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# Inkjet printed thin and uniform dielectrics for capacitors and organic thin film transistors enabled by the coffee ring effect



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#### ABSTRACT

The deposition of a thin and uniform dielectric layer is required for high performance printed capacitors and thin film transistors (TFTs), however this is difficult to achieve with printing methods. We have demonstrated inkjet-printed dielectrics with a uniform thickness from 70 nm to 200 nm by taking advantage of the coffee ring effect. A high capacitance per unit area of 230 pF/mm<sup>2</sup> is achieved from capacitors with linear morphologies fully printed onto flexible substrates. We also demonstrate organic TFTs with an average mobility of 0.86 cm<sup>2</sup>/Vs and a source drain current of 57  $\mu$ A obtained with a supply voltage of 15 V. This performance was shown to be consistent, with a standard deviation of 15% obtained from hundreds of printed organic TFTs on PET substrates. This consistency was further validated by the production of functional NAND, NOR, AND and OR logic gates. Our results demonstrate that the coffee ring effect, which is usually viewed as undesirable, can enable higher performance in printed electronic devices.

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#### 1. Introduction

The field of printable electronics is one of intense research focus. Printable electronics has the potential to enable low cost, large area and flexible devices to be produced with a myriad of functionalities. Recently reported devices fabricated using printing techniques include photovoltaics [1], organic light emitting diodes [2], radio frequency identification tags [3] and logic circuits [4]. As the number of proposed applications increases, so do the performance requirements for printed components, both in terms of functionality and form.

The use of printing methods for electronic device fabrication results in many challenges. One key challenge that affects many of the aforementioned applications is the printing of a thin, uniform and pinhole-free layer. This is especially crucial for the deposition of dielectrics for capacitors and transistors. Dielectric layer performance is defined by the relative permittivity (k) of the material, planar area of the layer and the layer thickness. Popular dielectric inks are usually polymer based, such as poly-4-vinylphenol (PVP) [5,6], polyimide (PI) [7] and poly(methyl methacrylate) (PMMA) [8],

all of which are limited to low-*k* values between 2.6 and 4.3 [9,10]. This limits the capacitance per unit area, especially in printed applications where very thin dielectric layers are hard to achieve. In order to increase the *k* value of the dielectric it is common to add high-*k* materials such as barium titanate (BaTiO<sub>3</sub>). This approach has been often reported in the literature [6,11–13], with *k* values of printed dielectrics reported as high as 102 [13]. However the approach has limitations [14], chiefly of which is the difficulty in obtaining a thin, defect free film with a suitable nanoparticle loading. Lim et al. [12] demonstrated that the *k* value of a hybrid BaTiO<sub>3</sub> inkjet printed film is dependent upon the particle size, with 100 nm diameter particles resulting in a k value of 46, compared to 62 for 500 nm particles. Larger particle sizes will have a significant impact on minimum film thickness and surface roughness. For example, of the aforementioned BaTiO<sub>3</sub> articles the reported printed dielectric layer thickness varies between 1.06 µm [6] and 15 µm [12].

Thinner dielectric layers can be achieved using polymer inks. However obtaining a thin and pinhole-free film is problematic using printing techniques, with many factors influencing the film quality. These include substrate roughness, drying parameters and environmental conditions. Noh et al. [8] demonstrated ultra-thin polymer dielectric layers down to 30 nm by use of a blending PMMA with a crosslinking agent. This was then deposited by spin coating onto glass. Repeating this result onto flexible substrates



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using high-throughput patterning techniques such as printing will be problematic due to instabilities not present in the spin coating process. Rotary printing methods such as gravure or flexography introduce layer instabilities during the ink splitting phase, while inkjet printing deposits droplets in a discrete fashion, all of which can result in non-uniform layer deposition.

A further problem with solution deposited dielectrics is the 'coffee ring effect', wherein fluid dynamics during the drying process results in thicker films at the edges of printed features [15]. This effect is well studied, with the exact morphology of the resulting film dependent upon many variables, including substrate temperature [16,17], drop spacing [16,17], humidity [18], solvent vapour pressure [19], drying conditions [20] and ink formulation [21]. It has been shown that this effect can be suppressed by careful solvent selection or optimised printing parameters [16]. Although the coffee ring effect is usually seen as undesirable, useful applications have been demonstrated such as microwells [22], microelectromechanical relays [23] and narrow features [24]. It has been shown that the coffee ring effect can lead to thin and uniform films in the centre of a feature [18,20]. We propose that the control of this effect in a printed line can lead to thin and reliable films which can be used for printed dielectric applications.

We propose devices which take advantage of the coffee ring effect in order to minimise the dielectric layer thickness. The proposed technique is to control the flow towards the extremities of the feature to leave a thin and uniform valley region in the centre. This effect is easiest to achieve via inkjet printing single droplets or lines, due to the non-contact raster scan method used for printing. As a result devices should be constructed of lines of dielectric, requiring linear morphology capacitors or TFTs. The coffee ring effect needs to be optimised to obtain a wide and thin valley region for maximum capacitance per unit area.

We have realized high performance inkjet printed capacitors and organic TFTs on flexible substrates with ultra-thin dielectric layers. We achieve this by taking advantage of the coffee ring effect in order to achieve a thin and uniform layer in the centre of printed lines. The coffee ring effect was studied with respect to various printing parameters in order to understand the required printing conditions for optimal performance. Inkjet-printed dielectric layers with thickness as low as 70 nm have been achieved on printed silver electrodes. We prove the viability of these dielectric layers by producing fully printed capacitors with high capacitance per unit area. In addition, our 3-layer printed organic TFTs achieved an average mobility of 0.86 cm<sup>2</sup>/Vs with a relative standard deviation of 15%. This high performance and consistency enabled the production of printed logic gates.

### 2. Materials and methods

All printing was performed using a Dimatix 5000 series drop on demand inkjet printer using a nominally 10 pl droplet print head in ambient atmosphere. Printing parameters such as waveform and voltage were optimised for each ink.

For dielectric morphology characterisation prints were made on Si wafers onto which 20 nm of Ag had been thermally evaporated to simulate an ideal printed bottom electrode. The PVP based dielectric ink was used as purchased from Xerox Research Centre Canada (XRCC). The dielectric constant of 3.9 is obtained when the ink is cured for 10 min at 90 °C followed by 20 min at 130 °C. Morphology was investigated using stylus profilometry (Veeco Dektak 150) and AFM (Veeco EnviroScope). The effects of drop spacing, line width and substrate temperature upon the coffee ring morphology were studied.

Capacitors were printed onto planarised PET substrate (DuPont Melinex ST505). Bottom electrodes were printed using SunJet EMD5603 nanosilver ink which was cured at 130 °C for 20 min. The dielectric layer was then printed using previously optimised settings. Samples were then plasma treated in air at 25 W for 30 s prior to the top electrode deposition using the same parameters as the bottom electrodes. Devices were analysed using a HP 4285A LCR meter, assuming a parallel model.

Transistors were also fabricated on planarised PET. Au source and drain electrodes were fabricated using conventional lift off photolithography. The semiconducting polymer was DPP-Thieno [3,2-b]thiophene copolymer (PDBT-co-TT) [25], purchased from XRCC. This was dissolved in 1,2-dichlorobenzene at a concentration of 5 mg/ml. This was then inkjet printed at a drop spacing of 20  $\mu$ m using previously optimised print settings. The print was then heated at 90 °C for 10 min followed by 140 °C for 20 min in a vacuum oven. The dielectric layer was printed using previously optimised settings. Samples were then plasma treated in air at 25 W for 30 s prior to the top electrode deposition using the same parameters as the capacitor electrodes. Devices were analysed using a HP 4155C semiconductor parameter analyser.

#### 3. Results and discussion

## 3.1. Dielectric morphology

The morphology of the printed dielectric is dependent upon a number of printing conditions which include drop spacing, print width and substrate temperature. The effects of these parameters upon the coffee ring morphology are shown in Figs. 1 to 3. In particular we examine two parameters of the printed lines, namely the ratio between the valley width and the total width of the printed line and the average height of the valley. The ratio between valley and total width is important as the outer peaks contribute significantly to the planar area whilst being significantly thicker than the centre valley. Therefore it is useful to maximise the valley width with regards to the total width for optimal capacitive structures. The central valley height is the key parameter, as the capacitance is inversely proportional to the dielectric thickness.

Fig. 1 shows the effect of drop spacing upon the morphology of a single droplet wide line. Single droplet wide lines were printed with varying drop spacing between 15 and 55  $\mu$ m. Below 15  $\mu$ m the centre area thickness was too high to be of interest for this application, above 55  $\mu$ m the line became irregular. This drop spacing range is larger than expected based on the results of Soltman et al. [16], however there are two significant differences between the tests. In their tests the jetting frequency was much lower, which changes the fluid dynamics during drying as the timescales for the drops to merge are different. Also the fluid properties of their ink are significantly different to the ink used in this study, as is emphasised by the significant coffee ring effect observed in our results.

Increasing the drop spacing results in a narrower line, with a thinner and wider valley section. This is caused by the reduced volume of ink deposited. The minimum measured thickness decreases to a minimum of approximately 60 nm at 55  $\mu$ m drop spacing. It is also interesting to note that the minimum valley height and maximum peak height appear to be directly proportional and independent of drop spacing, with a constant of proportionality of 0.17  $\pm$  0.01. This is similar in behaviour to the printed Ag ink seen by Kang et al. [17] which had a constant value of 0.65  $\pm$  0.05. The lower magnitude seen in our results may be due to the high vapour pressure and lower viscosity of the dielectric ink. This ratio describes the amount of flow from the centre of the printed drop to the edges, and should be minimised to obtain thinner films in the valley region.

To maximise the planar area of any devices it would be

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