Roll-to-roll patterning of Al/Cu/Ag electrodes on flexible poly(ethylene terephthalate) by oil masking: a comparison of thermal evaporation and magnetron sputtering

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ARTICLE INFO

Keywords:
Flexible electronics
Roll-to-roll
Physical vapor deposition
Patterning
Flexography

ABSTRACT

Here we show in-line-patterning of Al (37 nm)/Cu (58 nm)/Ag (55 nm) electrodes on flexible poly(ethylene-terephthalate) at 1–25 m min⁻¹, using a flexography printing apparatus retrofitted to a commercial roll-to-roll vapor deposition system. A Krytox® 1506 lift-off mask was printed for simultaneous evaporation during metal deposition. Heat through Al thermal evaporation facilitated single-step patterning with 99.99% masking efficiency, and 5% area shrinkage compared to the 4 × 6 mm photopolymer stamp. Al with nominal line widths of 28–58 μm (average. 47 μm) was also demonstrated using a commercial nitrile sleeve. Sputtering was trialed using powers 1–2 kW, substrate speeds of 1–25 m min⁻¹, and was unable to achieve mask lift-off, leading to metallic over-coating, removed via secondary isopropanol cleaning. Dynamic deposition rates of thermal evaporation exceeded sputtering (928 vs. 775 nm·m min⁻¹ respectively, with ten inline/confocal sputtering sources theoretically required). Resistivities of Al/Cu/Ag were 7.2 × 10⁻⁸/8.2 × 10⁻⁷/6.8 × 10⁻⁸ Ω·m; 2.6/48.2/4.2× greater than respective bulk values whilst work functions of electrodes varied 4.21/4.93/5.22 eV. Resistivities were critically impaired in proximity/on sputtered Cu/Ag. Electrodes were “printed” without inks/post-deposition heat-treatments, and whilst challenges remain, selective metallization is ready for high-throughput flexible electronics whilst sputtering may be used in a two-step process, requiring additional development for single-step patterning.

1. Introduction

Roll-to-Roll (R2R) manufacturing is desirable for high throughput deposition of electronic devices and integrated circuits such as transistors, solar cells, batteries and thermoelectric devices onto flexible materials for incorporation into the next generation of wearable electronics.

Prevalent in-line R2R printing techniques include offset, gravure, screen-printing, slot-die, and inkjet, each of which present tradeoffs between cost, speed and resolution. Commercial flexography printing employs a photopolymer/nitrile elastomer with a raised relief pattern to collect and transfer a printing medium (ink or oil) to a flexible substrate [1,2]. Flexography is widely used for printing decorative images onto packaging materials including polyethylene terephthalate (PET), polypropylene, paper, foils and corrugated cardboard. Compared to ink-jet, gravure and screen printing, flexography is chosen for its superior printing speeds (up to 180 m min⁻¹), low cost print plates, and ability to overcome substrate surface irregularities [3]. Inkjet has emerged as a modern non-contact frontrunner, however in electronic applications ink jetting can suffer from to nano/micro scale discontinuities in the print to impair circuit continuity [4]. Flexography and inkjet printing have demonstrated resolutions of 10 and 1 μm respectively relying on specialized techniques such as micro-contact printing which uses patterns in polydimethylsiloxane (PDMS) stamps via lithographically patterned molds [5] or inkjet printing of chemically repelling inks as shown by Grubb et al. to create a separation gap between transistor channels [6]. Typical commercial resolutions of inkjet is dependent on aperture sizes limiting resolution to 10 μm [7] whilst flexography has general limitation ~30 μm [1], limited by laser spot size for engraving of nitrile print sleeves. In addition liquid reliant techniques are also limited by fluid viscosity, surface properties of contact surfaces [8]. However, recent advances, reported in a 2016 publication from the Massachusetts Institute of Technology, showed that the 10 μm floor could be surpassed for relief-based stamps based on polymer-coated carbon nanotubes with tailored nano-porosity to contain the liquid ink during stamp-to-substrate compression, achieving...
1 μm features with 0.2 μm edge roughnesses [8]. These advances show that stamp-based technologies may be the future of high throughput printing of electronics with resolutions approaching that of inkjet.

Publications about patterned electrode tracks for flexible electronics have generally been limited to atmospheric processes whereby conductive silver/copper/carbon nanoparticle containing inks [9] have been printed by flexography and inkjet for polymer solar cells [4,10] and transistors [6,10]. Additionally printed insulators, dielectrics and semiconductors have been reported for both organic and inorganic devices including, but not limited to transistors, photovoltaics, solid state batteries and light emitting diodes. An extensive list of printed organics in, or suitable for, R2R fabrication can be found in a review by Sondergaard et al. [11]. Examples include the printing of an n-octanol interlayer to improve PEDOT:PSS-to-substrate adhesion [12], or deposition of In$_2$O$_3$ [10] and InZnO semiconductor inks in transistors [13].

Amongst thousands of reported studies on flexo applied conductive inks, those considering high-throughput continuous processing include Hosel et al., who produced 1 μm thick silver paste electrodes with resistivity of $16 \times 10^{-8} \, \Omega \cdot m$ at 10 m min$^{-1}$ [4] whilst Faddoul et al. obtained 1.5 μm thick conductive silver ink tracks printed at 25 m min$^{-1}$ with bulk resistivity $2.8 \times 10^{-8} \, \Omega \cdot m$ following a 850 °C heat treatment [14], a noteworthy attempt to approach the properties of pure silver thin-films, reported as 1.6 $\times 10^{-8} \, \Omega \cdot m$. Curing/sintering of inks to achieve optimized conductivity often requires minimum processing temperatures beyond those suitable for low cost polymer films such as PET. However, flash sintering has shown promising compatibility with PET substrates on a R2R system as used by Chung et al. to deposit silver based ink with sheet resistance of 0.95 Ω/sq for a 400 nm thick film (equivalent to $38 \times 10^{-8} \, \Omega \cdot m$) printed by gravure at 0.6 m min$^{-1}$ [15]. Conductive inks have been developed as a means to adapt metals for high throughput printing, however their conductivities fall short of their bulk metallic properties, and the choice of metal is extremely limited. Ink track thickness is often in the micron scale, to obtain necessary conductivity, which creates undesirably large steps for deposition of subsequent device layers [14,15]. Therefore an in-line patterning method, compatible with R2R for deposition of thin metal films would represent a significant step change in manufacturing of electronic devices. Process optimization could lead to single pass deposition of complete devices by incorporating multiple in-line print and deposition sources.

Researchers have stressed the necessity to move away from sputtering due to its inability to be adapted to high speed manufacturing [16]. Although vacuum deposition allows for a wide variety of materials, good multilayer and thickness control and good functional materials properties, the development of in-line patterning under vacuum lags behind that of ambient printing processes. Nevertheless, encouraging advances in selective metallization by flexography patterning would enable the extensive list of vacuum deposited thin-films including metals, dielectrics and semiconductors to be applied to low-temperature polymers such as PET. By combining flexography printing and vapor deposition, bulk conductors (Al/Cu/Ag) may be deposited as electronic circuitry components. Flexography printing with vapour deposition was primarily adapted for aluminum evaporation on a commercial scale for production of holographic displays and decorative packing [17,18] in which low vapor pressure fluorinated oils temporarily mask the substrate in vacuum, which if applied to electronics would prevent complications such as edge shadowing and material-on-mask build associated with conventional shadow masks [19], and be an attractive roll-to-roll solution. In a proof of concept publication, Cosnahan et al. used a pilot scale flexography system in an Edwards 306 with thermal evaporation to produce 30 nm thick Al electrodes as top contacts for OTFTs at 1.2 m min$^{-1}$ with resistivity $(4.8 \times 10^{-8} \, \Omega \cdot m)$ and channel width (165.1 μm) in which single pass oil printing and oil removal were achieved by consideration of oil thickness and induced radiative heating from the metalized region [20]. Similar techniques as shown by Lo et al. were used for deposition of sputtered 20 nm thick Ag electrodes where sacrificial inks were printed by R2R flexography and cured to mask electrode channels prior to carrying out the vacuum sputtering process; a method termed “flexography printing lift-off” [21]. Volkman et al. also printed 25–70 μm patterned ink photore sist at 10 m min$^{-1}$ prior to 100 nm of Ag evaporation to produce bottom electrodes in OTFTs [22]. Whilst promising, at present both techniques had drawbacks such as requirement to reduce roll speed for ink drying/ resist removal. Criticality the flexo printing, mask curing, electrode deposition and mask removal were not in either study entirely completed in a single R2R pass requiring separate machines for flexo/deposition and ink mask removal, which was not completed on a R2R system [21,22].

In the work presented here, a commercial scale in-vacuum flexography system was designed, retrofitted and employed to manufacture thin-film Al, Cu and Ag electrodes on flexible PET substrates to demonstrate the potential of R2R patterning for production of low-cost, large-area and high-throughput electronics. Crucially, this work demonstrates the speed and masking potential of Al by thermal evaporation and early potential of Cu and Ag by magnetron sputtering during operating conditions suitable for commercial scale application, involving relatively short, 30 min pump down times, whilst employing a commercially applicable webcoater. The distinct advantages of vacuum techniques over solution-based ambient printing processes are i) the wider variety of materials, e.g. pure metals that can be deposited than with ink and therefore ii) higher conductivity achievable via thin layers at the nano scale, which is important to minimize topography of patterned layers for deposition of subsequent layers. As compared to work on flexo printed lift-off inks and resists, oil mask patterning with vapor deposition has already been shown to be possible in a single R2R processing step. Furthermore 10 μm resolution source drain gaps have been shown in brief by Bobst® group using a similar oil masking method [23], however to the knowledge of the authors this is the first publication outlining the challenges of using an evaporating masking oil and simultaneously deposited metal to understand implications for resultant electrode resistivity and work functions; a necessary step in development of patterned electronics by this method. Additionally this work seeks to use sputtering (not previously shown), and if successful could make it possible to deposit the full range of sputtered semiconductors, dielectrics and metals, as well as co-sputtering of novel alloys. Successful compatibility of sputtering with oil patterning would offer greater adhesion, reproducibility, less material waste and an opportunity for producing wider ranges of novel high-functionality materials by co-deposition [24].

Al, Cu and Ag were chosen here due to the trade-off between low cost in the case of Al and the lowest resistivity metal in the case of Ag. The bulk resistivity of Al, Cu and Ag are 2.7, 1.7 and $1.6 \times 10^{-8} \, \Omega \cdot m$ [25] and at the time of writing costs ranged 1.8, 5.8 and 472.6 USD kg$^{-1}$ respectively [26]. These metals additionally represent a reasonable range of work functions from 4 to 5 eV where specific orientations of Al, Cu and Ag, have been reported as 4.06–4.41, 4.48–4.98 and 4.28–4.74 eV respectively; dependent upon the orientation of the crystallographic plane [27]. Furthermore Al is amongst the most commonly evaporated metal due to low cost and low vaporization temperature of ~1060 °C at 5.5 × 10$^{-4}$ mbar allowing for reasonable thickness during R2R high throughput manufacturing. Limited material usage during sputtering as compared to evaporation could make utilization of Cu and Ag (with two of the fastest pure metal sputtering rates), suitable materials for moderate throughput deposition, if shown to be successful [28]. Sputtering, if viable, would also prove advantageous over evaporation for patterning of a wide range of materials e.g. semiconductors, and materials such as diamond-like carbon or co-sputtered metals to add dopants for reducing work functions and/or resistivities.
2. Methodology

2.1. Oil patterning, magnetron sputtering and thermal evaporation

A photopolymer printing plate was acquired from Phoenix Printing Plates Ltd. Mylar® A (36 μm thick) PET film and mechanical grade (1196) silicon wafers acquired from University Wafer were used as substrates. Dupont™ Krytox® 1506 Oil was selected as a printing medium. A custom designed flexography system was manufactured for pattern printing (see Fig. 1A, B, C). Printing pressure was pneumatically applied for anilox-to-print plate and print plate-to-impression roller interfaces and both were kept constant at 0.5 and 1.0 bar, respectively.

All electrodes were deposited in an Aerre Machines Vacuum web coater equipped with a six-source thermal evaporator and a magnetron sputtering cathode as shown in (Fig. 1A). A base vacuum pressure of \(3.5 \pm 0.5 \times 10^{-4}\) mbar was achieved following 30 min of pumping by consecutive rotary (2 min), roots (8 min) and diffusion (20 min) pumping stages. For Al evaporation, 1.67 mm diameter Al wire was continuously fed at 8 cm min\(^{-1}\) and evaporated at \(\sim 440 \pm 15\) Amps from two resistively heated \(10 \times 2\) cm, TiB\(_2\)/BN ceramic source boats acquired from Sintec Ceramics, using a source to substrate distance of 180 mm. Vacuum pressure during deposition increased to \(5.5 \pm 0.5 \times 10^{-4}\) mbar. Magnetron sputtering of 99.99%, Al, Cu, and Ag was conducted from a 75 mm diameter water cooled, planar cathode at a target to substrate distance of 60 mm with argon flow set to 350 ± 5 SCCM prior to oil printing. A 100 μm thick stainless steel shadow mask, purchased from Newbury Electronics Ltd. was fixed to the drum as an industry standard comparison.

The time between oil printing and metal deposition has been specified for each run in Table 2. Thermal evaporation of Al was conducted by continuous R2R, allowing an oil wetting time of 1 s at 25 m min\(^{-1}\), whilst magnetron sputtering utilized multiple pre passes leading to extended oil wetting times of 266 or 156 s at 1 m min\(^{-1}\) (see Table 2).

2.2. Physical characterization (microscopy, thickness and deposition rates)

Light microscopy images were acquired using a Leica M165C. Electrode areas and mask efficiency were measured over \(n = 4\) electrodes and randomly selected 13.3 mm\(^2\) regions using ImageJ. Efficiency was calculated by measuring the proportional area of masking defects relative to the overall intended mask area.
A Bruker Dektak 6M stylus profilometer was used to measure the step height of coatings applied to partially masked silicon wafers. Thickness represented an average of \( n = 4 \) locations spaced at \( -3 \) mm apart per sample. Static deposition rates were obtained from wafers which were attached to a static drum. Dynamic deposition rates were calculated as deposited coating thickness multiplied by substrate speed.

### 2.3. Contact angle

Contact angle measurements were obtained at room temperature and atmospheric pressure for Krytox® 1506 Oil on PET from 4 independent drops via Dino-Lite digital microscope. Images were taken 1, 5, 10, 20, 60, 156 and 266 s after the droplet and analyzed using the imageJ plugin Low-Band Axisymmetric Drop Shape Analysis for Surface Tension and Contact Angle Measurements of Sessile Drops (LB-ADSA) produced by Stalder et al. [29].

### 2.4. Sheet resistance

Sheet resistance was calculated using Ohms law by acquiring voltage outputs using a Jandel Engineering Ltd. cylindrical 4-point probe with probe separation distance of 1 mm, under applied currents of 1, 2, 4, 6, and 8 \( \mu A \). Voltage outputs were measured via an Agilent 34420A Nano Volt/Micro Ohm meter. Current-voltage sweeps were collected at \( n = 4 \) locations. Sheet resistance was determined as the average of the slopes of each I-V curve and was converted to resistivity based on coating thickness. Calculations for sheet resistance required correction factor of 4.53 for semi-infinite plane where sample dimensions was greater than 40 mm (40 \( \times \) the 1 mm probe separation distance). Measurements acquired on the 6 by 4 mm patterned electrode where \( s = 4 \) and \( a/d = 1.5 \) respectively required correction factor of 3.16 using finite plane for samples where geometry was less than 40 \( \times \) the 1 mm probe separation distance. Derivation of correction factors and their use have been described by Smits et al. and Valdes et al. [30,31].

### 2.5. Kelvin probe

Work functions were collected using a KP Technology SKP5050 Scanning Kelvin Probe. Gold and aluminium reference electrodes were measured for calibration as the mean value of 25 scans and 3 spatially distinct points and correlated to literature values [32]. Collecting the relative work functions of the samples in the same way allowed for the calculation of their absolute work functions by plotting them along a linear relationship between the two reference electrode values. Error values were calculated using the maximum and minimum gradient of the linear reference relationship in conjunction with the respective minimum and maximum deviation in the sample measurements.

### 2.6. Absorption spectroscopy and X-ray photoelectron spectroscopy

UV-VIS and Fourier Transform Infrared Spectroscopy (FTIR) spectra of Krytox® 1506 oil and Mylar® A PET were acquired at wavelengths of 200–3600 nm and wavenumber 400–4000 \( \text{cm}^{-1} \) respectively. UV-Vis and FTIR were carried out using Varian Cary 5000 and Varian Excalibur FTS 3500 spectrometers in transmission and Attenuated Total Reflectance (ATR) modes respectively. In ATR mode Krytox® 1506 oil was placed on the diamond crystal whilst oil layer was pressed in contact with the crystal. For UV-Vis Krytox® 1506 oil was measured in a 10 \( \times \) 10 mm cuvette whilst oil layer was measured by UV transmission through the film of PET with surface oil.

A ThermoFisher Scientific K-alpha X-ray Photoelectron Spectrometer (XPS) system with an Al Ka X-Ray source was used to probe the surface/subsurface of Cu, Al and Ag thin films. Surfaces were etched with an EX06 ion gun for 10 s per step as specified in the results. The profiling depth over the 30 s period was estimated as \(~5\) nm for Al, by etch profiling for 450 s to detect Oxygen in the substrate beneath after 230 s.

#### 2.7. Buckling tests

Al-, Cu- and Ag-coated PET (from coating sections 80+ mm away from the oil masking regions) were cut into samples of 60 \( \times \) 10 mm. A 40 mm central length (original length between the grips) was buckled at a compression rate of 0.22 mm \( \text{s}^{-1} \) by 10 mm (creating a 30 mm distance) using an electromechanical actuator, at 30 mm a maximum bending radius of \(~15\) mm was induced. The resistance through the device was monitored via a Tenma 72-8720 multimeter and recorded at 1 s intervals. 3 independent samples were tested with each cycled 3 times between buckling and recovery.

### 3. Results and discussion

#### 3.1. In-vacuum flexography

A custom flexography system was manufactured and retrofitted to an Aerre Machines Vacuum Webcoater capable of R2R speeds of up to 300 m \( \text{min}^{-1} \) and maximum web widths of 350 mm (Fig. 1A). Commercially viable flexo systems utilize anilox, plate and impression rollers to collect media, transfer to the print plate and substrate respectively. The retrofitted assembly and geometries of components are shown in Fig. 1A, B and C. A 30° reverse-angle rounded edge geometry doctor blade was incorporated as a critical component for print media metering, intended here to thin the Krytox® oil layer by liquid splitting for consistent anilox-to-print plate transfer. In the principal study on selectively metalized Al electrodes by thermal evaporation the optimal printed oil thickness was suggested as 1.63 \( \mu m \) to achieve simultaneous oil on substrate removal and metal deposition [17]. In application, the required oil thickness is dependent upon applied heat, dependent upon heat source proximity, power, radiation, roll drum speed (exposure time), and working pressure to tune vapor pressure for optimal mask removal.

Anilox and plate roller diameters were designed to maximize the radius of curvature and to minimize lateral stretching of the photopolymer plate, which is a widely reported challenge leading to partial elongation of the printed pattern parallel to the print roller. To prevent this, print plate distortion factors may be applied to account for elongation caused by plate curvature [33]. In this case, the printed electrode pattern is intended for future production of thermoelectric generators by deposition of n-type and p-type semiconductor strips across the metal junctions.

#### 3.2. Electrode patterning and deposition (thermal evaporation vs. magnetron sputtering)

Deposition parameters for Al, Cu and Ag electrodes via substrate speeds of 1, 5 and 25 m \( \text{min}^{-1} \) are presented in Table 1. Electrodes were primarily deposited using Al at 25 m \( \text{min}^{-1} \) by thermal evaporation to demonstrate the functionality and upscale potential of the retrofitted flexography apparatus by the previously proven methodology of selective metallization. Subsequently, electrode materials were deposited by magnetron sputtering of Al (not shown), Cu, and Ag at 1, 5 and 25 m \( \text{min}^{-1} \), tailoring processing parameters to probe the capabilities of magnetron sputtering to initiate mask evaporation. Sample nomenclature (Table 1) denotes material and drum speed as specified within Table 1, eg. Cu-1 (Cu, 1 m \( \text{min}^{-1} \)). The sputtered Al film was not presented due to observed dielectric behavior in the deposited material (even without oil patterning), attributed to the insufficient pump-down regime (30 min), necessary to prevent oxidation in sputtered Al, where Al sputtering often requires medium to high vacuum, and removal of outgassing sources such as the PET roll [34,35].
Selective vapor deposition requires the following properties:

1. **Oil Mask Heating** – A vapor cloud of the masking oil must be formed by increasing the vapor pressure by simultaneous heating.

2. **Atomic Momentum** – The momentum of the Krytox® oil vapor cloud evaporating from the substrate must exceed the inwards momentum of the depositing coating.

Previous theory of selective metallization by thermal evaporation showed that heating of printed Dupont® Krytox® 1506 generated an oil vapor over the substrate to repel a condensing Al metal layer [20]. Pargellis [36], when examining substrate heating during deposition through holes onto printed circuit boards (and hence for a case in which there is no significant vaporization from the substrate) described three substrate heating mechanisms during vapor deposition as (1) heat of condensation, (2) radiant heating and (3) kinetic energy heating. For evaporation (1) & (2) will dominate, with their relative contributions dependent upon the deposition rate and the absorptivity of the substrate (in this case the oil). For sputtering, Pargellis concluded that (1) and (3) were the most important factors [36].

The vapor pressure of the Krytox® 1506 oil mask at room temperature, of $1.3 \times 10^{-13}$ mbar increases to within the vacuum pressure range in this study of $5.5 \times 10^{-4}$ mbar (vacuum level used for thermal evaporation, upon source heating) or $3.5 \times 10^{-3}$ mbar (argon gas inclusive vacuum for magnetron sputtering) at temperatures of either ~60 or ~100°C for the respective deposition processes [37]. The maximum operating temperature of the Mylar® A, PET substrate was 150°C [38], consequently a processing window for oil evaporation is between ~60 or ~100 to 150°C at $5.5 \times 10^{-4}$ or $3.5 \times 10^{-3}$ mbar for selective metallization or sputtering, respectively. The vapor pressure/temperature relationship was obtained from Dupont Teijin sales literature for Krytox® 1506 [37].

Successful oil masking was achieved here for thermal evaporated Al-25 with the oil vaporized and removed. In all sputtering trials Cu and Ag films coated over the oil mask as illustrated in Fig. 3B. Cu-25, Cu-5 and Cu-1 were sputtered immediately upon plasma ignition whilst the cathode was cold. A shutter was incorporated to simultaneously pre-heat the cathode source to a steady state prior to commencing deposition.

3.2.1. Heat of condensation

The dynamic deposition rate per rotation (a measure of the volume of material deposited per unit time for a given deposition width) of the evaporated Al was 928 nm·m min−1 compared with a maximum of 115 nm·m min−1 (in a single rotation) for sputtering. Harsha et al. suggested an average heat of evaporation of 5 eV per atom during thermal evaporation [24] processes whilst Thornton et al. measured heat of condensation to be 3.3–3.5 eV for Al ion mass ~120 m·m −2 cathode power density) for Cu and Al sputtered from a cylindrical post magnetron, intended to diminish the component of heating associated with plasma surface bombardment [39]. Our power densities used here ranged from ~28 to 113 kW·m −2 serving as a useful comparison to Thornton’s experiment. Hence, due to variation in deposition rates and therefore the number of atoms deposited per unit time here between sputtering and evaporation (eight times greater during evaporation), the amount of heating per unit time due to condensation of metal would be significantly lower for the sputtering, and so if metal begins to condense onto the oil, the amount of heating due to the heat of condensation to initiate vaporization of the oil is lower.

3.2.2. Radiation

Thermal evaporation requires heating to threshold temperatures to initiate deposition, where Al must reach ~1060°C at $5.5 \times 10^{-4}$ mbar [40], and significant IR radiation is emitted from the heat source. In line with Pargellis’ [36] conclusion, we would expect only modest IR radiation to be emitted from the (water cooled) sputter source, along with Ultraviolet (UV) and visible radiation from the plasma. UV-Vis and Infrared absorption spectra for Krytox® 1506 and the Mylar® A PET substrate (Fig. 2A and B) showed that Krytox® 1506 did not absorb in the UV to visible region, but as expected for organic molecules, did absorb in the IR. IR absorption by the oil begins at wavelengths as low as 2500 nm, as indicated in the UV-Vis spectrum (Fig. 2A). Comparisons between the absorbance of the oil and the polymer and between that measured with the UV-Vis and FTIR spectrometers should be treated with caution because of the different optical path lengths between the oil (in a cuvette: 10 mm) and the polymer film (36 µm) and with the ATIR interaction with the top 1 µm or so of the sample in the FTIR measurement. What this data does show is that IR radiation will be absorbed by the oil and could make a significant contribution to the heating of the oil, particularly for the case of evaporation, but UV-Vis absorption from the sputtering is minimal.

3.2.3. Kinetic energy

Magneton sputtering relies on ionized gas and neutrals to bombard the surface of the metal target and eject material towards the substrate by momentum exchange. The sputtering cathode is moderately heated...
from inelastic collisions at the surface of the metal target, whilst ionization and recombination of ions with electrons in the plasma emit UV and visible radiation [24]. The kinetic energy of sputtered particles may exceed evaporated particles by up to 100×, and has been suggested to be an important heating mechanism [36] in the case of sputtering. The high kinetic energy may be a limiting factor in functionality of a masking oil vapor cloud, as any generated oil vapor cloud could be unable to overcome and repel incoming sputtering atoms and molecules. The sputtering cathode here was operated at its maximum power output of 1–2 kW, with minimal substrate speed of 1 m min⁻¹ suggesting that either substrate heating was insufficient for vapor cloud formation, or vapor cloud momentum was inadequate for repulsion of depositing atoms/molecules. The incoming momentum could be reduced by low power deposition, at the expense of deposition rates, and the vapor cloud could be enhanced by additional heating of the oil, or utilizing a more volatile oil.

Following consideration of the three heating mechanisms, and suggestions that radiation is predominately emitted in the IR region for evaporation and in the UV region for sputtering, based on deposition rates and experimental observation here (i.e. no effective condensation of metal vapor onto the substrate in the case of evaporation and observed over-coating of the oil layer) we suggest radiative heating to be the dominant mechanism for oil vaporization during evaporation of Al-25. In contrast, during sputtering heat of condensation and kinetic energy remain the dominant factors and were insufficient for achieving oil mask evaporation.

The equivalent static evaporation and sputtering rates were measured here as 13.1 μm min⁻¹ and 0.9–2.0 μm min⁻¹ respectively (Table 1), to confirm depositions within both regimes described by Pargellis et al. Pargellis [36] concluded that either radiant heating or heat of condensation would dominate surface heating when depositing at the static equivalent of > 2 μm min⁻¹ on a dynamic substrate, and further suggested a similar magnitude of substrate heating for evaporation and sputtering at deposition rates < 3 μm min⁻¹. Beyond 3 μm min⁻¹ Pargellis suggested that kinetic energy heating during sputtering would exceed radiative and condensation heating during evaporation. This comparison was based on the similar substrate emissivity’s (Ɛ), where Pargellis assumed Ɛ = 0.08 for a thick aluminum substrate whilst Cosnahan et al. approximated Ɛ = 0.03 for a thin oil layer (1.63 μm thick) [20,36]. Thornton et al. considered heat of condensation, plasma radiation and kinetic energy during sputtering and reported cumulative measured heat fluxes 13–17 eV per atom for Al and Cu using similar power density to this work [39]. Substrate heating would be greater for thermal evaporation due to infrared radiation and the greater number of atoms condensing per unit time as deposition rates were a minimum of eight times faster for evaporation vs. sputtering in our experiments.

3.3. Print quality and masking efficiency

Al-25, manufactured by R2R evaporation was effectively masked and deposited onto PET in a single-step process (Fig. 3A). Although the maximum speed limitation was not explored here, the retrofitted flexography system was used for oil printing at speeds of up to 25 m min⁻¹. In contrast, for all sputter depositions the condensed Cu/Ag film coated atop the oil layer without the intended mask evaporation (Fig. 3B). A post-cleaning stage by rubbing with iso-propanol successfully removed the oil mask and the Cu overcoat (Fig. 3C) to leave the desired pattern of metal. However in the case of Ag-1 (1.0, 0.75 and 0.5 kW deposition powers) all electrodes were unintentionally abraded during the cleaning stage. Adhesion optimization of Ag with the substrate should be explored if a secondary cleaning stage is required.

The printed oil mask could function as a release layer in a two-step masking/removal process as evidenced by the optical micrograph in Fig. 3C to match conventional production by using a shadow mask (Fig. 3D).

The procured photopolymer print plate and shadow mask dimensions were distorted from their intended geometries from (6.00 × 4.00 mm) to (6.12 × 4.10 mm) and (6.05 × 4.04 mm) respectively (Table 2). Flexography print quality was defined here as masking efficiency and percentage area conformity to the photopolymer pattern. Print quality was assessed for single pass depositions that remained adherent to the substrate (which had not received any pre-treatment); specifically, Al-25 and Cu-1. The elapsed time between oil patterning and metal deposition was varied as 1, 156, 266 s as specified in Table 2 where respective electrode areas shrunk with respect to the photopolymer plate to 95%, 90–94%, 85%, with similar length and width contractions to suggest either dynamic wetting of the Krytox® 1506 oil on the substrate or incomplete oil transfer due to surface tension. Cu-1 was measured in two independent batches to show variation of 90–94%. Masking efficiency was above 99.9% for all electrode patterns (Table 2). Contact angle measurements of Krytox® 1506 oil on PET were carried out (Fig. 4A) to observe any liquid advancement with time and to confirm whether oil wetting with time at the macro scale could be expected to affect print resolution and therefore to explain observed shrinkage in electrode size with wetting time (varying from 1 to 266 s...
leading to respective electrode area conformities of 95.2 down to 85.1%). Results presented in Fig. 4A tracked contact angle between 1 and 266 s after the liquid drop and showed contact angle advanced from 33.1° to 23.2° to suggest that on the macroscale fluid dynamics would reduce resolution with time. At the lower micron range and even nano range of liquid volumes, in the realm of micro/nano-fluidic behavior, liquid/surface spreading is dominated by capillary forces and surface tension, almost unaffected by gravitation effects which greatly affect the advancing contact angle at the macroscale [41] leading to expectation of a lower rate of liquid spreading than observed by contact angle.

Whilst large scale electrodes for future thermoelectric generators is the main topic of this work, attempts have been made to reduce feature size down to the current commercial limit using a laser engraved nitrile sleeve supplied by Phoenix Printing Plates Ltd. As shown in Fig. 4B, Al-25 was patterned on PET using an oil mask applied with 50 μm nominal electrode widths/channels. Measured line widths varied from 28 to 58 μm with mean of 47 ± 1 μm (Fig. 4B). Commercially the limit of flexo print plate resolution remains ~11 μm (2150 dpi) governed by the minimum laser spot size in plate laser engraving technology demonstrated by Kodak’s Flexcel Technology [42] whilst ink print resolution itself is limited to ~30 μm [1], accounting for liquid spreading during plate to substrate compression [8]. It is encouraging to note here that contrary to traditionally ink printing where the ink final print would spread outwards under plate-substrate compression thereby increasing print size over nominal print plate dimensions, in the case here the Kyrtox® 1506 oil mask would spread outwards to effectively narrow the line width of the metal deposited pattern as metal is deposited in the gaps between the oil leading to a final print below the plates nominal line width. Therefore oil masking liquid spreading could be optimized and controlled in future to reduce print resolution to the lower micron scales limited by intermolecular liquid attraction which would eventually lead to coalescence of print oil. Additionally here we showed patterning of the University of Oxford Crest to demonstrate capability to manufacture complex shapes suitable for future circuitry design containing a range of line widths and shapes down to 50 μm.

3.4. Coating thickness during dynamic and R2R operation (see Table 1 and Fig. 5)

3.4.1. Al evaporation

Continuous R2R manufacturing was employed for Al-25 deposited at an average of 37 ± 2 nm pass−1. To observe process uniformity, thickness was measured at 5 m intervals from 5 to 45 m, and varied from 30 to 48 nm; a 37.5% variation (Fig. 5A). Variation is the result of challenging source temperature control as the boat resistance changes, relying on a feedback control loop [43].

3.4.2. Cu and Ag sputtering

Several drum rotations (1, 6 and 10 at substrate speeds of 1, 5, 25 m min−1) were assessed for sputtered Cu to mimic integration of multiple in-line or confocal sputtering cathodes. Average Cu thickness ranged from 31 to 58 nm, requiring between 1 and 10 drum rotations (Fig. 5B and C). The thickness per pass increased from 3.1 to 58.0 nm pass−1 based on rotational speeds and deposition powers of (25 m min−1 and 2.0 kW) and (1 m min−1 and 1.0 kW) respectively. Power was reduced from 2 kW for Cu-25 to 1 kW for subsequent depositions for continuous use as associated power densities can cause magnetic degaussing, as temperatures may rise to above curie temperatures [44]. The thicknesses of Cu-1 over 4 independent batches were measured.

| Material | Oil wetting Time (s) | Electrode length (mm) | Electrode width (mm) | Electrode area (mm²) | Area conformity to plate (%) | Mask Efficiency (%) |
|----------|----------------------|-----------------------|----------------------|----------------------|-----------------------------|--------------------|
| Shadow Mask | – | 6.05 ± 0.01 | 4.04 ± 0.1 | 24.63 ± 0.05 | – | – |
| Print Plate | – | 6.12 ± 0.01 | 4.10 ± 0.01 | 25.05 ± 0.06 | – | – |
| Al-25 | 1 | 5.94 ± 0.04 | 3.88 ± 0.03 | 23.85 ± 0.33 | 95.21 ± 1.36 | 99.99 ± 0.01 |
| Cu-1 | 266 | 5.82 ± 0.04 | 3.81 ± 0.01 | 22.14 ± 0.19 | 85.06 ± 0.95 | *99.99 ± 0.01 |
| | 156 | 5.96 ± 0.05 | 3.94 ± 0.04 | 23.45 ± 0.30 | 93.61 ± 1.24 | *99.90 ± 0.04 |
| | 156 | 5.91 ± 0.02 | 3.89 ± 0.03 | 22.53 ± 0.19 | 89.95 ± 0.80 | *99.96 ± 0.02 |
| Ag-1 | 156 | | | | | |

* Post cleaning stage required to remove un-evaporated mask and metallic overcoat.
ranged from 51 to 64 nm thick, ~20% batch-to-batch variation. Ag-1 was similarly deposited at 1 kW, increasing thickness to 115.3 nm pass⁻¹. Deposition power was reduced to 0.75 and 0.50 kW to obtain comparable thickness of 55 nm (see Fig. 5B and C).

3.4.3. Dynamic deposition rates

Dynamic deposition rates by both sputtering and evaporation, critical to future commercial manufacturing were calculated based on coating thickness irrespective of number of rotations (Fig. 5B) and were presented in (Fig. 5D). Al-25 was evaporated at 928 nm·m min⁻¹, showing superior capabilities whilst utilizing a pair of thermal evaporation sources (arranged in the transverse direction for good coverage of the web width) for high throughput manufacturing. Dynamic
3.5. Electrode resistivity and work functions

The resistivities of Cu-25, and Cu-5 were measured without Krytox® oil present in the process and were compared to Cu-1 where oil was used, to assess any negative effects of Krytox® 1506 or its vapors on potential electrode performance. Firstly, resistivity of all patterned samples was measured 80+ mm from commencement of an oil region (Fig. 6A and B). In this case, no significant difference was found between any samples (oil present or absent) with all Cu coatings having resistance of ~5.6-6.6× greater than bulk Cu of 1.7 × 10⁻⁸ Ω·m. Similar increases have been widely reported in literature for Cu thin films due to increases in electron-surface, electron-grain boundary and electron-phonon scattering as film thickness approaches the mean free path of the electron (~39 nm) in Cu to cause a significant reduction in electron transport [46]. Cemin et al. showed that DC sputtered copper thin films often have insufficient grain sizes for optimal conductivity [47] whilst perhaps of greatest concern here, Su et al. also suggested that CuO and Cu₂O defects could be readily formed when using moderate vacuum pressures due to affinity of residual oxygen atoms [48].

Resistance/sheet resistance data was generated at on the electrode and 80 mm from commencement of the oil masked region for Al-25 and Ag-1 whilst a complete profile was ascertained for Cu-1 at 180, 80, 22, 15, 3 mm and on the electrode (Fig. 6C). A crucial observation of the inset photograph of Fig. 6B inset showed darkening of both Cu-1 and Ag-1 films towards the oil masked region as well as yellowing of the over coated masked regions for Ag-1. The yellowing may have been attributed to formation of silver carbonate, as well as yellowing of the electro-deposited materials due to affinity of residual oxygen atoms [49].

Notably, the resistivity of thermal evaporated Al-25 between 80 mm and measured on the Al electrodes reduced marginally based on measured uncertainty (8.4 ± 0.4 × 10⁻⁷ vs. 7.2 ± 0.6 × 10⁻⁷ Ω·m) (Table 3). Residual oxygen is highly reactive with Al and deposition of high-quality Al electronics have been limited by the presence of outgassing sources such as the PET substrate, and the base vacuum limit of the webcoater employed (2.5 × 10⁻⁴ mbar). The resistivity of Cu-1 on the electrode was 8.2 × 10⁻⁷ Ω·m; 48× greater than bulk Cu. Improved performance for Ag-1 (55 nm) on the electrode was found as 6.8 × 10⁻⁸ Ω·m; ~4.2 greater than bulk Ag. Both Cu and Ag showed characterized by reduced resistivity at 80 mm from the oil region (Table 3). Work functions were acquired for electrodes (Table 3) that were within expected literature ranges for Al and Cu. In the case of Ag-1 electrodes the work function was 5.22 eV, significantly higher than the theoretical range.

XPS was used to ascertain any compositional and/or bonding variation which may have led to a modified resistivity at 180 mm from the oil region and on a deposited electrodes for Cu-1, Ag-25 and Cu-1. In the case of Cu-1 where the greatest change in resistivity was observed, at all three locations, the surface layer was rich in F (23–62 at%) and C (28–36 at%), associated with a possible re-deposition of Krytox® 1506 oil onto the surface.

The Cu-1, Ag-1 and Al-25 electrode surfaces were ion etched for 10, 20 and 30 s to obtain a compositional depth profiles (Fig. 7A–D), where estimated profiling depth after 30 s was ~5 nm for Al which is well known to have the lowest sputtering yield amongst Cu, Ag and Al [28]. After 30 s of etching F remained minimally present in all subsurface layers (1.2–2.9 at%) whilst O was found in trace amount for Ag (<1 at%), more for Cu-1 (9 at%) and in considerable quantities Al-25 (36 at%).

Scans of the F 1s suggested metal fluorides for Ag [51] and Al [52] in addition to the presence of organic fluorides in all three materials (Fig. 7E). The O 1s also suggested the presence of metal oxides [53], substantially present in the Al-25 sample (Fig. 7F). Oil contamination may have contributed to the observed 48× reduction in sheet resistance of the thin-film with respect to bulk Cu. Furthermore, despite significant color changes associated with blackening of the Cu electrode.
as compared to depositions 180 mm from the oil regions, the compositions at the two locations were not found to be significantly different (Fig. 7A–B). Therefore the further reduction and color change of the electrodes in the proximity of the oiled region in both Ag and Cu could have been an optical effect from nano scale porosity, perhaps due to imparting Krytox® Oil vapors forming defects, however its cause remains unconfirmed. It is clear that both fluorine and oxygen contamination from Krytox® Oil (both constituents of the Krytox® 1506 oil structure) are reacting in the vapor phase or becoming trapped within the structure, later likely acting as a oxidizing agent within the electrode sublayers in the case of Ag, Cu and Al [54]. The significant conductivity, the metallic appearance of the evaporated Al layer and

|                | Theoretical Bulk Resistivity (Ω·m) [25] | Electrode Resistivity (Ω·m) | Times Bulk (x) | Electrode Work Function (eV) | Theoretical Work Functions (eV) [27] | 80 mm from oil region Resistivity (Ω·m) | Times Bulk (x) |
|----------------|----------------------------------------|----------------------------|----------------|-----------------------------|--------------------------------------|----------------------------------------|----------------|
| Al-25 (37 nm)  | 2.74 × 10⁻⁸                             | 7.2 × 10⁻⁸                 | 2.6            | 4.21 ± 0.05                | 4.06-4.41                            | 8.4 × 10⁻⁸                             | 3.1            |
| Cu-1 (51 nm)   | 1.70 × 10⁻⁸                             | 8.2 × 10⁻⁸                 | 48.2           | 4.93 ± 0.03                | 4.48-4.98                            | 9.5 × 10⁻⁸                             | 5.7            |
| Ag-1 (55 nm)   | 1.61 × 10⁻⁸                             | 6.8 × 10⁻⁸                 | 4.2            | 5.22 ± 0.05                | 4.28-4.74                            | 3.54 × 10⁻⁸                             | 2.2            |

*Four-point probe measurements acquired at distance from the oiled regions and on the electrode utilized correction factors of 4.53 and 3.16 to account for edge effects assuming semi-infinite and finite planes respectively [31].

Table 3

Bulk metal resistivities and measured values on the electrode and 80 mm from oiled regions. Increases in metal resistivity have been calculated as “Times Bulk”.

Fig. 7. Atomic composition by XPS analysis of the surface/through thickness depth profiles following argon ion etching for 10, 20 and 30 s of (A) Cu electrode (Fig. 3), (B) Cu deposited 180 mm from oil region (C) Ag electrode deposited (D) Al electrode (E) and (F) High resolution F 1s and O 1s photoelectron emission spectrum of on electrode post 30 s etching to determine bonding states of oil residuals in the coating.
XPS data suggested the combined presence of metallic Al and Al₂O₃ whilst majority metallic Al was confirmed by the Al 2P spectrum even after 30 s of etching. Further complete depth profiling to the substrate suggested an increasing detection of metallic Al from 66% to 88% after 30 and 230 s of etching respectively with 34 and 12% Al₂O₃ respectively (see supplementary data). In contrast, whilst visually apparent, metallic Ag and Cu could not be differentiated based on high resolution scans of Ag 3d and Cu 2P spectra, due to proximity of metallic Oxide and metallic and Fluoride peaks.

3.6. Oxidation

For sputtered electrodes, achieving thin-film purity is challenging due to presence of residual atmospheric gases, and particularly in commercial scale R2R web-coating, where moisture-absorbing polyester substrate rolls [55] are situated within the chamber. As an illustration of the challenge, Lee et al. identified that the equilibrium partial pressures were 2.5 × 10⁻¹¹⁴ and 10.0 × 10⁻₂⁷ Pa to prevent Al and Cu oxidation respectively [55]. At the moderate vacuum used here to produce the highest purity films, the rate of film formation must exceed the rate of the oxidation reaction [35,55], which explains the superior performance of Al electrodes deposited by thermal evaporation, where deposition rates can reach 25 μm min⁻¹, an order of magnitude higher than magnetron sputtering [56]. To maximize film quality and reduce oxidation reactions with residual gas atoms, high vacuum levels are required where the masking process with Krytox® 1506 oil may be conducted down to 5.3 × 10⁻⁷ mbar (the vapor pressure at 20 °C)[37] if radiation/heat of condensation applied to the oil from the deposition source is carefully balanced. However where the focus here remains on commercial manufacturing, moderate vacuums, large chambers, pump down time limitations and necessity to utilize substrate materials which readily outgas will impair the applicability and performance of oxidizing metallic electrodes.

3.7. Fluorination

The oil masking method at present has some drawback when applied to electrodes, specifically contamination with fluorine and oxidation which could create metal fluoride and dielectric oxide phases during the vapour condensation stage leading to reduced resistivity. Even in trace amounts, fluorine can act as an oxidizer when in metallic structures to enable metals to achieve their highest oxidation states, due to fluorine’s highest elemental electronegativity. Fluorides in particular are well known oxidizers [54], which could explain partial oxidation of the Cu-1 electrodes and the observed 48 × increase in resistivity. In improving the oil masking techniques for electrodes efforts should be made towards reducing use of fluorinated oil, with other liquids such as hydrocarbon oils being a point of future interest.

Fig. 8. Al-25, Cu-1 and Ag-1 were buckled by a distance of 10 mm to create a bending radius of ~15 mm. In each case there was no variation in resistance, examined over 3 cycles. The buckling apparatus utilized an electromechanical actuator for constant buckling speed.
However in the case of Al-25 here where resistivity of the electrode was only 2.6×10⁻⁷ that of the bulk values this method could be promising for production of low-cost high throughput flexible electrodes. Secondly, beyond the intended application here of pure metal electrodes for thermoelectric devices in this work, many authors have also reported positive effects of fluorine dopants in semiconductor devices where oxidation is intended such as Fluorine Doped Tin Oxide where Koo et al. reported that fluorine was attributed to increasing carrier concentration and hall mobility attributed to a reduction in oxygen vacancies [57]. Aluminium Fluoride has been recently suggested as a novel cathode material for lithium ion batteries, where its benefits are attributed to a reduction of AlF₃ to LiF/Al and subsequent reverse during recharge [58].

3.8. Flexibility of metal coated PET (buckling)

Whilst metallization with oil patterning has been used commercially for many years and robustness and flexibility of metalized Al on PET is well-established [18,59] and the flexibility of thin metal films up to foils is widely recognized, variation in electrical performance during bending will be critical to performance in future device fabrication. In brief, the resistance across Al-25, Cu-1 and Ag-1 layers (at 80+ mm from the oiled region) on PET was measured whilst buckled to a distance of 10 mm creating a ~15 mm buckling radius and re-expanded in three cycles, showing no notable alteration in resistance as shown in Fig. 8 to support suitability of these layers on PET for flexible electrodes.

4. Conclusion

Selective thermal evaporation with Kryton® 1506 oil masking was implemented in a single step with 99.99% masking efficiency to produce 37 nm thick Al electrodes on flexible PET substrates at 25 m min⁻¹, with resistivity of 7.2 × 10⁻⁸ Ωm (~2.6× greater than bulk Al) and work function of 4.21, similar to theoretical Al.

Sputtered metal layers with up to 99.99% masking efficiency could also be patterned by a two-step process (in the case of Cu only) in which the deposited metal over-coated the patterned oil, and then could be removed by washing with isopropanol. In the case of Ag, inadequate adhesion prevented a secondary cleaning stage. To understand why the sputtering over-coated the oil, a comparison of the relative substrate heating by radiation, heat of condensation and kinetic energy was made for evaporation and sputtering. Maximum cathode powers (1–2 kW) and exposure times (1 m min⁻¹) were insufficient for raising substrate temperature by radiation and kinetic energy transfer to initiate mask evaporation, resulting in Cu and Ag coatings over the oil layer, or the kinetic energy of the sputtered species was sufficient to penetrate any vapour arising.

The appearance and resistivity of sputtered Cu and Ag varied as measured on the electrode and with distance from the oil patterned region, increasing to 8.2 × 10⁻⁷ and 6.8 × 10⁻⁸ Ωm, ~48.2× and 4.2× greater than bulk Cu and Ag. XPS depth profiling of Cu, Al and Ag suggested oxygen and fluorine contamination whilst metal fluorides and metal oxides were present.

Roll-to-roll, high throughput (25 m min⁻¹) patterning by selective metallization of Al can produce high quality patterns with good electrical conductivity, ready for the production of flexible electronic devices with potential to drastically reduce costs associated with shadow mask, bath processes. Whilst thermal evaporation has some drawbacks including material wastage, coating uniformity (30–48 nm over 45 m substrate distance) in our system, and limitation in evaporation capabilities of exotic/novel materials, further manufacturing iterations are necessary to achieve single-step selective sputtering by means of imparting more energy to vaporize the oil to sufficient density and to reduce fluorine contamination/oxidation which was attributed to considerable increase in resistivity and work function.

Acknowledgements

This work was supported by the Engineering and Physical Sciences Research Council [grant number EP/M015713/1] via the Wearable and flexible technologies enabled by advanced thin-film manufacture and metrology (WAFT) Collaboration. The authors would like to acknowledge Oxford Materials Characterization Services (OMCS) for equipment access and Phil Holdway for acquiring XPS data and Robin Vincent, Gideon Ring and Richard Turner for Technical Assistance.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2019.144294.

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