The Challenges of Printing Functional Materials on Cellulose Based Substrates

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Abstract

Cellulous substrates offer flexible character; they are cost-effective, readily available and are environmentally friendly. However, using paper as a substrate for printed electronics might be a challenging task. In this work, various paper substrates were employed as a base for printing of conductive and semiconductive materials including conductive polymer (poly(3,4-ethylenedioxy-thiophene)-poly(styrene-sulfonate), commonly known as PEDOT-PSS, and poly 3-hexylthiophene semiconductor. These materials were printed using a piezoelectric inkjet printer and printed features were evaluated in terms of print quality and electrical performance. Paper substrate properties were characterized using standard methods. The most critical substrate and ink properties are presented and their influence on the printability and electrical performance are discussed.

Introduction

The field of printed electronics has become a widely researched area with some applications already entering the market. Applications that could benefit from the use of printing in electronics manufacture include printed organic light emitting diodes (OLEDs) for display and lighting applications, printed batteries and memory devices, solar cells, sensors, smart labels and radio frequency identification (RFID) and other low-cost electronics [1]. The manufacture of traditional electronics is based on solid-state technology using rigid silicon as a base substrate [2]. However, for successful roll-to-roll production of low cost electronics by printing, there is a need for flexible substrates. Among flexible substrates, most of the reports are focused on polymer films such as polyethylene terephthalate or other polyesters [3]. However, printing of electronics on cellulose based materials such as paper or paperboard is of big interest, especially for RFID applications [4]. Printing both, antenna and integrated circuit directly on the package is the most aggressive approach to lowering the price of RFID tags. In fact, it is one of the main driving forces pushing the development of new materials and processes forward.

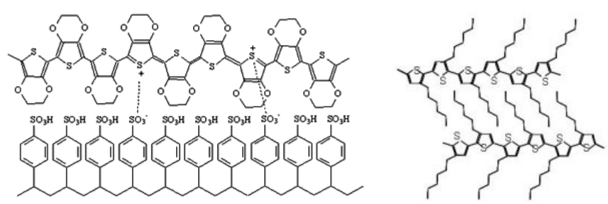
Electronic circuits contain various building blocks, such as transistors, diodes, interconnecting wires, etc. There are at least three main types of materials required for their construction and these include conductors, semiconductors and dielectrics (insulators) [1]. Moreover, the substrate, on which the components are constructed, is also an essential part of the system.

Among all printing methods, inkjet is probably the most versatile process and researchers are employing it as a first option for testing of new functional material intended to be printed [5, 6, 7]. The inkjet process itself is improving rapidly and provides better performance of printed features [8].

This paper deals with printability and performance of two types of functional materials deposited with ink jet printing on paper based substrates for applications in printed electronics.

Materials and Instrumentation

One conductor, (poly(3,4-ethylenedioxy-thiophene)-poly(styrene sulfonate) complex [PEDOT: PSS]) and one semiconductor, (poly(3-hexylthiophene) [P3HT]) have been studied. Both polymer materials were formulated into the printable liquids (inks) and deposited on different substrates. PEDOT: PSS is commercially available as a water-soluble polyelectrolyte system. The chemical structure of PEDOT-PSS is shown in the Figure 1. The PSS acts as a source for the charge balancing counter ion. It also keeps the PEDOT chains dispersed in water [9]. P3HT is probably the most widely studied and readily available polymer semiconductor for printed transistors [10]. The chemical structure of P3HT is also shown in the Figure 1. It can be processed at ambient conditions; however, prolonged exposure to oxygen can lead to decreased electrical performance [11].



PEDOT-PSS P3HT

***Figure 1** Chemical structure of polymers used in ink formulations*

The Dimatix DMP-2831, piezoelectric ink jet printhead system, was used to print functional inks to test their printability and functionality. Dimatix system uses MEMS-based cartridge-style printheads with 16 nozzles, each 254 µm apart (drop volume of 10 pL) and 1.5 ml volume reservoir for printed fluid.

Overall, three paper substrates (P1, P3, and P4) and one polyethylene terephthalate (PET) film were used for material deposition. Paper substrate P1 is a commercially available label stock substrate. Substrates P2 and P3 are modifications of substrate P1. PET film was chosen for comparisons because it is being widely used as a substrate for for printed electronics.

Experimental

The properties of inks (viscosity and surface energy) were adjusted to meet requirements for jetting with the Dimatix system.

Prior to printing, each liquid (ink) was processed using the following steps:

- Filtration of ink using 0.45 μm syringe filter
- Degassing the ink in an ultrasonic bath for at least 30 min prior to loading the ink into the printer cartridge
- The loaded cartridge was allowed to set for 30 min. with the nozzles facing down so the fluid could flow into each nozzle and ensure proper wetting of the nozzles.

To prevent the drying of the ink at the nozzles, cleaning pads were soaked with solvent used for the particular ink system. For each ink, the printing waveform was modified and voltage adjusted to ensure the best jetting results. The nozzles temperature was set to 28°C for both inks. The substrate platform was also kept at a constant temperature of 28°C. During printing, a few cleaning cycles were used to provide stable and consistent jetting. The drop size of jetted ink for given printer configuration was approximately 4 pL.

Each substrate was printed with conductive and semiconductive ink at two different resolutions (distance of jetted drops from center-to-center), 20 μm and 16 μm. These values were chosen based on preliminary testing. Printed design included fine lines of different widths (20, 30, 40, 50, and 100 μm) for the printability study and 500 μm wide lines for electrical measurements. All lines were printed in parallel and perpendicular direction to print head movement. Results for lines printed in cross direction to head movement are reported here.

Prepared and adjusted PEDOT ink and P3HT ink were inkjet printed on all studied paper substrates and PET film. In the case of PEDOT ink, multiple layers were printed and resistance properties were compared. Samples printed with PEDOT ink were dried in the oven at 80 °C for 5 min after jetting. No drying was applied between depositions of additional layers of PEDOT ink. Samples printed with P3HT were air dried at ambient temperature for 24 h before further testing.

Print quality of printed features was evaluated using an ImageXpert (KDY Inc.) image analysis system comprised of a motion table for sample positioning, two calibrated cameras for image capture and ImageXpert image analysis software (IX 10.0b63). The line fidelity was measured as a deviation in measured line width from nominal (designed) dimension. Also line definition was studied visually in terms of line edge raggedness (edge smoothness).

The resistivity values of printed PEDOT lines were measured using a Keithley 2400 digital multimeter in the 4-wire sensing mode. The behavior of the P3HT ink printed at different drop spacing was also examined in terms of electrical characteristics. This time three drop spacings were used, 16, 20 and 25 μm. The electrodes, needed for testing of semiconductive P3HT were printed with silver based conductive ink using a laboratory gravure K-proofer and/or screen-printing on all tested substrates. Then the P3HT was inkjet printed overlaying the gap and electrodes to ensure good contact. The electrical performance was evaluated in terms of I-V (voltage-current) curves and sheet resistivity was calculated from Ohms's law and dimensions of tested sample. Again, a Keithley 2400 controlled with Labview software was used to collect data.

Results and Discussion

Two different non-pigmented coatings were applied to the substrate P1 using a bar applicator at 8-9 gsm coat weight. The objective was to improve surface smoothness, control ink absorption and at the same time retain optimal surface energy of substrates for sufficient wetting. Modified substrates P2 and P3 were smoother than the original substrate P1 with some variance in surface energy values (Table 1).

Table 1 Surface properties of substrates used for printing

	Surface Energy [mN/m]	Roughness [μm] (stylus profilometer)
P1	46.4	1.24
P2	30.7	1.15
P3	47.7	0.81
PET	43.8	0.44

Printability of PEDOT ink

It was observed that only one layer of PEDOT ink did not provide adequate coverage, which led to poor conductivity of printed lines. Therefore, one and two additional layers of PEDOT ink were applied. One layer of the ink printed on substrates P3 and PET also provided very poor visibility of printed lines and printability quality could not be evaluated by image analysis system. In the case of PET, visibility, did not improve even after applying two more layers and therefore PET was eliminated from printability examination.

In general, it was found that printing with resolution 16 μm led to greater spreading than 20 μm resolution (Figure 2). As the drops are jetted closer together, more ink is applied per printed area. If the ink is not immediately dried or absorbed into the substrate, more spreading occurs.

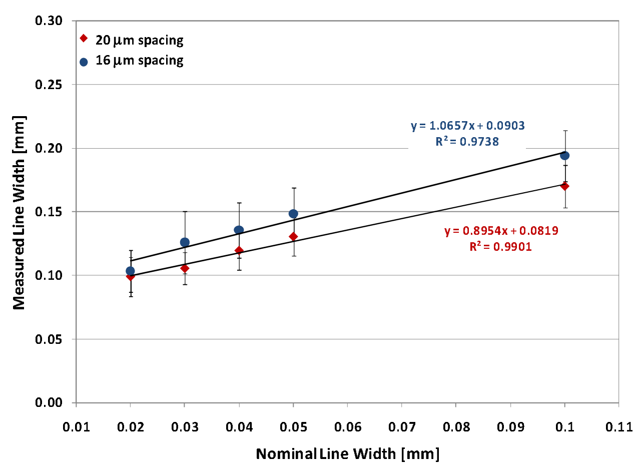


Figure 2 *Example of linear relationship between measured widths and nominal line widths at two different drops spacing (3 layers of PEDOT ink printed on substrate P1)*

The fidelity of printed lines was the best for P2 with approximately 110 % gain for 100 μm and 320 % gain for 20 μm designed lines at lower resolution (20 μm drops spacing). Substrate

P1 and P3 showed higher line width gain. Substrate P2 was also the best substrate in terms of line edge definition (edge raggedness) (Figure 3).

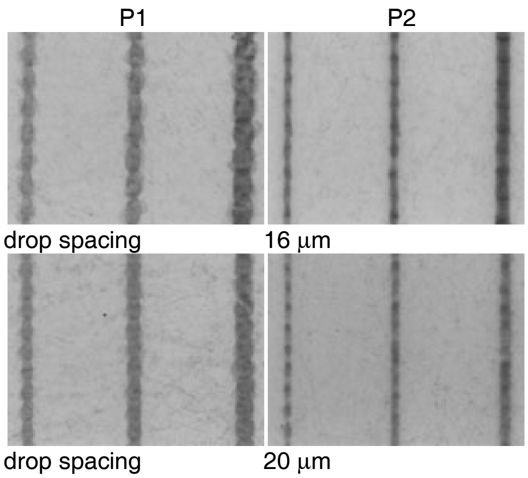


Figure 3 *Example of PEDOT ink printed on substrate P1, P2 (3 layers, lines with designed widths of 40, 50, and 100 μm)*

Electrical characteristics of features printed with PEDOT ink

DC resistance values measured for printed PEDOT traces had similar trends for all substrates (Figure 4). With increasing in numbers of layers, conductivity improved (decrees in resistance value). In addition, as it was expected, printed lines revealed better conductivity at 16 μm drop spacing then 20 μm as the volume of ink per area increases.

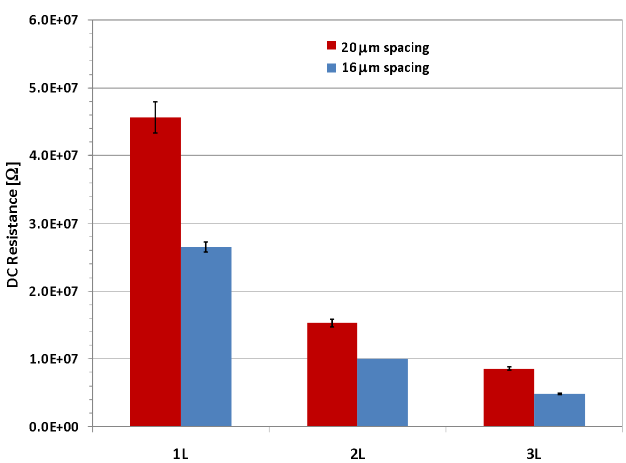


Figure 4 *Example of DC resistance of PEDOT multiple layers printed on substrate P1 at different spacing*

Among the tested substrates, the lowest resistance values were measured for substrate P2 and were the closest to the reference substrate PET (Figure 5). For PEDOT ink printed on substrate P3 at 20 μm drop spacing, a finite resistance value was not obtained, which is probably due to the PEDOT material being absorbed into the substrate. Absorption plays a very important role in printing of functional materials on cellulous substrates. Because of that, PEDOT material printed on such substrates will less likely to reach electrical performance of that printed on non porous polymer films. Nevertheless with controlling the surface properties of cellulous substrates by application of an appropriate coating, absorption can be controlled and optimized for required electrical performance.

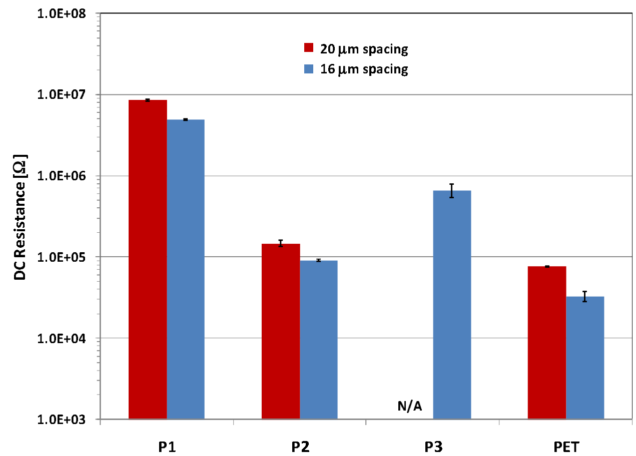


Figure 5 *DC resistance of PEDOT printed on different substrates at different drop spacing (3 layers)*

Printability of P3HT ink

Preliminary tests show that, unlike for printing with PEDOT ink, there was no need to print more than one layer of P3HT ink to reach good coverage which resulted in sufficient electrical performance. Similarly to the PEDOT ink, higher spreading was observed for lines printed with P3HT ink at 16 μm then for line printed at 20 μm drops spacing (Figure 6).

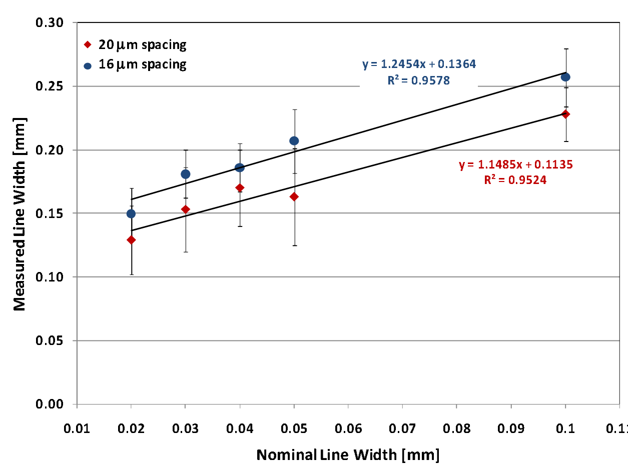


Figure 6 *Example of linear relationship between measured widths and nominal line widths at two different drop spacing (P3HT printed on P2).*

Lines printed on substrate P3 showed better line fidelity than lines printed on substrate P1 or P2. Line width gain for P3 substrate was around 170 % for 100 µm lines and 370 % for lines designed as 20 µm width for lower resolution. Similar to the samples printed with PEDOT ink, the substrate that showed the best fidelity of printed lines showed also the best edge definition of printed line (Figure 7).

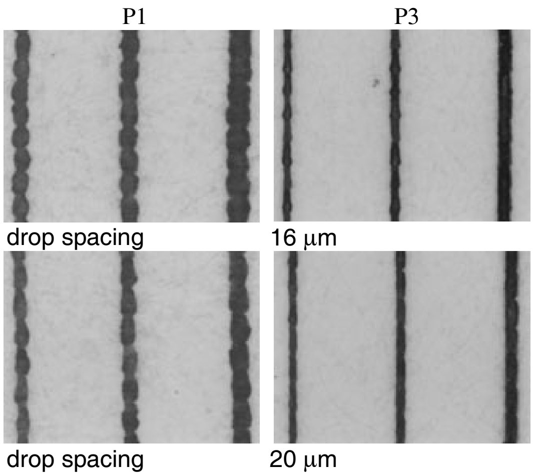


Figure 7 *Example of P3HT ink printed on substrate P1, P3 (line with designed width 40, 50, and 100 µm)*

Electrical characteristics of features printed with P3HT ink

First, three different drop spacings were tested in terms of their electrical performance. Figure 8 shows the I-V curves for P3HT ink printed on the substrate P1 and it can be seen that the polymer shows Ohmic behavior for all tested drop spacing values. The highest current was measured for 16 µm drop spacing, which is due to more P3HT being deposited in the gap between silver electrodes. No significant differences were observed between samples printed with drop spacing of 20 µm and 25 µm.

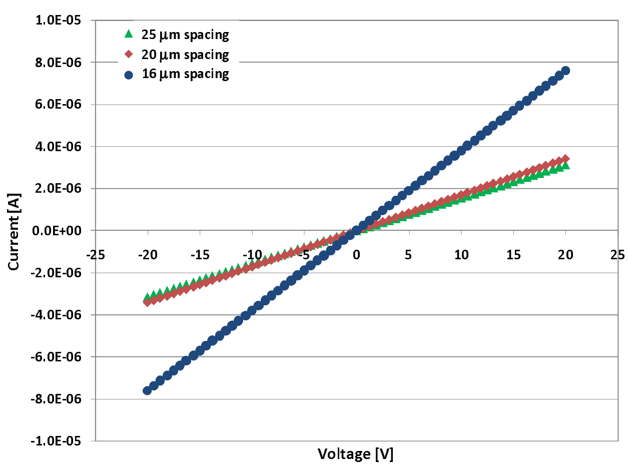


Figure 8 *I-V curves for P3HT inkjet printed on P1 at various drop spacing settings.*

The effect of the substrate on the electrical performance was evaluated by printing P3HT onto all studied paper substrates. PET was again used as a reference substrate.

Based on the findings reported above, the 16 µm drop spacing was used for higher conductivity. Prior to P3HT printing, the distance between silver electrodes (gap length) was measured and later used in the calculation of sheet resistivity. After printing and drying of P3HT ink, I-V curves were again measured. All measured samples showed Ohmic behavior enabling the resistance to be calculated from Ohm's law (R=V/I). These values were then used to calculate the sheet resistivity of the P3HT on each of the tested substrates using gap length and width. Results for the sheet resistivity, reported in the Figure 9 are showing the best conductivity values for substrate P3.

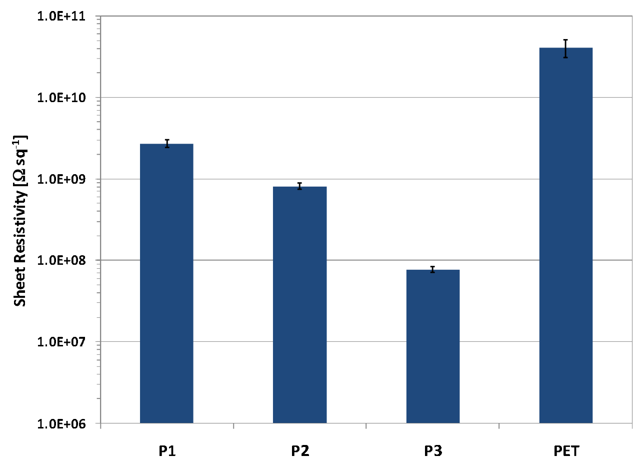


Figure 9 *Sheet resistivity of P3HT printed on different substrates at 16 µm drop spacing*

One reason for the difference in sheet resistivity between tested substrates can be attributed to ink absorption into the substrate. Surprisingly, high resistance was measured for the non-porous PET substrate. This might be due to poor wetting of the PET substrate, which caused the ink to spread more on top of the electrodes, leaving only a thin P3HT layer in the gap. Figure 10 shows pictures from the fiducial camera integrated with the Dimatix inkjet system taken right after printing. More of the P3HT ink printed on paper substrate is left in the gap to provide less resistance to the electric current.

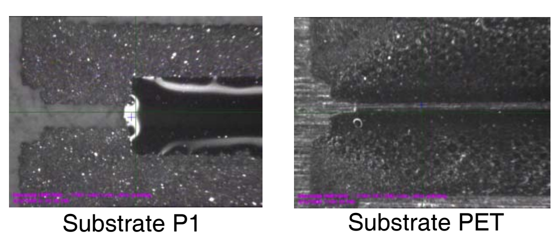


Figure 10 *Comparison of inkjetted P3HT on two of the tested substrates immediately after printing showing the spreading behavior of the ink*

Conclusion

Printing of graphic inks on paper substrates has been well optimized over years, but when it comes to printing of functional materials, paper properties need to be optimized in order to provide desired functionality of materials being printed.. Porosity, smoothness and surface energy are probably the most important to control.

In the case of PEDOT ink, a different number of layers has to be printed to reach the required conductivity of functional features determined by the application. For P3HT, resistance measurements showed that one layer provided sufficient performance.

In terms of printability, the best substrate for PEDOT ink was P2 while for P3HT ink it was the substrate P3. By including a surfactant in to the formulation of water based PEDOT ink, its final surface tension was close to surface tension of solvent based P3HT ink. However, a very important characteristic for ink-substrate interaction is a ratio of dispersive and polar forces contribution in the particular ink [12]. Therefore, even though two inks have very similar surface energy, printability on the same substrates could be different.

Printed lines showed edge raggedness for both inks at both tested resolutions. The shape of these edges is termed as a scalloped pattern and it can be eliminated by decreasing the drop spacing when printing on nonporous substrates [13]. However further lowering in drop spacing leads to more spreading while printing on paper substrates.

Better line fidelity was found for lower resolution (higher drop spacing) for both studied inks. However, conductivity had the opposite trend and lines printed at higher resolution showed better performance. According to these results, the compromise between holding the line dimension and required conductivity performance has to be found to obtain adequate performance.

Adjusting of substrate surface properties by application of additional coating, electrical performance and print quality were improved. The results obtained in this work provide good data for further study of functional material and their interactions with cellulose based substrates, which can be further used for applications by conventional roll-to-roll printing applications such as gravure and flexography.

References

[1] D. R. Gamota, P. Brazis, K. Kalyanasundaram, J. Zhang (Ed.), “Printed Organic and Molecular Electroncis,” Kluwer Academic Publishers, Norwell, Massachusetts, 2004, pg. 695

[2] A. S. Sedra, K. C. Smith, “Microelectronic Circuits,” 5th Ed., Oxford University Press, Oxford, NY, 2004, pg. 1283

[3] W .A. MacDonald, et.al., ‘Latest advances in substrates for flexible electronics’ Journal of the SID, 15/12: 1075-1083 (2007)

[4] M. Rebros, E. Hrehorova, B. J. Bazuin, M. K. Joyce, P. D. Fleming, A. Pekarovicova, “Rotogravure Printed UHF RFID Antennae Directly on Packaging Materials,” TAGA 60th Annual Technical Conference, San Francisco, CA, 16-19 March, 2008

[5] S. Sanaur, A. Whalley, B. Alameddine, M. Carnes, C. Nuckolls, “Jet-printed electrodes and semiconducting oligomers for elaboration of organic thin-film transistors”, Organic Electronics, 7, 423, (2006)

[6] S. M. Bidoki, D. M. Lewis, M. Clark, A. Vakorov, P. A. Millner, D. McGorman, “Ink-jet fabrication of electronic Components”, J. Micromech. Microeng. 17, 967, (2007)

[7] T. Kawasea, T. Shimodaa, Ch. Newsomeb, H. Sirringhausc, R. H.Friend, “Inkjet printing of polymer thin film transistors”, Thin Solid Films, 438 –439, 279, (2003)

[8] T. Sekitani, Y. Noguchi, U. Zschieschang, H. Klauk, T Someya, “Organic transistors manufactured using inkjet technology with subfemtoliter accuracy”, PNAS, 105, 4976, (2008)

[9] S. Kirchmeyer, K. Reuter, “Scientific importance, properties and growing applications of poly(3, 4-ethylenedioxythiophene),” J. Mater. Chem., vol. 15 (2005) pp. 2077 – 2088

[10] I. Mcculloch, et. al., “Liquid-crystalline semiconducting polymers with high charge-carrier mobility,” Nat. Mat.,5,(2006) , pg. 328

[11] B. S. Ong, Y. Wu, Y. Li, “Organic Semiconductors Based on Polythiophene and Indolo[3,2-b]carbazole,” in Organic Electronics: Materials, Manufacturing and Applications, ed. H. Klauk, Wiley-VCH Verlag GmbH&Co. KGaA, Weinheim (2006) pg. 80

[12] J. M. Bradley, “Determining the dispersive and polar contributions to the surface tension of water-based printing ink as a function of surfactant surface excess” J. Phys. D: Appl. Phys., 38, 2045, (2005)

[13] D. Soltman, V. Subramanian, “Inkjet-Printed Line Morphologies and Temperature Control of the Coffee Ring Effect”, Langmuir, 24, 2224, (2008)

Author Biography

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