

Easy synthesis of hybrid hydrophilic-hydrophobic patterned surfaces by atmospheric plasmas

A. Demaude¹, C. Poleunis², E. Goormaghtigh³, A. Delcorte², M. Gordon⁴, F. Reniers¹

¹CHANI, Université Libre de Bruxelles, Brussels, Belgium

²IMNC, Université Catholique de Louvain, Louvain-la-Neuve, Belgium

³SFMB, Université Libre de Bruxelles, Brussels, Belgium

⁴Chemical Engineering, University of California, Santa Barbara, United States

Abstract: Two different hybrid coatings with a 100 μ m-mm scale hydrophilic-hydrophobic patterns showing high wettability contrast (from $>125^\circ$ to $<25^\circ$) were synthesized by atmospheric dielectric barrier discharge. The different areas were characterized by water contact angle measurements and by IR imaging.

Keywords: Atmospheric plasma, patterned surface, wettability contrast

1. Introduction

Hydrophilic and hydrophobic coatings and surfaces are nowadays easily synthesized and find applications in daily life as well as in advanced technological industries. A new interest is brought to surfaces that combine both properties over different length scales. Such hybrid surfaces having micro- or nano-hydrophilic—hydrophobic patterns are useful for many applications[1,2]. For example, they can be used for water/fog harvesting, mimicking the back of the *Stenocara* beetle (*physasteria cribripes*)[3,4], for controlling the location and movement of fluids, or for improving heat transfer on certain materials[5,6]. This type of surfaces can also be needed in biology research, to control cell growth, to study cell-cell or cell-material interactions, or to fix, manipulate and detect biomolecules[7,8]. Methods to synthesize these surfaces already exist but are based on the use of advanced technologies (lithography for example), in low pressure environment that are difficult to implement at larger scale, and using fluorinated chemicals to produce the hydrophobic areas[9–12]. Here we propose the deposition of hydrophilic and hydrophobic films by an atmospheric dielectric barrier discharge (DBD), and a post-treatment of Ar/O₂ DBD through a PVC physical mask to obtain hydrophilic-hydrophobic patterned surfaces. The only chemicals used are acrylic acid (AA) and propargyl methacrylate (PMA), which is less harmful to the environment and less controversial than fluorinated molecules. Besides, these coatings can virtually be deposited on any surfaces, unlike most of the coatings reported in the literature that use the intrinsic wettability of the substrate.

2. Experimental

The deposition of the coating was done on silicon wafers and aluminium, using a dielectric barrier discharge reactor (see Fig. 1) that has been described in previous paper[13]. In this device, the lower electrode moves along the upper electrode during deposition.

Argon was used as the plasmagen gas (with a flow of 18 L.min⁻¹ for depositions or post-treatment), and as the carrier gas (with flows ranging from 1 to 2 L.min⁻¹).

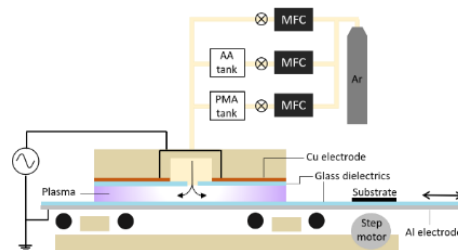


Fig. 1. Schematic setup of the dielectric barrier discharge reactor[13].

Hydrophobic films were deposited by flowing 2 L.min⁻¹ of Ar through the PMA precursor and by applying 60 W of plasma power, for two passes (i.e. one displacement of the upper electrode from one side of the reactor to the other, back and forth, that is 300s in the discharge)

Hydrophilic films were deposited from:

- A mix of AA and PMA with 1 L.min⁻¹ of carrier gas flow for each precursor, and at a plasma power of 60 W for two passes.
- Post treatment of the hydrophobic film with an Ar/O₂ plasma for one pass of the electrode, with 0.1 L.min⁻¹ of O₂.

Chemical heterogeneity of the hybrid coatings was assessed using IR imaging and water contact angle (WCA).

3. Results

Films with water contact angle of more than 135° could be obtained from the deposition of pure PMA. These show remarkable hydrophobic properties compared to the fluorinated counterparts, though it was possible to obtain lower WCA by applying lower plasma power.

A first type of hydrophilic film was obtained by co-deposition of AA (which can be of interest for biocompatibility) with PMA. The double and triple bond located at both ends of PMA insure not only a high deposition rate, but also crosslinking, rendering the films exceptionally stable and non water-soluble, contrary to most pure AA films[14–16]. By tuning the PMA versus AA precursors ratio injected in the discharge, surfaces

with different wettability properties were produced. The presence of PMA increases the water-stability but also the hydrophobicity of the film. The film corresponding to the best compromise between hydrophilicity and water-stability showed a WCA $\sim 50^\circ$.

A second type of hydrophilic film was developed by treating the hydrophobic PMA film with an Ar/O₂ plasma, which induces the grafting of polar oxygen-containing functionalities on the surface. The resulting film shows WCA $\sim 20^\circ$.

Two stable hydrophilic/phobic 2D patterns in the 100's μm to mm length scale regime were synthesized using sequential deposition of the hydrophobic and the two hydrophilic films described above through a PVC mask. First, the PMA-Mix coating consists of a mix (AA+PMA) hydrophilic pattern deposited on a first hydrophobic PMA layer. Second, the PMA+O₂-PMA coating consists of a hydrophobic PMA pattern deposited on a first hydrophilic PMA layer post-treated by Ar/O₂ plasma.

The WCA measurements performed on these two hybrid coatings revealed a high wettability contrast between each chemically different area (see Fig.2), and particularly for the PMA+O₂-PMA sample.

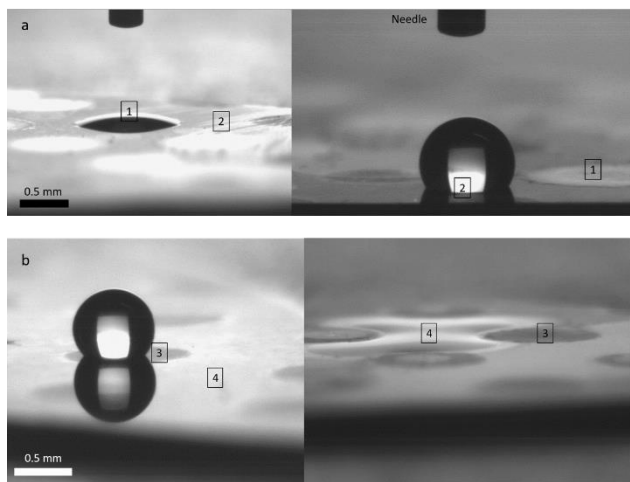


Fig. 2. Images of the droplets during WCA measurements on a) the PMA-Mix coating, and b) the PMA+O₂-PMA coating. The chemical differentiation of regions 1 and 2 from panel a), and regions 3 and 4 from panel b) is pictured on Fig 3a and Fig 3b, respectively[17].

Chemical characterization of the patterned coatings was done by micro IR imaging at the wavenumber corresponding to the C=O stretching band, as it shown on Fig. 3. For each sample, a mean spectrum of the hydrophilic areas was compared with one of the hydrophobic areas (see Fig. 4).

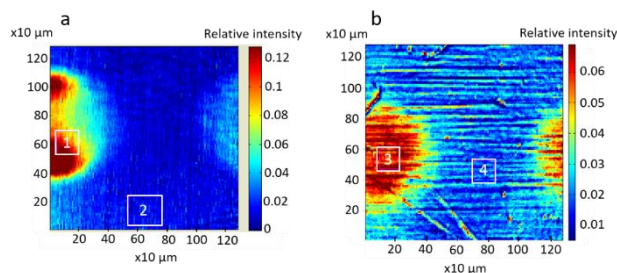


Fig. 3. Micro-IR imaging of C=O stretch intensity for hybrid patterned hydrophilic/phobic films. a) Mix pattern on PMA (1722cm⁻¹) and b) PMA pattern on O₂-plasma treated PMA (1734 cm⁻¹). Spectra from regions 1 and 2 in panel a), and 2 and 3 from panel b) are shown in Fig. 4a and Fig 4b, respectively[17].

The difference between the hydrophilic and the hydrophobic areas in the PMA-Mix coating was evidenced by the shoulder appearing in the C=O stretching band spectrum of the mix area (see the arrow on Fig. 4a). The latter can be related to the presence of carboxylic acid moieties in the film.

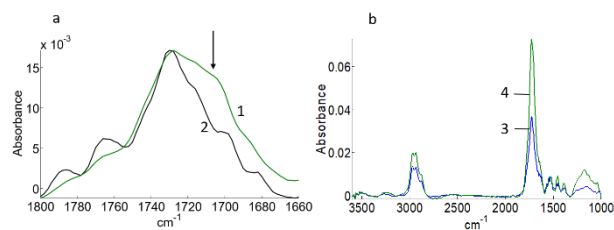


Fig. 4. a) Comparison of the mean IR spectra between the hydrophilic mix area (1) and the PMA hydrophobic area (2) taken in the regions shown in Fig. 3a. b) Comparison of the mean IR spectra between the hydrophobic PMA area (3) and the hydrophilic O₂-plasma treated PMA area (4) taken in the regions shown in Fig. 3b[17].

For the PMA+O₂-PMA coating, the hydrophilic and hydrophobic areas were chemically differentiated by comparing the intensity of the OH stretching band (see Fig. 4b). The later was greater in the areas treated by the Ar/O₂ plasma than in the non-treated ones.

4. Conclusion

A new method to synthesize stable hybrid sub-mm patterned hydrophilic/hydrophobic using an atmospheric pressure dielectric barrier discharge with PMA and AA as precursors was demonstrated. The deposited coatings exhibit high wettability contrast, with WCA varying from $>125^\circ$ to $<25^\circ$ depending on the experimental parameters. The pendant reactive groups of PMA facilitate cross-linking and insure the rapid formation of a hydrophobic layer. The combined precursors (AA + PMA) deposition lead to stable, non-water-soluble layer, with hydrophilic properties brought by the carboxylic acid and the other oxygen-containing moieties from the AA. Hydrophilic layer is also obtained by performing an Ar/O₂ plasma

post-treatment of the PMA layer, that lead to the grafting of polar functionalities. The chemical differences between the hydrophilic and the hydrophobic areas could be highlighted by micro IR imaging.

5. References

- [1] S. Zhang, J. Huang, Z. Chen, Y. Lai, *Small*, **13** (2017).
- [2] E. Ueda, P.A. Levkin, *Advanced Materials*, **25**, 1234 (2013).
- [3] A.R. Parker, C.R. Lawrence, *Nature*, **414**, 33 (2001).
- [4] R.P. Garrod, L.G Harris, W.C E. Schofield, J. McGettrick, L.J. Ward, D.O.H. Teare, J.P.S. Baydal, *Langmuir*, **23**, 689 (2007).
- [5] A.R. Betz, J. Jenkins, D. Attinger, *International Journal of Heat and Mass Transfer*, **57**, 733 (2013).
- [6] K. Tsougeni, A. Bourkoulou, P. Petrou, A. Tserepi, S. E. Kakabakos, E. Gogolides, *Microelectronic Engineering*, **124**, 47 (2014).
- [7] A.M. Leclair, S.S.G. Ferguson, F. Lagugné-Labarthet, *Biomaterials*, **32**, 1351 (2011).
- [8] S.D. Gillmor, A.J. Thiel, T.C. Strother, L.M Smith, M. G. Lagally, *Langmuir*, **16**, 7223 (2000).
- [9] V. Liimatainen, A. Shah, L-S. Johansson, N. Houbenov, Q. Zhou, *Small*, **12**, 1847 (2016).
- [10] S. Nishimoto, M. Becchaku, Y. Kameshima, Y. Shirosaki, S. Hayakawa, A. Osaka, M. Miyake, *Thin Solid Films*, **558**, 221 (2014).
- [11] G.S. Malkov, I.T. Martin, W.B. Schwisow, J.P. Chandler, B.T. Wickes, L.J. Gamble, D.G. Castner, E.R. Fisher, *Plasma Processes and Polymers*, **5**, 129 (2008).
- [12] I. Graz, A. Ebner, S. Bauer, C. Romanin, H. Gruber, *Applied Physics A*, **92**, 547 (2008).
- [13] B. Nisol, J. Ghesquière, F. Reniers, *Plasma Chemistry and Plasma Processing*, **36**, 1239 (2016).
- [14] Y. Arima, H. Iwata, *Acta Biomaterialia*, **26**, 72 (2015).
- [15] P. Cools, H. Declercq, N. De Geyter, R. Morent, *Applied Surface Science*, **432**, 214 (2018).
- [16] D. Ben Salem, O. Carton, H. Fakhouri, J. Pulpytel, F. Arefi-Khonsari, *Plasma Processes and Polymers*, **11**, 269 (2014).
- [17] A. Demaude, C. Poleunis, E. Goormaghtigh, A. Delcorte, M. Gordon, F. Reniers, Manuscript submitted for publication, (2019).