


COMMUNICATION

The wrinkling concept applied to plasma-deposited polymer-like thin films: A promising method for the fabrication of flexible electrodes

Damien Thiry¹  | Nathan Vinx¹ | Pascal Damman² | Francisco J. Aparicio³ | Pierre-Yves Tessier⁴ | David Moerman⁵ | Philippe Leclère⁵ | Thomas Godfroid⁶ | Sylvain Desprez⁶ | Rony Snyders^{1,6}

¹Chimie des Interactions Plasma-Surface, CIRMAP, University of Mons, Mons, Belgium

²Laboratoire Interfaces and Fluides Complexes, CIRMAP, University of Mons, Mons, Belgium

³Instituto de Ciencia de Materiales de Sevilla, CSIC-Universidad de Sevilla, Sevilla, Spain

⁴Université de Nantes, CNRS, Institut des Matériaux Jean Rouxel, IMN, Nantes, France

⁵Laboratory for Chemistry of Novel Materials, CIRMAP, University of Mons, Mons, Belgium

⁶Materia Nova Research Center, Parc Initialis, Mons, Belgium

Correspondence

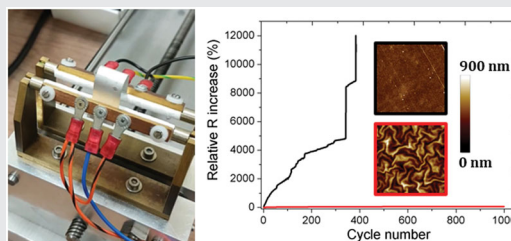
Damien Thiry, Chimie des Interactions Plasma-Surface, CIRMAP, University of Mons, Place du Parc 20, B-7000 Mons, Belgium.

Email: damien.thiry@umons.ac.be

The name of Sylvain Desprez was corrected on 28 July 2020 after the original publication. Also, a missing sentence was added into Acknowledgements.

Abstract

In this communication, we report on an innovative solvent-free method that allows for the design of nano-/micropatterns with tuneable dimensions. Our approach is based on the spontaneous wrinkling phenomenon taking place in a bilayer system formed by a mechanically responsive bottom plasma polymer layer and a top aluminum thin film. The dimensions of the wrinkles can be adjusted in a wide range (i.e., from nanometer to micrometer range) by modulating the cross-linking density as well as the thickness of the plasma polymer layer. Finally, it is demonstrated that these wrinkled surfaces could efficiently be used as flexible electrodes. The whole set of our data unambiguously reveals the attractiveness of our method for the fabrication of the micro-/nanopattern with dimensions on demand.



KEYWORDS

flexible electrode, nano-/micropattern, plasma polymer, wrinkling

1 | INTRODUCTION

In the last 50 years, plasma polymerization has become a well-established method for the synthesis of organic thin films, referred to as plasma polymer films (PPF), with applications in many fields such as photonics,^[1] biology/medicine,^[2] and surface protection.^[3] Briefly, the growth mechanism of a PPF is based on the activation of an

organic precursor in the plasma. The complex scheme including numerous gas phase and surface reaction pathways is responsible for the uniqueness of the PPF, as, for instance, the absence of repeating units in comparison with conventional polymers.^[4–6] The intrinsic substrate-independent nature of the process, the outstanding properties of the formed layers (i.e., high thermal stability and insolubility in most of the solvents), the low

environmental impact (i.e., the absence of solvents in the process), the industrial scalability of the technique, and the exquisite control over the physicochemical properties of the PPF justify the popularity gained by the plasma polymerization method.^[5,6]

Nano-/micro-organized surfaces are often a prerequisite for many applications in flexible electronic,^[7] sensor,^[8] antifouling coatings,^[9] and so forth. One of the most documented approaches to generate such kinds of surfaces consists of the use of bilayer systems formed by a stiff top layer on a compliant polymer film, which, under an external stimulus, gives rise to the formation of a wrinkled surface.^[10–15] It has been reported that the dimension of the wrinkles depends on both the stiffness and the thickness of the layers.^[13,16–18] The objective of this study is to demonstrate that this concept can be utilized using a PPF as the compliant material. Considering that both the mechanical properties and the thickness of PPF can be tuned by adjusting the process parameters,^[5,19,20] this achievement would represent the emergence of a new versatile method for the design of tailor-made micro-/nanopatterns. Furthermore, owing to the intrinsic good adhesion properties of the PPF to any kind of surfaces, this method would also be potentially applicable to a large variety of materials.

As a first step, our experimental strategy (described in Scheme 1) involves the deposition of PPF presenting different cross-linking densities. This is obtained by varying the substrate temperature (T_s), which has been demonstrated to be a key parameter in recent works related to the growth of propanethiol PPF.^[21,22] In the second step, an aluminum thin film is deposited on the PPF by the magnetron sputtering technique. The strong mismatch between the elastic properties of the inorganic and organic materials is expected to result in the wrinkling phenomenon.

If the methodology is performed using silicon wafers as model substrates, the bilayers are also grown on polyethylene terephthalate (PET) substrates to demonstrate their potential as a flexible thin-film electrode. Indeed, wrinkled surfaces have been identified as good candidates for developing such a kind of material.^[23,24] For this purpose, the electrical sheet resistance of the material is measured under severe and repeated deformation experiments.

2 | EXPERIMENTAL SECTION

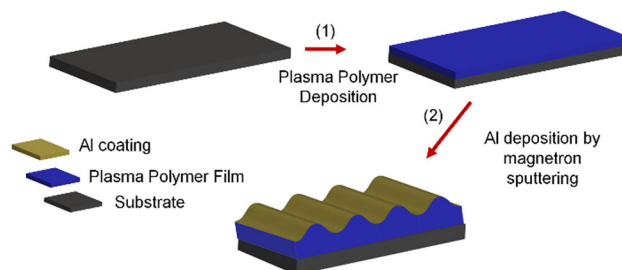
The PPF were grown from 1-propanethiol on cleaned $1 \times 1 \text{ cm}^2$ silicon wafers or $4 \times 1 \text{ cm}^2$ PET substrates. Propanethiol-based PPF were chosen as a case study in view of our previous works.^[21,22,25,26] The depositions were carried out in a metallic vacuum chamber (65-cm

and 35-cm diameter) where the plasma was sustained by an internal one-turn inductive Cu coil (10 cm in diameter). More details about the chamber can be found elsewhere.^[26] The coil was connected to an advanced energy radio frequency (13.56 MHz) power supply via a matching network. The precursor flow rate, the injected power, and the working pressure were fixed at 10 sccm, 40 mTorr, and 40 W for all experiments, respectively.

The substrate temperature (T_s), measured using a thermocouple affixed to the substrate holder, can be accurately controlled ($\pm 2^\circ\text{C}$) by combining two independent heating and cooling (using liquid nitrogen) systems. More details about the regulation of the substrate temperature can be found elsewhere.^[21] In this study, the influence of T_s on the physicochemical properties of the layers was investigated in the range 0–45°C.

The deposition of the top aluminum thin film (thickness fixed at 50 nm) was carried out by magnetron sputtering in a second chamber with an Al target ($450 \times 150 \text{ mm}^2$) in a pure Ar atmosphere. The working pressure and the power applied to the target were 5 mTorr and 1,000 W, respectively. More details about the experimental setup can be found elsewhere.^[27] After the deposition of the propanethiol PPF, the samples were directly transferred to the second reactor.

The thickness of the PPF was obtained by measuring the difference of height between coated and uncoated parts by AFM. The cross-linking density of PPF is evaluated by static time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements acquired using ToF-SIMS IV instrument from IONTOF GmbH. A 25-keV Ga^+ ion beam at a current of 0.8 pA is raster-scanned over a scan area of $200 \times 200 \mu\text{m}^2$ for 150 s. Topographical analyses of the multilayer system are carried out with a Bruker Multimode Atomic Force Microscopy (AFM) in tapping mode, equipped with a Nanoscope III controller and a phase extender module. An etched Si probe (PPP-NCHR Nanosensors GmbH) was used. The AFM images were treated according to the spectral imaging processing power spectrum density (PSD) method.^[28] With regard to the



SCHEME 1 A schematic description of the strategy developed in this study: (1) the synthesis of the plasma polymer film for different T_s and (2) deposition of an aluminum top coating by magnetron sputtering

evaluation of the electrical resistance of the Al/PPF bilayer system deposited on the PET substrate, bending tests were carried out using a homemade setup.^[29] In this study, repeated bending deformations (i.e., 1,000 times) were applied. The electrical sheet resistance was measured after each deformation cycle using a two-probe method.

3 | RESULTS AND DISCUSSION

First, the cross-linking density of the PPF is semi-quantitatively evaluated by ToF-SIMS technique. It has been reported that for PPF material, the cross-linking

degree is inversely correlated with the total secondary ions intensity for spectra recorded in the positive mode.^[30,31] Within our experimental window, it can be concluded that the cross-linking density increases with T_s (Figure S1), which suggests an increase in the stiffness of the layer. This trend has been already reported and is explained through a decrease in the energy density brought by positive ions to the growing film with respect to the total amount of matter deposited.^[22]

Figure 1 shows the morphologies of the bilayer system consisting of the Al thin film (50 nm) deposited on 250-nm-thick propanethiol PPF grown at $T_s = 0, 10,$ and 20°C .

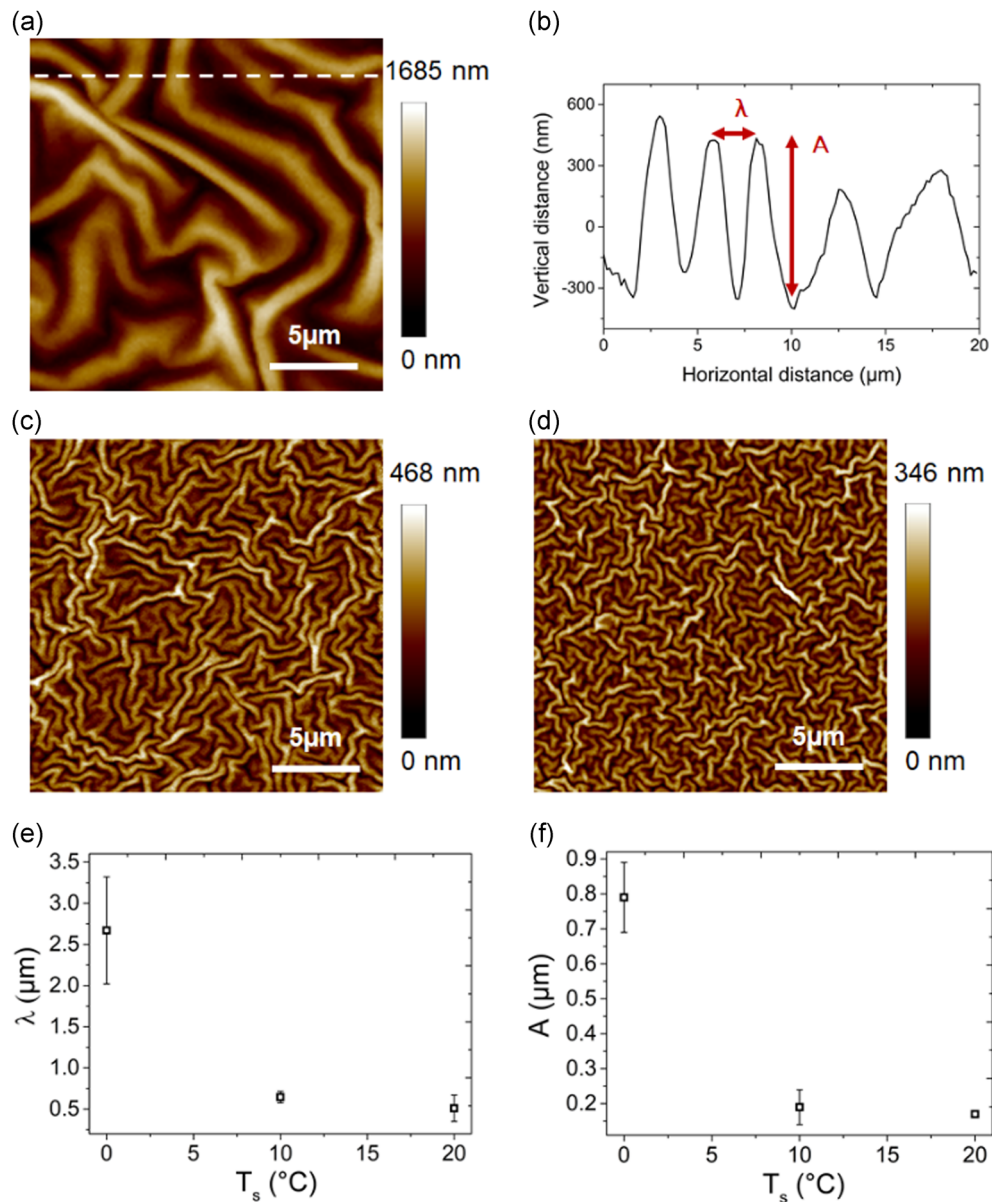


FIGURE 1 Two-dimensional atomic force microscopy images of 250-nm-thick plasma polymer film (PPF)/Al bilayer with varying T_s during the growth of the PPF: (a) 0°C with (b) the corresponding cross-section, (c) 10°C , and (d) 20°C . Evolution of (e) λ and (f) A as a function of T_s

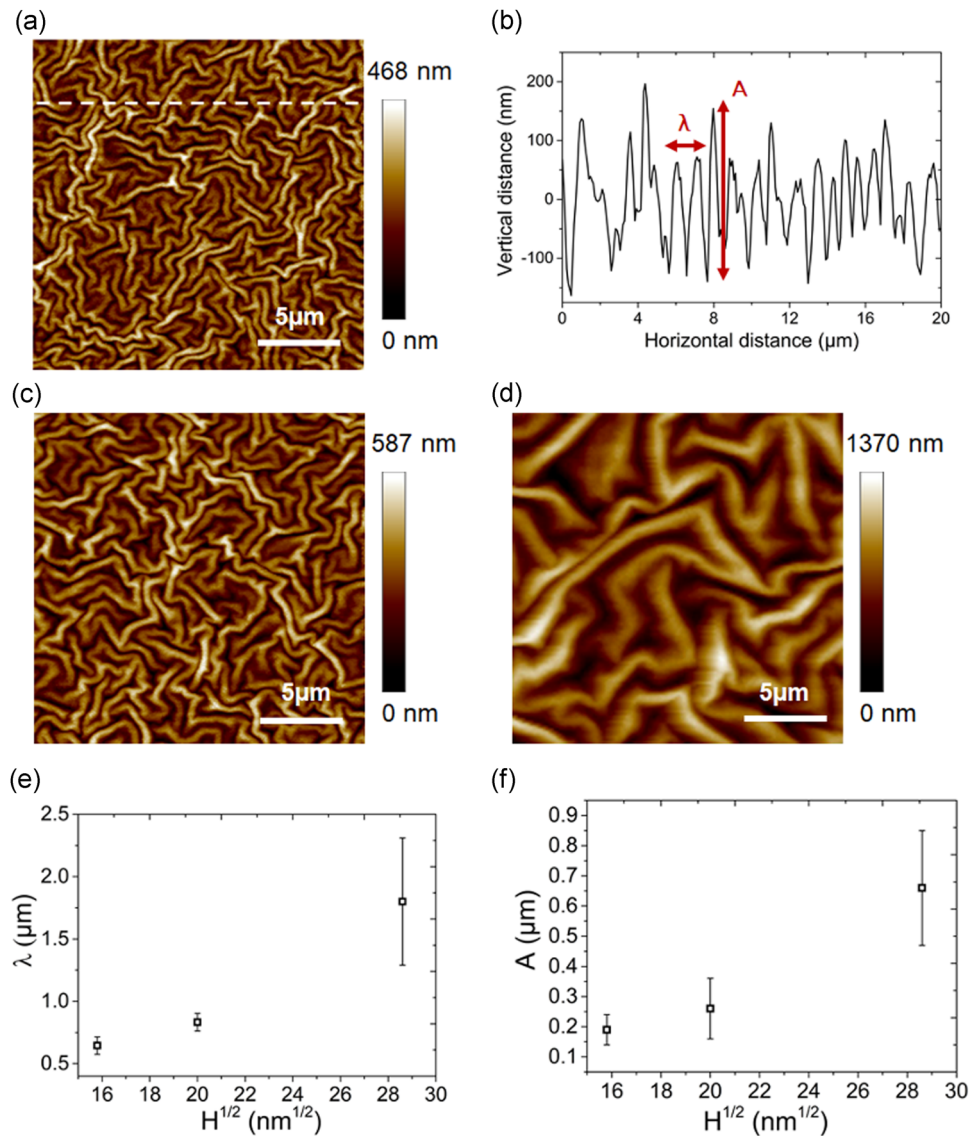


FIGURE 2 Two-dimensional atomic force microscopy images of 10°C-prepared plasma polymer film (PPF)/Al bilayer with varying thickness of the PPF: (a) 250 nm with (b) the corresponding section, (c) 400 nm, and (d) 820 nm. Evolution of (e) λ and (f) A as a function of \sqrt{H}

The analysis of the AFM images unambiguously reveals, for the first time, that the wrinkling phenomenon takes place using PPF as a compliant bottom layer. From these results, we also learn that the wrinkle wavelength (i.e., peak-to-peak distances, λ) and amplitude (i.e., peak-to-valley distance, A) strongly depend on T_s , and hence the cross-linking density of the polymeric layer. As plotted in Figure 1e,f both λ (from 2.67 ± 0.65 to $0.51 \pm 0.09 \mu\text{m}$) and A (from 0.79 ± 0.1 to $0.17 \pm 0.01 \mu\text{m}$) decrease with the increase in the cross-linking density of the PPF (through an increase in T_s from 0°C to 20°C). For the sake of completeness, the surface roughness evolves from 265 ± 8 to 56 ± 1 nm when T_s is increased.

These observations could be rationalized by considering the theoretical evolution of the wavelength,

$\lambda \sim \sqrt{hH} (E_{Al}/E_{PPF})^{1/6}$, where h , H , E_i represent metal/PPF thickness and elastic moduli, respectively.^[32] The increase in the cross-linking density of PPF induces an increase in its elastic modulus and thus a decrease in the wavelength. The evolution of the wrinkle amplitude is related to the conservation of the film surface. At constant strain, $\delta \propto (A/\lambda)^2$, we thus expect a similar trend for both the amplitude and wavelength, as shown in Figure 1e,f. These observations are in line with previously reported studies using conventional polymers.^[16,18] It should be noted that a further increase in the cross-linking degree of the PPF (for $T_s = 45^\circ\text{C}$) eliminates the wrinkling phenomenon (Figure S2). At this temperature, the critical strain for wrinkling, $\delta_c \sim (E_{PPF}/E_{Al})^{1/3}$, related to the stiffness of

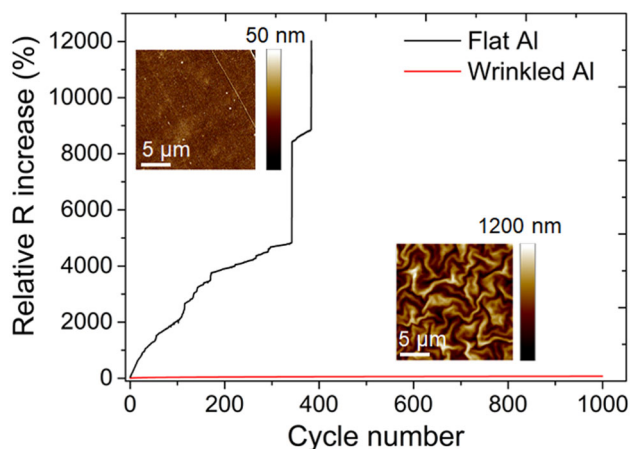


FIGURE 3 Evolution of the relative resistance (R) increase for flat Al and wrinkled plasma polymer film/Al ($\lambda = 1.13 \pm 0.17 \mu\text{m}$ and $A = 0.56 \pm 0.05 \mu\text{m}$) deposited on polyethylene terephthalate substrate with the corresponding atomic force microscopy images as a function of the number of cycles of repeated bending events

the PPF becomes too high to enable the morphological reorganization.^[32]

For a given T_s (i.e., 10°C), the influence of the thickness of the PPF on the morphological features is investigated in the range 250–820 nm, and it follows the expected behavior (i.e., $\lambda \propto \sqrt{H}$), namely an increase from 0.64 ± 0.07 to $1.8 \pm 0.51 \mu\text{m}$ (Figure 2).^[12] The amplitude, related to λ , also increases (i.e., from 0.19 ± 0.05 to $0.66 \pm 0.19 \mu\text{m}$) as shown in Figure 2f, whereas the surface roughness evolves from 74 ± 1 to $220 \pm 12 \text{ nm}$.

On the basis of these data sets, it can be concluded that our methodology allows for the design of nano-/micropattern with a large control over the dimensions of the structures (i.e., from the nanometer to the micrometer scale) by simply adjusting the deposition time (i.e., thickness) and T_s (i.e., the cross-linking density of the PPF). Another major point is that owing to the use of magnetron sputtering for the deposition of the metal top layer, the wrinkling phenomenon spontaneously takes place without the need of any external stress in contrast with other studies.^[10,17] On the basis of the literature, this is explained as follows: during metal deposition, exothermic surface condensation reactions as well as ionic bombardment encountered by the PPF substrate could lead to a spontaneous increase in the system temperature. After deposition and as a consequence of the significantly different thermal expansion coefficient of the metal and the organic-like coating, compressive stress would be generated. When the latter gets relieved, surface undulation spontaneously takes place.^[13,33,34]

Finally, we have examined the feasibility of our approach for the design of a flexible thin-film electrode. In this case, the wrinkled PPF/Al bilayer has been grown on

a PET substrate using the experimental procedure established in this paper (see the AFM image in Figure 3).

To evaluate the mechanical stability of the electrode, the bilayer system has been bent for 1,000 times. In this experiment, for each bending cycle, PPF/Al layers on the PET film ($125 \mu\text{m}$ thick) were submitted to a positive radius curvature (6.5 mm), corresponding to a positive strain of $0.97 \pm 0.08\%$. The evolution of the sheet resistance measured after each bending cycle (red curve) as a function of the number of bending events reveals a relative increase in the resistance of about 70% for the entire procedure, corresponding to an evolution of the sheet resistance from 1.3 to $2.3 \Omega/\square$. The electrode remains electrically conductive, indicating that the wrinkles can, to some extent, be reversibly stretched in response to the bending deformation. In contrast, if a flat smooth Al thin film (roughness of $\sim 7 \text{ nm}$) is directly deposited on a PET substrate, the electrical resistance dramatically increases by 12,000% after ~ 500 cycles, indicating that the material is no longer conductive, likely due to the failure of Al layer under the repetitive strain (Figure 3). This behavior could be ascribed to a distribution of the applied strain over a longer length for the wrinkled morphology in comparison with the smooth deposited layer.^[23]

4 | CONCLUSION

In this study, we establish an entire solvent-free process for the design of tailor-made nano-/microwrinkled surfaces. The method is based on the spontaneous generation of surface patterns in bilayer systems consisting of a mechanically responsive PPF and a magnetron-sputtered Al layer. The method, herein developed, offers a remarkable control over the dimensions of the surface topography by modulating the physicochemical properties (i.e., thickness and cross-linking degree) of the PPF. Furthermore, thanks to our approach, the wrinkled surface can be produced even on a solid substrate that cannot be stretched or compressed by sandwiching a plasma polymer layer, offering an additional degree of freedom for material engineering. It is finally demonstrated that the established methodology also enables to design a flexible electrode, opening the door to numerous research domains including stretchable solar cells, bioinspired devices, and so forth.

ACKNOWLEDGMENTS

Scanning probe research activities in Mons were supported by the FRS-FNRS PDR Project “Hybrid Organic/Inorganic Nanomaterials for Energy Conversion and Storage Devices on Flexible and Stretchable Substrates” (ECOSTOFLEX). Ph. L. is Senior research Associate from FRS-FNRS (Belgium). D. T. acknowledges the “Région Wallonne” through the CLEANAIR project for its financial support.

ORCID

Damien Thiry  <http://orcid.org/0000-0001-6703-1512>

REFERENCES

- [1] F. J. Aparicio, M. Holgado, A. Borrás, I. Blaszczyk-Lezak, A. Griol, C. A. Barrios, R. Casquel, F. J. Sanza, H. Sohlström, M. Antelius, A. R. González-Elipé, A. Barranco, *Adv. Mater.* **2011**, *23*, 761.
- [2] Z. Chen, A. Bachhuka, S. Han, F. Wei, S. Lu, R. M. Visalakshan, K. Vasilev, Y. Xiao, *ACS Nano* **2017**, *11*, 4494.
- [3] R. Morent, N. De Geyter, T. Jacobs, S. Van Vlierberghe, P. Dubruel, C. Leys, E. Schacht, *Plasma Processes Polym.* **2009**, *6*, S537.
- [4] D. Thiry, F. Reniers, R. Snyders, *Surface Modification of Polymers: Methods and Applications* (Eds: J. Pinson, D. Thiry), Wiley, Weinheim **2019**, p. 67.
- [5] D. Thiry, S. Konstantinidis, J. Cornil, R. Snyders, *Thin Solid Films* **2016**, *606*, 19.
- [6] J. Friedrich, *Plasma Processes Polym.* **2011**, *8*, 783.
- [7] D. Y. Khang, J. A. Rogers, H. H. Lee, *Adv. Funct. Mater.* **2009**, *19*, 1526.
- [8] F. Greco, L. Ventrelli, P. Dario, B. Mazzolai, V. Mattoli, *Int. J. Hydrogen Energy* **2012**, *37*, 17529.
- [9] K. Efimenko, J. Finlay, M. E. Callow, J. A. Callow, J. Genzer, *ACS Appl. Mater. Interfaces* **2009**, *1*, 1031.
- [10] L. T. De Haan, P. Leclère, P. Damman, A. P. Schenning, M. G. Debije, *Adv. Funct. Mater.* **2015**, *25*, 1360.
- [11] J. Rodríguez-Hernández, *Prog. Polym. Sci.* **2015**, *42*, 1.
- [12] H. Vandeparre, S. Desbief, R. Lazzaroni, C. Gay, P. Damman, *Soft Matter* **2011**, *7*, 6878.
- [13] N. Bowden, S. Brittain, A. G. Evans, J. W. Hutchinson, G. M. Whitesides, *Nature* **1998**, *393*, 146.
- [14] E. Cerda, L. Mahadevan, *Phys. Rev. Lett.* **2003**, *90*, 074302.
- [15] F. Brau, H. Vandeparre, A. Sabbah, C. Poulard, A. Boudaoud, P. Damman, *Nat. Phys.* **2011**, *7*, 56.
- [16] A. Das, A. Banerji, R. Mukherjee, *ACS Appl. Mater. Interfaces* **2017**, *9*, 35086.
- [17] M. D. Huntington, C. J. Engel, A. J. Hryn, T. W. Odom, *ACS Appl. Mater. Interfaces* **2013**, *5*, 6438.
- [18] S. K. Park, Y. J. Kwark, J. Moon, C. W. Joo, B. Yu, J. I. Lee, *Macromol. Rapid Commun.* **2015**, *36*, 2006.
- [19] A. Choukurov, I. Gordeev, D. Arzhakov, A. Artemenko, J. Kousal, O. Kylián, D. Slavínská, H. Biederman, *Plasma Processes Polym.* **2012**, *9*, 48.
- [20] B. Cechalova, M. Branecky, P. Klapetek, V. Cech, *Materials* **2019**, *12*, 539.
- [21] D. Thiry, F. J. Aparicio, P. Laha, H. Terryn, R. Snyders, *J. Vac. Sci. Technol., A* **2014**, *32*, 050602.
- [22] F. J. Aparicio, D. Thiry, P. Laha, R. Snyders, *Plasma Processes Polym.* **2016**, *13*, 814.
- [23] S. P. Lacour, S. Wagner, Z. Huang, Z. Suo, *Appl. Phys. Lett.* **2003**, *82*, 2404.
- [24] J. Won, S. Mondal, J. Park, W. Wang, H. Lee, S. Kim, B. Shin, S. G. Sathi, C. Nah, *Polym. Compos.* **2020**, *202*, 122715.
- [25] D. Thiry, N. Vinx, F. J. Aparicio, D. Moerman, R. Lazzaroni, D. Cossement, R. Snyders, *Thin Solid Films* **2019**, *672*, 26.
- [26] D. Thiry, F. J. Aparicio, N. Britun, R. Snyders, *Surf. Coat. Technol.* **2014**, *241*, 2.
- [27] C. Nouvellon, R. Belchi, L. Libralesso, O. Douh ret, R. Lazzaroni, R. Snyders, D. Thiry, *Thin Solid Films* **2017**, *630*, 79.
- [28] F. D. S. Teixeira, W. W. R. D. Ara jo, M. Salvadori, *J. Appl. Phys.* **2016**, *119*, 145305.
- [29] A. Chauvin, W. T. C. Heu, J. Buh, P.-Y. Tessier, A.-A. El Mel, *npj Flexible Electron.* **2019**, *3*, 5.
- [30] U. Oran, S. Swaraj, J. F. Friedrich, W. E. Unger, *Plasma Processes Polym.* **2004**, *1*, 141.
- [31] D. Thiry, M. Pouyanne, D. Cossement, A. Hemberg, R. Snyders, *Langmuir* **2018**, *34*, 7655.
- [32] H. Vandeparre, J. L opold s, C. Poulard, S. Desprez, G. Derue, C. Gay, P. Damman, *Phys. Rev. Lett.* **2007**, *99*, 188302.
- [33] S.-J. Yu, Y.-P. Du, Y.-D. Sun, Q.-L. Ye, H. Zhou, *Thin Solid Films* **2017**, *638*, 230.
- [34] K. Wu, H. Yuan, S. Li, J. Zhang, G. Liu, J. Sun, *Scr. Mater.* **2019**, *162*, 456.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.

How to cite this article: Thiry D, Vinx N, Damman P, et al. The wrinkling concept applied to plasma-deposited polymer-like thin films: A promising method for the fabrication of flexible electrodes. *Plasma Process Polym.* 2020;17:e2000119. <https://doi.org/10.1002/ppap.202000119>