSO₄-based plating bath for 20 min., followed by rinsing in deionised water. PPy(DBSA) was electro-deposited at a potential of 1.5V for 10 min. in an aqueous solution of 0.05 M pyrrole and 0.05 M DBSA. The completed multilayer was rinsed using deionised water and dried for 24 hours at 60°C.

RESULTS: PPy(DBSA) films were successfully deposited on electropolished copper at potentials of 1.5 V and higher due to partial surface passivation by Cu₂O. XPS showed doping levels were highest, (ratio of charged N species to total N species = 0.55) at 1.5V deposition potential. In contrast, deposition on mechanically polished copper failed with substrate

dissolution dominating in the presence of a much thinner surface oxide.

XPS and TOF-SIMS showed the formation of oxygen-containing functional groups during plasma treatment and subsequent reaction of these with TMS. PdCl₂ formed a complex with nitrogen groups in the TMS and activated the surface for electroless deposition of copper. The copper surface oxide was similar to that observed for electropolished copper, with a significant concentration of Cu₂O. PPy(DBSA) was successfully deposited on this surface due to the passivation action of the oxide, completing the desired multi-layer film (Table 1).

Table 1. Multi-layer film forming basis of μ CP-fabricated conducting polymer sensor devices.

Layer	Material/Treatment
substrate	poly(tetrafluoroethylene)
plasma treatment	Ar ⁺ plus air exposure
silane coupling	TMS
activator	palladium chloride
metallization	electroless copper
conducting polymer	PPy(DBSA)

μ CP, via a polydimethylsiloxane stamp, was used to apply a TMS silane pattern on a plasma-treated PTFE surface, allowing the formation of copper patterns and providing a pathway to PPy(DBSA) sensor arrays.

DISCUSSION & CONCLUSIONS: The formation of patterned structures on PTFE has been demonstrated. Migration of silicon-containing species remains a potential limitation to reducing features sizes from the current 200 μ m to 10 μ m and below. Current work is directed at identifying enhanced μ CP pathways.

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ACKNOWLEDGEMENTS: The authors acknowledge the assistance of the Australian Research Council (ARC) and the State Government of Victoria Science, Technology and Innovation Initiative for provision of TOF-SIMS infrastructure, and the ARC for project funding (DP0209965).