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Influence of Etching Solvent Evaporation on the Size of Micro-Via Holes in PVP Thin Films

Yan Zhang, Changqing Liu and David C Whalley

Wolfson School of Mechanical and Manufacturing Engineering, Loughborough University
Loughborough, Leicestershire, United Kingdom

Abstract

Via holes are a necessary component in traditional PCBs and IC interconnections. Such structures will also be required in organic electronics to achieve vertical communication between multiple layers. Inkjet printing has demonstrated its applicability in both hole creation and for other pattern generation requirements in various polymeric layers. However, the technique has not been systematically investigated. This paper is focused on a study of the effect of solvent evaporation rate on the size of inkjet-etched via holes for organic electronics, which is part of a more extensive investigation and evaluation of inkjet etching as a via hole fabrication technique.

In this work, holes were etched in thin layers of poly(4-vinyl phenol) (PVP), which is a potential dielectric material for organic electronic structures. Ethanol, isobutanol and ethylene glycol were used as the etchants in order to study the effect of solvent boiling point and vapour pressure on the size evolution of via holes with the total number and the frequency of the solvent drops used to dissolve them. Isobutanol and ethylene glycol have higher boiling points than ethanol, leading to slower evaporation, which is believed to allow the dissolved polymer to flow backwards to the central area before complete solvent evaporation, resulting in hole refill. However it will be shown that applying temperatures higher than room temperature can accelerate solvent evaporation and eliminate the refill issue.

1. Introduction

Printed electronics has emerged as a fast developing technology in terms of both academic research and industrial application. The global market for printed electronics continues to grow and many products are either already or expected to be commercially available to markets. Commercialised examples include LG's 55 inch organic light-emitting diodes (OLED) TV and 6 inch e-ink plastic electronic paper display (EPD). The global market for printed electronics is expected to increase to over US \$44 billion by 2021 [1].

Inkjet printing, as a noncontact, maskless and digitally-driven direct-write technique, is a candidate process for printed electronics manufacturing and has the potential to allow fully printed structures by using arrays of nozzles loaded with different functional inks such as conductive, semi-conductive and insulating materials. Researchers have also demonstrated the use of inkjet as an etching technique for polymer layers. The mechanism of polymer etching and pattern generation is attributed to the coffee ring effect, during which dissolved material is deposited at the periphery of an evaporating sessile drop. This polymer re-deposition is due to the faster evaporation rate at the perimeter, which also results in micro-flows from the centre to the perimeter due to solvent replenishment [2-4]. In this case, a pinned contact line also plays a significant role, i.e. the receding wetting angle of the solvent is sufficiently low that as the droplet shrinks in

volume the wetted area does not reduce. de Gans, *et al.*, demonstrated the use of inkjet etching to produce holes in polystyrene and grooves in poly(benzyl methacrylate) layers [5,6]. Bonaccorso, *et al.* [7] and Pericet-Camara, *et al.* [8] deposited liquid drops onto polystyrene substrates to make microlenses. Karabasheva, *et al.* [9] and Grimaldi, *et al.* [10] studied the different shapes obtained in a polystyrene substrate with varying solvent mixture ratios. Siringhaus and Kawase, *et al.* first used inkjet to etch via holes in PVP thin films for all polymer thin film transistors [11-13]. Xia, *et al.* [14,15] used the etched holes as a structure for OLEDs and detected a thin residual polymer layer at the bottom, but showed that repeated deposition of solvents eventually removed this polymer residue. Zhang, *et al.* [16] utilised electroplating to demonstrate the completeness of via hole etching after several drops.

Although inkjet etching has been studied for over ten years, the etching process is still not fully understood and its strengths and limitations have not been thoroughly investigated. This paper is focused on the effect of solvent properties on the resulting via hole size evolution with the number of solvent drops (N_d) dispensed.

2. Experimental Setup

A Microfab Jetlab 4 printing system was used throughout this work. A 60 μ m nozzle was employed to dispense the solvent drops. To achieve good quality printing results, proper jetting needs to be established by adjusting the triggering waveform for each material jetted due to their different properties such as viscosity. Both unipolar and bipolar waveforms, as shown in Figure 1, can be used as the triggering waveform for the inkjet printer. However, a unipolar waveform was adopted in this work as satisfactory results could be achieved, but with less parameters to adjust.

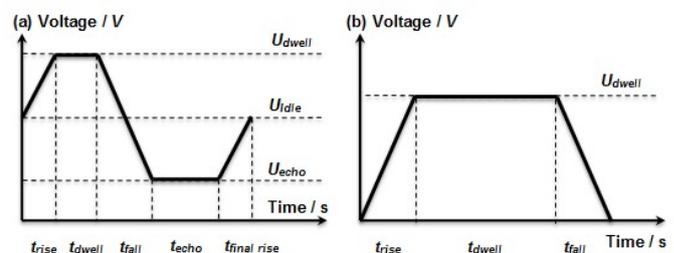


Figure 1. (a) Bipolar and (b) unipolar waveforms used for droplet generation in a drop-on-demand (DoD) inkjet printer.

For this via hole etching application, the dwell voltage (U_{dwell}) and dwell time (t_{dwell}) needed to be adjusted so that no satellite drops formed behind the main drop, and the ejection velocity was sufficient to ensure the droplet trajectory from the tip of the nozzle to the landing location on the printing

surface was straight and normal to the substrate. This is significant as deviation in the droplet trajectory can severely affect the quality of the resulting via holes. Figure 2 shows an example of good droplet formation ready to be used in the etching process. The droplet ejection frequency was set to 1Hz for all tests, except where noted.

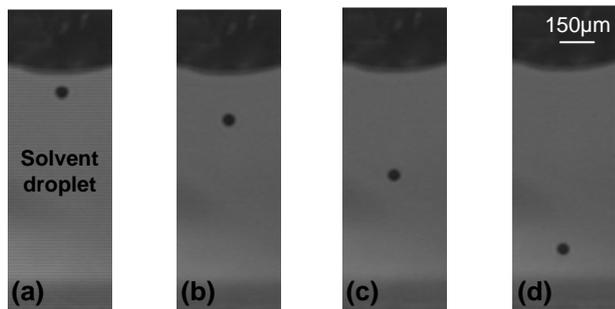


Figure 2. Images of an ethanol drop jetted by a 60µm inkjet nozzle travelling through the gap between the print head and the substrate.

Poly(4-vinyl phenol) (PVP) was dissolved into isopropyl alcohol (IPA) to form a 20.3wt% polymer solution for spin coating onto a glass substrate. The spin coating speed and time were set to 2000rpm and 40s respectively. The sample was stored at ambient temperature for 24 hours to dry. The thickness of the resulting PVP film was measured using a white light interferometry (WLI) microscope to be 2.336µm. Table 1 lists some of the physical properties of ethanol, isobutanol and ethylene glycol. The higher boiling point and lower vapour pressure at room temperature of isobutanol and ethylene glycol was expected to result in much slower droplet evaporation, whilst their higher surface tension and viscosity requires a higher drive voltage to ensure satisfactory droplet ejection from the jetting nozzle.

Table 1. Main physical properties of the solvents at 20°C (at 1.01325kPa for boiling point)

Solvent (Linear formula)	Boiling Point (°C)	Vapour Pressure (kPa)	Surface Tension (10 ⁻³ J/m ²)	Viscosity (mPa·s)
Ethanol (CH ₃ CH ₂ OH)	78.3	5.95	22	1.078
Isobutanol (C(CH ₃) ₂ CHCH ₂ OH)	108	0.8	23	4
Ethylene Glycol (HOCH ₂ CH ₂ OH)	197.3	0.016	47	16.13

The jetting parameters and resulting drop sizes for the solvents are listed in Table 2.

Table 2. Jetting parameters for different solvents and the corresponding drop size at 20°C

Solvent	U_{dwell} (V)	t_{dwell} (s)	D_{drop} (µm)	V_{drop} (pl)
Ethanol	24	35	40.00	33.49
Isobutanol	27	29	61.47	121.55
Ethylene Glycol	45	31	57.34	98.66

3. Results

The typical resulting via hole profile generated by inkjet etching is illustrated in Figure 3.

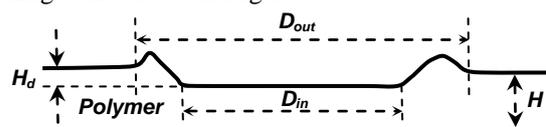


Figure 3. An illustration of the profile of a via hole etched by jetting of solvents.

3.1. Ethanol

Our previous study showed that, for the etchant ethanol, once the entire polymer layer is penetrated, both D_{out} and D_{in} do not change with the number of drops used to etch the holes at an ejection frequency of 1Hz, as shown in Figure 4 [16]. This is a result of the low boiling point and high vapour pressure of ethanol, as listed in Table 1.

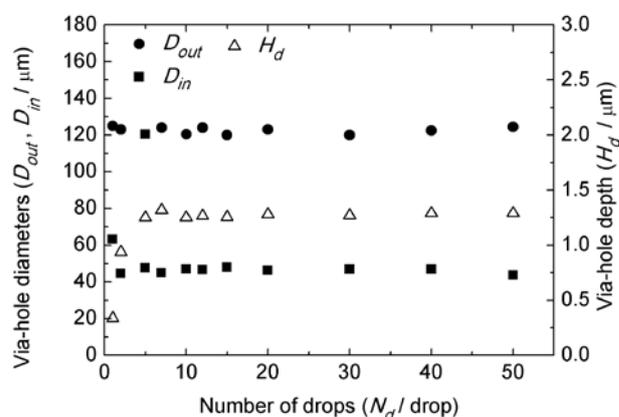


Figure 4. D_{out} , D_{in} and H_d versus N_d for via holes produced by ethanol drops at intervals of 1s.

3.2. Isobutanol

Figure 5 presents the evolution of D_{out} and D_{in} with N_d . As can be observed in Figure 5, D_{out} is independent of N_d while D_{in} varies with N_d .

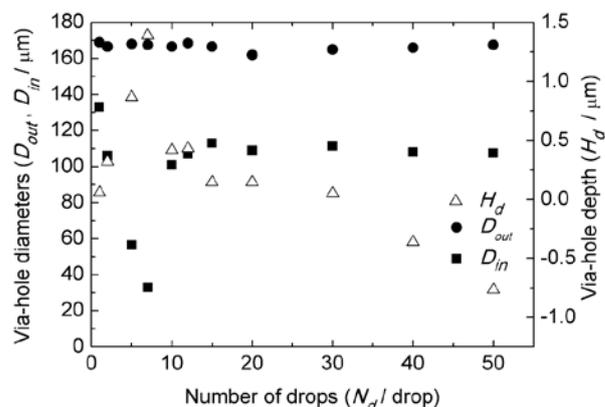


Figure 5. D_{out} , D_{in} and H_d versus N_d for via holes produced by isobutanol drops at intervals of 1s.

It is believed that the slower evaporation rate of isobutanol contributes to this different evolution of D_{out} and D_{in} with N_d . Isobutanol drops evaporate at such a rate that the accumulating solvent does not enlarge D_{out} , but does alter D_{in} with increasing N_d . During the first several drops, the flow of

polymer solution back to the centre and deeper excavation in the polymer all contribute to a narrower D_{in} . As N_d further increases, the accumulating residual solvent renders the polymer solution less viscous, so that it flows back to refill the hole. This is shown by the rapid D_{in} increase and H_d drop when N_d exceeds 7.

To provide further evidence for this attribution of feature evolution to the solvent evaporation rate, the same experiment was carried out again with an extra 90s delay between consecutive droplet dispensing, adding up to a total time interval of 91s. The extra jetting delay was achieved by writing a script recalling subroutines in the main script.

Figure 6 schematically presents the evolution of D_{out} , D_{in} and H_d with N_d for the 91s printing delay. As shown in Figure 6 this evolution resembles that when ethanol was used with a 1s delay. D_{out} stays constant throughout the process and D_{in} begins to level off to a constant when the polymer is completely penetrated.

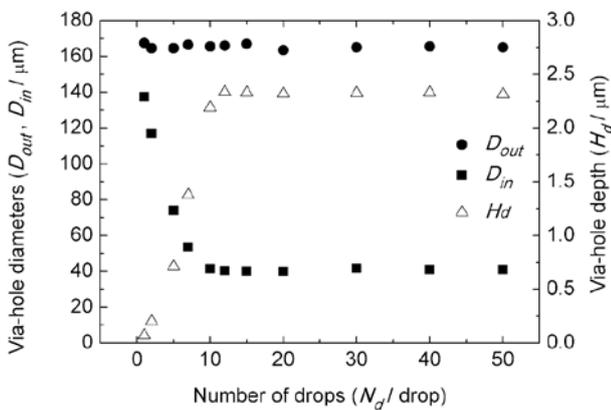


Figure 6. D_{out} , D_{in} and H_d versus N_d for via holes produced by isobutanol drops at intervals of 91s.

3.3. Ethylene Glycol

From the results above, it could be foreseen that jetting ethylene glycol at 1s intervals would cause the via holes to quickly enlarge with increasing N_d because of the significant amount of residual solvent left before the next drop merges in, due to its even higher boiling point and lower vapour pressure. Ideally via holes produced by ethylene glycol could still be independent of N_d if sufficient time was allowed for the sessile drop to evaporate substantially before dispensing the next drop. However this encounters practical difficulties as jetting becomes inconsistent in terms of satellite drop formation, drop trajectory deviation, and drop volume fluctuation when the inkjet printer sits idle for so long. All these issues can contribute to poor quality via hole formation, since multiple droplets will not land at the same location and their contact lines may overlap. A higher temperature (100°C) was, therefore, applied to the printing stage to accelerate evaporation of the ethylene glycol.

As illustrated in Figure 7, D_{out} and D_{in} still gradually increased with N_d at 100°C when the ejection frequency was set to 1Hz. However it should be mentioned that, even though the via holes are enlarged with increasing N_d , the depths of the holes equalled the polymer thickness, which indicates the holes are etched through the entire polymer layer. This can be potentially used for tuning the diameter of the via holes

produced without compromising penetration. When an extra jetting delay of 30s is applied, both D_{out} and D_{in} stay constant after 10 drops, as shown in Figure 8.

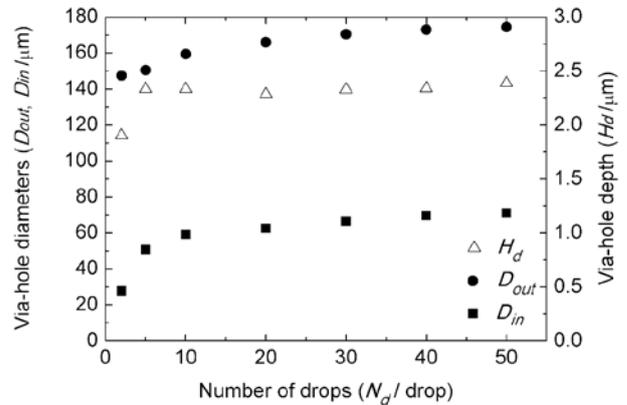


Figure 7. D_{out} , D_{in} and H_d versus N_d for via holes produced by ethylene glycol drops at intervals of 1s at 100°C.

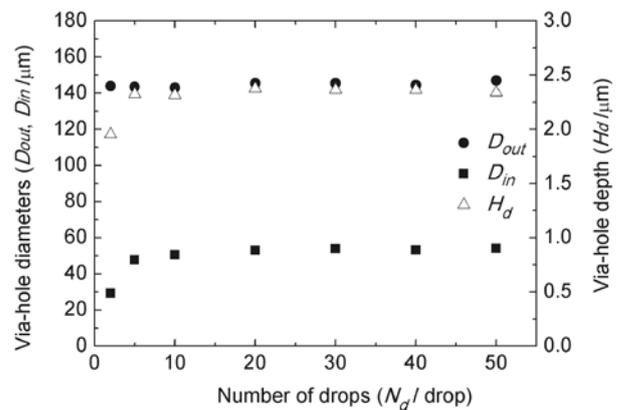


Figure 8. D_{out} , D_{in} and H_d versus N_d for via holes produced by ethylene glycol drops at intervals of 31s at 100°C.

It can be seen from Figure 8 that at 100°C and with a jetting delay of 31s, D_{out} and D_{in} follow the same evolution with N_d as ethanol at 1Hz and isobutanol with a 91s jetting delay.

4. Summary

This paper explores the influence of solvents with different evaporation properties, i.e. boiling point and vapour pressure, on hole size evolution with the number of etchant drops. This is part of an investigation into factors which can affect the size and shape of via holes produced by inkjet etching, aimed at evaluating inkjet printing as a via hole creation method. Experiments have shown that solvent evaporation properties are very important in the size development with N_d in inkjet etching via holes. Volatile solvents evaporate quickly and little residual solvent remains before the next drop arrives, even at a 1s dispensing interval. Solvents with high boiling points and low vapour pressures need more time to evaporate and are less likely to substantially evaporate before the next drop merges into the etching sessile drop, which enlarges the sessile drop contact line, thereby contributing to the enlargement of the resulting via holes.

5. References

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