High throughput soft embossing process for micro-patterning of PEDOT thin films

Fanzio, Paola; Cagliani, A.; Peterffy, Kristof G.; Sasso, Luigi

DOI

[10.1016/j.mee.2017.01.011](https://doi.org/10.1016/j.mee.2017.01.011)

Publication date

2017

Document Version

Accepted author manuscript

Published in

Microelectronic Engineering

Citation (APA)

Fanzio, P., Cagliani, A., Peterffy, K. G., & Sasso, L. (2017). High throughput soft embossing process for micro-patterning of PEDOT thin films. *Microelectronic Engineering*, 176, 15-21.
<https://doi.org/10.1016/j.mee.2017.01.011>

Important note

To cite this publication, please use the final published version (if applicable).
Please check the document version above.

Copyright

Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights.
We will remove access to the work immediately and investigate your claim.

High throughput soft embossing process for micro-patterning of PEDOT thin films

Paola Fanzio^{1*}, Alberto Cagliani^{2,3}, Kristof G. Peterffy¹ and Luigi Sasso¹

¹Delft University of Technology, Dept. of Precision and Microsystems Engineering (PME), Mekelweg 2, 2628 CD Delft, The Netherlands

²DTU-Nanotech, Department of Micro and Nanotechnology, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

³CAPRES A/S, Diplomvej 373, DK-2800 Kgs. Lyngby, Denmark

*Corresponding author: p.fanzio-1@tudelft.nl

Highlights

- Development of a soft embossing process for micro-patterning a PEDOT layer
- A post processing treatment to increase the conductivity and decrease the solubility of PEDOT
- Evaluation of replication reliability and structure functionality

Abstract

The patterning of conductive polymers is a major challenge in the implementation of these materials in several research and industrial applications, spanning from photovoltaics to biosensors. Within this context, we have developed a reliable technique to pattern a thin layer of the conductive polymer poly(3,4-ethylenedioxythiophene) (PEDOT) by means of a low cost and high throughput soft embossing process. We were able to reproduce a functional conductive pattern with a minimum dimension of 1µm and to fabricate electrically decoupled electrodes. Moreover, the conductivity of the PEDOT films has been characterized, finding that a post-processing treatment with Ethylene Glycol allows an increase in conductivity and a decrease in water solubility of the PEDOT film. Finally, cyclic voltammetry demonstrates that the post-treatment also ensures the electrochemical activity of the film. Our technology offers a facile solution for the patterning of organic conductors with resolution in the micro scale, and can be the basis for the realization and development of polymeric microdevices with electrical and electrochemical functionalities.

Keywords

Micro-patterning, PEDOT, Soft embossing, Ethylene Glycol, Conductivity, soft electrodes

1. Introduction

The interest of the scientific research community in the use of conductive polymers is constantly growing [1]. This is due to their tuneable and attractive features [2] and to the broad range of applications that would benefit from their introduction: the realization of wearable Lab-On-Chip devices aimed at revolutionizing medical screening and diagnosis, the improvement of solar cell efficiency, energy storage, and the realization of organic LED [3].

One of the most commonly used conductive polymers is poly(3,4-ethylenedioxythiophene) (PEDOT) thanks to its high conductivity, transparency and environmental stability [4]. In order to increase the PEDOT water-solubility for spin-coating or inkjet printing, the polyelectrolyte poly(styrenesulfonic acid) (PSS) is added [5]. Despite the advantages for PEDOT processing, the presence of negatively charged PSS molecules reduces the conductivity [6] and often the water solubility is unwanted in the final device, especially for bioanalytical platforms which are in contact with water based solutions.

A major challenge in introducing this material into industrial processes is the development of a low cost and high throughput strategy for the manufacturing of organic conductive patterns at the micro scale. Several techniques have been developed, such as in situ electro polymerization [7], inkjet-printing techniques, lithography assisted chemical polymerization [8] and laser ablation [9]. However, all these methods suffer from several drawbacks such as long fabrication times and high costs. Moreover, PEDOT is incompatible with standard lithographic techniques [10] and standard hot embossing [10,11]. To resolve this issue, plasticizers, such as Glycerol, have been added to increase the chain mobility (lowering viscosity) [12] but they produce instability in the imprinted dimensions due to evaporation [13]. A different approach is to use intermediate layer lithography (IIL) [14] in which an intermediate layer of thermoplastic polymer is used as a substrate for the conductive layer. In this way, the conductive polymer can be printed via hot embossing and, eventually, multiple structures (such as microchannels and electrodes) can be imprinted simultaneously in one single step [15]. In this context, an interesting approach to drastically reduce the production costs and to make the process easy to scale up and automated is soft embossing. It differs from a standard hot embossing process in the use of polymeric embossing stamps instead of hard ones (aluminium or silicon materials) [16]. This technique opens up the possibility to tune the properties of the mold by choosing among a broad range of polymeric materials and to reduce the problem of breaking the mold, yielding ultimately to a higher mold reusability.

Here we propose and describe a low cost and high throughput soft embossing process that allows to pattern a PEDOT:PSS film spin coated on a flexible thermoplastic polymer made of TOPAS®. This novel approach merges the advantages and high throughput of soft embossing with intermediate layer lithography (IIL) and allows patterning the PEDOT layer with a resolution in the micro range. As expected, we have found that the conductivity of the PEDOT layer is decreased by the soft embossing process. This problem has been solved by means of a treatment with Ethylene Glycol (EG), which increases the conductivity up to 10 times. This treatment also drastically decrease the solubility of PEDOT:PSS in water, overcoming an additional challenge in the implementation of this material into industrial settings. Finally we also show that electrically decoupled electrodes can be fabricated in one soft embossing step and that the PEDOT-EG layer is electrochemically active. The novelty of the proposed approach consists of the combination of soft embossing, IIL and EG treatment that can be effectively used for the realization of microdevices with sensing functionalities.

2. Materials and methods

2.1 Soft embossing process

The soft embossing process is basically a hot embossing process in which a polymeric mold (soft working stamp) is used instead of a standard hard mold (e.g. silicon, nickel or aluminium). **Figure 1** shows the fabrication procedure which is mainly divided into three steps:

- 1) The fabrication of the soft working stamp
- 2) The preparation of the substrate
- 3) The embossing process

Figure 1. The scheme of the fabrication process is divided into 3 steps. The soft working stamp fabrication is based on a soft lithography process. The substrate preparation consists of the spin-coating a PEDOT layer on a thermoplastic foil obtaining a TOPAS-PEDOT substrate. The soft embossing process is performed in order to replicate the pattern present on the soft working stamp into the TOPAS-PEDOT substrate.

2.1.1 Soft working stamp fabrication

The soft working stamp was fabricated by means of a soft lithography process from a silicon master mold, as shown in **figure 1**. The pattern consists of arrays of trenches of different dimensions (between $1\mu\text{m}$ and $10\mu\text{m}$) and spacing (between $1\mu\text{m}$ and $20\mu\text{m}$) and height of 300nm (see Supplementary information)

In order to reduce adhesion, an anti-stiction layer (Methyl nonafluorobutyl ether + Methyl nonafluoroisobutyl ether form EVG) was spin coated (2000rpm) on the patterned silicon master and baked for 10min at 120°C .

Then a glass wafer (Plan Optik) was treated with the adhesion promoter KR513 (Shin-EtsuMicroSi, Inc.). After baking the glass wafer 1 min at 180°C , the promoter was spin-coated $2000\text{ rpm}/1\text{min}$ and baked $160^\circ\text{C} - 180^\circ\text{C}/5\text{min}$.

The polymer used for the fabrication of the soft working stamp was MD700 (perfluoropolyether (PFPE)-urethane dimethacrylate from Solvay) mixed with a photoinitiator (Igracur 2022 from BTC Speciality Chemical Distribution GmbH). The polymer was cast on the patterned silicon master, covered with a glass wafer and was cured for 200s in UV light. The cured polymer adheres to the glass wafer and can be directly used as soft working stamp without the need of an anti-stiction layer thanks to the low surface tension of MD700.

2.1.2 Substrate preparation

The substrate for the embossing was a bilayer made of a thermoplastic cyclic olefin copolymer (COC) foil (300 μm thick TOPAS® foil with glass transition temperature equal to 70°C) and a thin layer of the conductive polymer poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS 1.3wt% dispersion in water from Sigma Aldrich), as shown in **figure1**. After cleaning with isopropanol and air plasma (5 minutes at 60W), the COC foil was covered with the PEDOT layer by means of a spin coating process at 1000rpm for 60s and dried at room temperature for 6 hours. The resulting thickness of the PEDOT layer was measured with a profilometer and it is equal to (135 ± 7) nm.

The morphology of the PEDOT layer is shown in the SEM image of **figure 2a**. The presence of the PEDOT film is also demonstrated with the SEM image of the edge of the TOPAS/PEDOT substrate acquired tilting the sample at 30deg (**figure 2b**). In this image the dark thin layer is the PEDOT and the white thick one is the TOPAS which is not conductive and tends to charge while imaging with the SEM.

Figure 2. a) SEM image of the PEDOT surface. b) SEM image of the edge of the TOPAS/PEDOT substrate acquired tilting the sample at 30deg.

2.1.3 Soft embossing

The embossing process, shown in **figure1**, has been performed with an EVG embosser machine. It was carried out by placing the soft working stamp against the substrate. The applied pressure and temperature have been controlled with dedicated software (EVG).

2.2 Treatment with Ethylene Glycol

The substrate was immersed in Ethylene Glycol (Sigma-Aldrich) for different durations, then cleaned with water and dried with compressed air.

2.3 Characterization

The conductivity has been evaluated by means of 4-point probe measurements (Signatone couple with a Keithley Sourcemeter 2400 and Nanovoltmeter 2182).

3D optical images were acquired with a white-light interferometer (Bruker).

The electrochemical experiment has been carried out with a Potentiostat (Metrohm Autolab B.V., Netherlands). We have used a TOPAS strip spin-coated with PEDOT or PEDOT-EG as working electrode (25mm^2), a TOPAS strip spin-coated with PEDOT-EG as counter electrode (2.5cm^2) and a gold electrode as reference. Cyclic voltammetry has been performed in KCl 0.1M.

3. Results and discussion

3.1 Embossing process

In this section, we describe the results of the soft embossing technique. The master mold (4 inches Si wafer), used to evaluate the fidelity and reproducibility of the soft embossing process, was patterned with arrays of trenches of different dimensions (between $1\mu\text{m}$ and $10\mu\text{m}$) and spacing (between $1\mu\text{m}$ and $20\mu\text{m}$).

Figure 3. 3D optical image of trenches with a dimension $d=1\mu\text{m}$ and spacing $s=1\mu\text{m}$. a) of the soft working stamp; b) for the parameter optimization (pressure and temperature); c) after embossing on TOPAS; d) after the embossing on TOPAS-PEDOT.

As mentioned in the introduction, an important aspect to take into account is that PEDOT:PSS is not a thermoplastic polymer so, in principle, it cannot be embossed. On the contrary TOPAS® is a cyclic olefin copolymer (COC) with a glass transition temperature of about 70°C and can be used as a substrate for the embossing process. With our approach, we were able to transfer a pattern to the conductive layer, a PEDOT film spin-coated on the TOPAS, during the imprinting.

Figure 3a shows a 3D optical image of the array with the smallest dimension ($d=1\mu\text{m}/s=1\mu\text{m}$) of the soft working stamp that has been used as a mold for the soft embossing process. **Figure 3b** shows the used imprinted parameters (pressure and temperature) related with the 3D optical images of the replicated structure in the PEDOT substrate after the embossing. The best parameters in order to obtain defined structures on a PEDOT/TOPAS substrate are a temperature of 90°C and an applied force of 6000N. The duration of the imprinting process has been set to 10 minutes. After that, the pressure on the substrate is maintained during the cooling phase till reaching the demoulding temperature (50°C).

Going below these values means losing the uniformity of the structures and increasing the presence of ripples and surface wrinkles that are the product of low viscous flow of the TOPAS polymer, and consequently a poor mobility of the PEDOT layer.

By using these values for the temperature and pressure we have performed soft embossing on a TOPAS sheet and on a TOPAS-PEDOT substrate. **Figure 3c** (TOPAS) and **3d** (TOPAS-PEDOT) show 3D optical images of two examples of the imprinted structures for the array with the smallest dimension ($d=1\mu\text{m}/s=1\mu\text{m}$). This result demonstrates that we are able to structure the TOPAS substrate down to the 1 μm dimension and that the pattern can be transferred to the PEDOT:PSS layer.

Figure 4a shows 3D optical images of different arrays in the embossed TOPAS-PEDOT sample with the corresponding height profiles. The shape is sharp and uniform for trenches with dimension equal to 10 μm , 5 μm and 1 μm . The quality of the embossing process has been evaluated for all the test structures present in the master. The result for all the trenches dimensions is shown in **figure 4b** and **4c**, where the trenches dimension obtained after the embossing (y-axis) is compared with the original dimension in the Si master mold (x-axis). The black line represents the linear fit. A slope equal to 1 means a perfect match between original dimension and imprinted dimension. For both lines and spaces we obtain a value that is quite close to 1 demonstrating that the soft embossing process allows to replicate the pattern with good accuracy till 1 μm dimension. The comparison has been performed both for the trenches dimension (**figure 4b**) and the spacing between the trenches (**figure 4c**).

It is also important to note that we have avoided the problem of stiction between the soft working stamp and the PEDOT:PSS substrate which is often a big issue in hot embossing. Indeed the MD700 polymer merges a low surface energy with hardness and a high curing speed [17] and it is an excellent candidate for the realization of stable and reusable working stamps.

Figure 4. a) 3D optical images of embossed TOPAS-PEDOT (top) with the corresponding height profiles (bottom). Comparison between the original dimensions in the Si master (x-axis) and the imprinted dimensions obtained from the 3D optical images (y-axis) b) of the trenches and c) the spacing between trenches.

However, the working stamp is much more prone to deformations under high temperature and pressure conditions and this issue can affect the stamp lifetime [18]. In fact, the quality of the polymeric mold decreases with multiple uses and we have evaluated that after 10 embossing cycles the height of the structures is reduced of about 30% (see Supplementary information). This can be due to thermal expansion mismatch between MD700 and TOPAS-PEDOT, degradation of the polymer itself under high temperature and pressure or presence of residuals during the demoulding phase. We have found that a mold can be used for 5 times without any modification in the pattern height. Compared with hard mold, that can be reused for dozens of times, this result is quite unsatisfactory but it is important to consider that an advantage in the use of a polymeric working stamp instead of a solid state one (such as silicon masters) is that, in case of breaking, it is possible to produce a new working stamp in an easy, cheap and fast way.

The structuring of PEDOT films with a superficial pattern (height in the nanometer range) can be useful for a wide variety of applications that require conductive functionalities, such as for photovoltaics. However, applications in biosensing require electrodes that are electrically decoupled from each other. In this case it is necessary to “break” the PEDOT film at the edge of each electrode.

This can be possible because the thickness of the PEDOT is relatively low (about 100nm) compared with the one of the TOPAS sheet (300 μ m). We have evaluated that fully electrically disconnected structures can be obtained with an height difference of 40 μ m (see Supplementary information).

3.2 Post processing treatment

Another aspect that must be taken into account is the conductivity of the PEDOT, which reflects the core functionality of this layer, especially for the realization of organic electrodes.

Initially, we have evaluated how the embossing process affects the conductivity. **Figure 5a** shows the comparison between the voltage/current curve, obtained by means of 4-point probe measurements, before (empty dots) and after (black dots) the embossing. The sheet resistance (R) has been evaluated by means of a linear fit of the voltage/current curve and increases significantly of about 20K Ω . The conductivity reduction due to the embossing process is due to the hygroscopicity of the PEDOT:PSS film. Indeed it has been demonstrated [19] that the presence of PSS molecules increases the PEDOT hygroscopicity affecting the stability of PEDOT subjected to temperature changes.

In order to resolve this problem and increase the electrical conductivity of the imprinted PEDOT:PSS layer we have performed a treatment with Ethylene Glycol (EG). The treatment is easy to implement into industrial settings as it consists of the immersion of the TOPAS-PEDOT substrate inside a beaker containing EG. **Figure 5b** shows the voltage current graph before (black dots) and after the EG treatment (empty dots). The sheet resistance after the treatment, evaluated by means of a linear fit, decreases of about 10 times, from 100 K Ω /sq to 7 K Ω /sq. This decrease in R depends on the duration of the treatment. **Figure 5c** shows the conductance of the PEDOT-EG layer in function of the duration of the treatment. It is necessary to perform the treatment for at least 10 minutes to reach a maximum level in the measured conductance. After this time, increasing the duration of the immersion of the substrate in EG does not greatly affect the conductance. We have also found that the temperature during the treatment does not influence the sheet resistance reduction of the PEDOT-EG layer (see Supplementary information).

In order to explain the conductivity enhancement after the EG treatment it is necessary to point out that the film has a lamellar structure in which PEDOT islands are surrounded by insulating PSS [20,21]. We believe that this lack of uniformity of the electrical properties at the micro and nanoscale is responsible for the local variability we measured in a line map of the sheet resistance of untreated PEDOT with micro a four-point-probe system (see Supplementary information).

The increased connection between adjacent PEDOT islands (i.e. the increased charge transfer in the film after the treatment with EG) is due to a conformational change in the polymer structure from a coiled conformation (benzoid structure) to a more linear one (quinoid structure), as demonstrated by J. Ouyang *et al* [22]. AFM images of the PEDOT surface before (**figure 6a**) and after (**figure 6b**) the EG treatment demonstrate that, as expected, we observe a decrease in roughness after the treatment which, coupled with conductance measurement (shown in **figure 5**), demonstrate that we have indeed produced a conformational change in the PEDOT film.

The conformational change due to EG treatment also decreases the water solubility of the PEDOT layer. To test the effect of the EG treatment on the water-solubility of the PEDOT:PSS layer we have compared, in **figure 5d**, the sheet resistance of a PEDOT (empty dots) and a PEDOT-EG sample (black

dots) versus the duration of the immersion in water. The conductivity does not change for the PEDOT-EG sample after 30 minutes immersion. On the contrary, the sheet resistance started to increase after only 5 minutes of immersion in water of the PEDOT:PSS sample and kept increasing. This is due to a gradual dissolution of PEDOT in water that leads to a complete damage of the surface (see Supplementary information).

Figure 5. a) Comparison between the voltage/current curve, evaluated by means of 4-point probe measurements, before (empty dots) and after (black dots) embossing. b) Voltage/Current curves obtained by means of 4-point probe measurements before (black dots) and after (empty dots) the treatment with Ethylene Glycol (EG). c) Conductance of the PEDOT layer in function of the duration of the treatment with EG. d) Sheet resistance plotted versus the immersion time in water for a PEDOT (empty dots) and a PEDOT-EG sample (black dots).

Figure 6. AFM images of a PEDOT surface a) before and b) after the EG treatment.

Figure 7. CV curves at different scan rates in KCl 0.1M for a) PEDOT and b) PEDOT-EG. C) Comparison between the CV curves at 10mV/s. d) CV curves for PEDOT-EG at low scan rates and, in the inset, graph of the square of the oxidation peak height (I_p^2) versus the scan rate.

The electrochemical properties of PEDOT and PEDOT-EG films have been evaluated by cyclic voltammetry (CV). **Figure 7a** and **7b** show the cyclic voltammograms at different scan rates obtained in KCl 0.1M by using respectively PEDOT and PEDOT-EG as working electrode. **Figure 7c** shows a direct comparison between the CV of PEDOT and PEDOT-EG films at 10mV/s scan rate. The PEDOT

response is mainly ohmic and no peak can be observed. On the contrary the CVs of PEDOT-EG show an increase in the amplitude of the current response due to the intrinsic PEDOT redox activity, demonstrating that the patterned film is electrochemically active. Particularly for low scan rates the peak corresponding to the PEDOT redox reaction can be observed, as shown in **figure 7d**. While we observed a linear increase in current peak amplitude with varying scan rates (see **the inset of figure 7d**), a potential shift with increasing scan rate describes a pseudo-reversible electrode behaviour for PEDOT-EG.

In conclusion, the EG treatment not only increases the conductivity of PEDOT:PSS but also improves the electrochemical current response of the film. The enhanced electrochemical response of PEDOT-EG demonstrates that the EG post treatment allows to obtain electrodes with an active surface, a property necessary for the realization of electrochemical biosensing devices.

4. Conclusions

In conclusion we propose a low cost and high throughput technique to pattern conductive polymers. The coupling between the soft embossing process and the intermediate layer lithography allows to imprint a thin PEDOT:PSS film even if it is not a thermoplastic polymer. We have achieved a good reproducibility and fidelity to a minimum dimension of 1 μ m for a surface pattern and we have evaluated that a structure height of 40 μ m allows to obtain decoupled electrodes. Moreover, we have underlined the advantages in the use of a soft working stamp, such as the simplicity of the realization, the low cost, the reduction of major challenges and the reduction of stiction. We have also found some limits, in terms of mold lifetime and pattern homogeneity. We have also found that the conductivity of PEDOT is affected by the embossing process and we have proposed a treatment with Ethylene Glycol that allows a decrease in resistivity about 10 folds. This treatment reduces also the water solubility of PEDOT and improves its electrochemical activity. These results demonstrate that our technology is a promising approach for patterning conductive polymers and in particular of the realization of organic electrodes.

Acknowledgments

This work has been supported by NanoNextNL (10A-03, www.nanonextnl.nl). We thank Marcel Tichem and Urs Staufer for the useful discussion and advices. We would like also to thank the lab manager Rob Luttjeboer for his support during the experiments.

References

- [1] M. Ates, A review study of (bio)sensor systems based on conducting polymers, Mater. Sci. Eng. C Mater. Biol. Appl. 33 (2013) 1853–1859. doi:10.1016/j.msec.2013.01.035.
- [2] R. Balint, N.J. Cassidy, S.H. Cartmell, Conductive polymers: Towards a smart biomaterial for tissue engineering, Acta Biomater. 10 (2014) 2341–2353. doi:10.1016/j.actbio.2014.02.015.

- [3] C.-T. Yen, F.-C. Wu, H.-L. Cheng, H.-S. Sheu, F.-C. Tang, W.-Y. Chou, Charge transfer highways in polymer solar cells embedded with imprinted PEDOT:PSS gratings, *RSC Adv.* 4 (2014) 58342–58348. doi:10.1039/C4RA10268A.
- [4] F. Louwet, L. Groenendaal, J. Dhaen, J. Manca, J. Van Luppen, E. Verdonck, L. Leenders, PEDOT/PSS: synthesis, characterization, properties and applications, *Synth. Met.* 135–136 (2003) 115–117. doi:10.1016/S0379-6779(02)00518-0.
- [5] L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, J.R. Reynolds, Poly(3,4-ethylenedioxythiophene) and Its Derivatives: Past, Present, and Future, *Adv. Mater.* 12 (2000) 481–494. doi:10.1002/(SICI)1521-4095(200004)12:7<481::AID-ADMA481>3.0.CO;2-C.
- [6] T. Stöcker, A. Köhler, R. Moos, Why does the electrical conductivity in PEDOT:PSS decrease with PSS content? A study combining thermoelectric measurements with impedance spectroscopy, *J. Polym. Sci. Part B Polym. Phys.* 50 (2012) 976–983. doi:10.1002/polb.23089.
- [7] L. Sasso, A. Heiskanen, F. Diazzi, M. Dimaki, J. Castillo-León, M. Vergani, E. Landini, R. Raiteri, G. Ferrari, M. Carminati, M. Sampietro, W. E. Svendsen, J. Emnéus, Doped overoxidized polypyrrole microelectrodes as sensors for the detection of dopamine released from cell populations, *Analyst.* 138 (2013) 3651–3659. doi:10.1039/C3AN00085K.
- [8] L. Sasso, † P.V., I. Vedarethinam, J. Castillo-León, J. Emnéus, W.E. Svendsen, Conducting Polymer 3D Microelectrodes, *Sensors.* 10 (2010) 10986–11000. doi:10.3390/s101210986.
- [9] B. Charlot, G. Sassine, A. Garraud, B. Sorli, A. Giani, P. Combette, Micropatterning PEDOT:PSS layers, *Microsyst. Technol.* 19 (2012) 895–903. doi:10.1007/s00542-012-1696-5.
- [10] H. Hlaing, X. Lu, C.-Y. Nam, B.M. Ocko, Water-Vapor-Assisted Nanoimprinting of PEDOT:PSS Thin Films, *Small.* 8 (2012) 3443–3447. doi:10.1002/smll.201201267.
- [11] Y. Yang, K. Lee, K. Mielczarek, W. Hu, A. Zakhidov, Nanoimprint of dehydrated PEDOT:PSS for organic photovoltaics, *Nanotechnology.* 22 (2011) 485301. doi:10.1088/0957-4484/22/48/485301.
- [12] R. Meier, C. Birkenstock, C.M. Palumbiny, P. Müller-Buschbaum, Efficiency-improved organic solar cells based on plasticizer assisted soft embossed PEDOT:PSS layers, *Phys. Chem. Chem. Phys. PCCP.* 14 (2012) 15088–15098. doi:10.1039/c2cp42918g.
- [13] R.M. Reano, Y.P. Kong, H.Y. Low, L. Tan, F. Wang, S.W. Pang, A.F. Yee, Stability of functional polymers after plasticizer-assisted imprint lithography, *J. Vac. Sci. Technol. B.* 22 (2004) 3294–3299. doi:10.1116/1.1825013.
- [14] C. Luo, Generation of micropatterns of conducting polymers and aluminum using an intermediate-layer lithography approach and some applications, *Microsyst. Technol.* 15 (2009) 1605–1617. doi:10.1007/s00542-009-0861-y.
- [15] J. Kafka, N.B. Larsen, S. Skaarup, O. Geschke, Fabrication of an all-polymer electrochemical sensor by using a one-step hot embossing procedure, *Microelectron. Eng.* 87 (2010) 1239–1241. doi:10.1016/j.mee.2009.11.137.
- [16] L. Peng, Y. Deng, P. Yi, X. Lai, Micro hot embossing of thermoplastic polymers: a review, *J. Micromechanics Microengineering.* 24 (2014) 013001. doi:10.1088/0960-1317/24/1/013001.
- [17] J.P. Rolland, R.M. Van Dam, D.A. Schorzman, S.R. Quake, J.M. DeSimone, Solvent-Resistant Photocurable “Liquid Teflon” for Microfluidic Device Fabrication, *J. Am. Chem. Soc.* 126 (2004) 2322–2323. doi:10.1021/ja031657y.
- [18] S. Gilles, M. Diez, A. Offenhäusser, M.C. Lensen, D. Mayer, Deformation of nanostructures on polymer molds during soft UV nanoimprint lithography, *Nanotechnology.* 21 (2010) 245307. doi:10.1088/0957-4484/21/24/245307.
- [19] J. Huang, P.F. Miller, J.C. de Mello, A.J. de Mello, D.D.C. Bradley, Influence of thermal treatment on the conductivity and morphology of PEDOT/PSS films, *Synth. Met.* 139 (2003) 569–572. doi:10.1016/S0379-6779(03)00280-7.
- [20] T. Takano, H. Masunaga, A. Fujiwara, H. Okuzaki, T. Sasaki, PEDOT Nanocrystal in Highly Conductive PEDOT:PSS Polymer Films, *Macromolecules.* 45 (2012) 3859–3865. doi:10.1021/ma300120g.

- [21] M. Kemerink, S. Timpanaro, M.M. de Kok, E.A. Meulenkamp, F.J. Touwslager, Three-Dimensional Inhomogeneities in PEDOT:PSS Films, *J. Phys. Chem. B.* 108 (2004) 18820–18825. doi:10.1021/jp0464674.
- [22] J. Ouyang, Q. Xu, C.-W. Chu, Y. Yang, G. Li, J. Shinar, On the mechanism of conductivity enhancement in poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) film through solvent treatment, *Polymer.* 45 (2004) 8443–8450. doi:10.1016/j.polymer.2004.10.001.