A Precision Capillary Coating System and Applications

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ABSTRACT
A precision direct patterning system based on capillary coating was developed to meet the requirements of a range of different applications. Silver ink with a viscosity of about 220 cP was initially used as a working fluid to study the effect of control parameters including the coater tip diameter, the coating velocity, the coating gap, and the back pressure. Quantitative analyses of the liquid bridge shape and wet film morphology, such as line thickness and width, were conducted to study the coating mechanism. A compact direct precision patterning desktop system with exchangeable coater modules was also developed for use in the laboratory, or even the home, to replace the tedious processes and cumbersome machines normally used. The application of a Hole Injection Layer on an OLED display panel was achieved and even the preparation of layers for costly biomedical processes involving antibodies were successfully demonstrated which shows the feasibility of this coating technique for different applications. The proposed coating system shows a very high material utility rate and has the potential to produce very complex patterns for research and industrial applications using material with a wide range of viscosity.

1. Introduction
In many industrial applications, ‘wet precision coating’ is an essential technique used in the manufacturing process. However, most precision coating is done using huge machines under conditions of mass production. The need for increasingly complex coating patterns has resulted in the design and development of a highly accurate direct pattern coating system. This precision patterning coating shows great potential in many different high-end applications. There are two main kinds of coating process; the first is continuous coating technology, which includes spin coating,[2] slot coating,[3,4] CVD,[5,6] PVD,[7] and others which all produce a flat uniform film. Standard photolithography can be used to remove unwanted parts of the film to produce the required pattern. The process is wasteful and can also become complicated if more than one kind of coating is needed. However, some etch-free methods, which save material, require the use of a...
Additive manufacturing has shown some recent development and small-scale customized manufacture seems to have great market potential. It is feasible now to operate a miniature coating machine in a laboratory or office environment or even at home. A small precision coating machine, with a user-friendly interface, that is not expensive to run, is feasible and can easily contribute to the realization of the personal microfactory concept. In this paper, the principle of capillary coating technique is explained, and the precision patterning systems on the workbench and desktop are introduced. Silver ink, with a viscosity of 220 cP, was used in the laboratory experiments, and the control parameters, including the tip diameter \((D_i)\) and \((D_o)\), the coating velocity \((V)\), the coating gap \((G)\), and the liquid pressure head \((H)\), were all investigated by studying the liquid bridge formed between the tip and the substrate. The physical and electrical properties were examined and measured. Two examples, which demonstrate the wide range of different uses to which the method may be put, are given: the application of a hole injection layer (HIL) on an OLED display and a biomedical procedure involving antibody/antigen reactions in a thin film.

2. The capillary coating method

2.1. Capillary coating

Capillary coating [12, 13] is a template-free direct-writing technique. The capillary tube fills itself by capillary action and there is no need for pumps or other devices. The basic working principle is the control of the relative motion between the fluid-filled capillary tube of the coater and the substrate.[14] The coating process is best explained in five steps as shown in Figure 1(a):

[Step 1] Installation of the capillary tube: The capillary tube is initially filled to a predetermined height with coating fluid before coating begins.

[Step 2] Formation of a liquid bridge: The capillary tube is lowered gently until it just makes contact with the substrate. The tube is then raised to specific preset height to form a gap \(G\) across which a bridge of liquid forms.

[Step 3] Fluid coating: After the formation of a stable liquid bridge, the substrate (on the coater table) is moved with a constant velocity \(V\) relative to the coater (or the substrate) to generate a stable shear force which pulls the liquid column out of the capillary onto the moving substrate.

[Step 4] Breaking the liquid bridge: At the end of the coated line, the capillary is raised to break the bridge and the section is completed.

[Step 5] The coater stage is moved to a new starting position and the process begins again.
Steps 1–5 are repeated until the full pattern has been completed. The relative position of the capillary with respect to the substrate is accurately controlled, as is the speed of movement and the gap \( G \). Careful programming of the substrate movement and capillary controls allows any kind of arbitrary pattern to be produced for use in a wide range of different applications.

As shown in Figure 1(b), the line pattern can be affected by several different parameters:

1. **The head pressure \( H \):** This has a direct effect on the coating liquid flow rate. It can be adjusted by changing the height of the liquid column or maintained constant by connecting the coater to a reservoir with a large cross section. The pressure head \( H \) can also be controlled by an active pressure source to increase the flow rate in different applications.

2. **Coating gap \( G \):** The coating gap influences the formation of the liquid bridge. To form a stable liquid bridge, \( G \) should typically be smaller than one-third of the nozzle tip diameter \( D_o \).

3. **Inner and outer diameters of the nozzle tip \( D_i \) and \( D_o \):** The outer diameter \( D_o \) of nozzle tip will determine the shape of the liquid bridge which also depends on different wetting conditions. As shown in Figure 2, the outer diameter \( D_o \) between 15 and 200 \( \mu m \) was investigated according to the line pattern required. The inner diameter \( D_i \) is linearly proportional to \( D_o \) and this plays an important role in viscous dissipation.

4. **Coating velocity \( V \):** The faster the substrate moves, the greater will be the shear force. Therefore, thinner films \( h \) and narrower lines \( w \) can generally be achieved with a high substrate velocity.

### 2.2. A precision patterning system on the workbench

As shown in Figure 3, the capillary coating system has four main parts.

1. **The Motion stage:** This has two linear motorized stages for moving the substrate in the \( X \) and \( Y \) directions, a microstep linear motorized stage for controlling the height of the coater module, a rotary motorized stage for adjusting the coating direction in the \( X-Y \) plane, and a 2-axes tilt platform for adjusting the levelness of the substrate. The substrate stage has six degrees of freedom and is capable of dealing with any complicated coating patterns. Each stage has a resolution of 1.0 \( \mu m \), and a maximum speed of 20 mm/s. The \( X-Y \) working range is 100 mm. The substrate is held to the stage by vacuum.

2. **Coater capillary module:** This module carries the coating head with the capillary and the reservoir. The minimum capillary tube diameter \( D_o \) that can be handled is 10 \( \mu m \) and the height of the capillary (the gap \( G \) above the substrate is dynamically controlled, see Figure 3(b). This allows the capillary to follow any changes in the contour of the substrate. The reservoir also helps to maintain a constant head of gravitational pressure for large area coating where flow rate is high.

3. **Image acquisition:** This includes a CCD camera with a high-magnification lens to observe the micro-coating process (which is too small for comfortable observation without magnification) in real time.

4. **Control unit:** All the mechanical motions are controlled from a desktop computer using a Graphical User Interface that was developed.
using LabVIEW software which not only controls but also allows online monitoring of the coating process. All the experimental devices were installed inside a laminar flow hood to reduce external disturbance and contamination during the coating process.

### 2.3. A precision patterning system on the desktop

A compact desktop direct precision patterning system was designed and developed for the experimental work and as such would be useful in any laboratory or office, see Figure 4(a). It has three main component parts:

(I) **Motion stage**: A linear translation stage was constructed using two stepper motors and linear slides to move the substrate in the X and Y directions. For the Z-axis, a translational and rotary stage was added to adjust the height and to set the capillary normal to the substrate.

(II) **Exchangeable coating module**: Coating modules can easily be exchanged for different coating purposes.

(III) **Control box and accessories**: Stage motion control was implemented using a precision position controller, and a vacuum suction plate was fitted to the stage to hold the substrate. An optional liquid pump can be utilized to deliver coating liquid from the reservoir to the coater on demand.

A transparent cover was designed for protecting the coater from dust to other outside disturbances. The customized graphical user interface allows easy programming to build whatever patterns are required. The design of the exchangeable coating module can be very helpful for different applications. For example, a module can hold several capillaries at the same time for high-throughput application, as shown in Figure 4(b), or a slot-die coater can be used for thin film coating.

### 3. Results of capillary coating

To demonstrate the superior capability of capillary coating when using highly viscous fluid, 20 wt% organic silver ink with a viscosity of around 220 cP (an order of magnitude higher than that of the upper viscosity limit for the inkjet printing method) was used as the coating material in this study. Because coating is affected by the outer tip diameter \( D_o \), the coating velocity \( V \), the coating gap \( G \), and the liquid head pressure \( H \), a real-time monitoring experiment was conducted. Front view and side view images were made to gain an understanding of the coating process. The surface morphology including line width \( w \), film thickness \( t \), and the electrical properties (resistance \( R \) and resistivity \( \rho \)) of the dried coated patterns, were all measured in a systematic study of the effect of each of these individual control parameters.

#### 3.1. Coating velocity \( V \)

As shown in Figure 5, the line width \( w \) and thickness \( t \) gradually decreases as the coating speed \( V \) is increased.
The fluid–substrate contact line becomes narrower as the coating speed increases, see the front view pictures. At a coating speed \( V \) of 10 mm/s, the line width was close to the outer diameter of the capillary tube \( (D_o) \). However, when \( V > 10 \) mm/s, the liquid bridge became unstable because the fluid feed was insufficient and the width and thickness of the line both shrank, see D in Figure 5.

Front and side diagrammatic views of the liquid bridge formed at different coating speeds between the capillary tip and the substrate are shown in Figure 6. From the front view (a), it can be seen that the contact lines change symmetrically about the center-line of the capillary tube and shrink toward the center as the speed \( V \) increases. This is caused by competition between the lateral fluid-wetting force and fluid–substrate shear force in the coating direction. As the speed \( V \) goes up, the line width becomes narrower. On the other hand, the side view (b) shows that the upstream contact line of the liquid bridge is pushed backwards by the opposing airstream. The strength of the airstream goes up as the coating speed rises. The curvature of the downstream portion of the liquid bridge becomes greater with increasing \( V \) and overlaps when \( V > 7 \) mm/s. To maintain a stable bridge and uniform line width and film thickness, the upstream contact line and downstream contours are clearly the most important factors for maintaining coating stability.

### 3.2. Coating gap (G)

The effect of gap widths \( G \) between 10 and 60 \( \mu \)m was investigated, and its effect on line thickness and width was measured at different coating speeds. As can be seen from the graphs in Figure 7(a) and (b), no big difference in line width and thickness is observed. It is worth noting that the bigger the gap, the smaller the operation range of coating velocity. Both the line thickness and width are strongly dependent on coating velocity for \( V < 5 \) mm/s, but relatively insensitive when \( V > 5 \) mm/s.

Similarly, the digitized upstream contact lines and downstream fluid bridge for different gaps were analyzed for \( V = 5 \) mm/s as shown in Figure 8. Except in the case of \( G = 10 \) \( \mu \)m, the results showed that the film thickness was not affected by \( G \) due to the overlapping of the downstream contours that determine the coating morphology. An increase in \( G \) would cause the upstream contact line to retreat further in the downstream direction due to more surface contact with the incoming airflow. In other words, a bigger \( G \) would cause instability and have an adverse effect on the usable coating velocity range. However, it was clear that the results using a gap \( G \) of 10 \( \mu \)m were different from the other cases, so a white light interferometer was used to scan the line contour as shown in Figure 9. Surprisingly, a discontinuity appeared in the center of the coated line which was clearly visible under a microscope. Interferometry revealed a distinct valley down the center of the line, see Figure 9(b) and (c). This could be the result of a strong shear force acting on the fluid between the tip and substrate which caused it to be drawn towards the edges of the line leaving an almost clear space down the center.
3.3. Liquid head pressure ($H$)

For a set gap size $G$ and inner capillary diameter ($D_i$), in other words for a fixed flow resistance, a higher liquid head pressure will allow more liquid flow. The results of an experiment using $H = 10$ and 30 mm under different $V$ and $G$ values are shown in Figure 10. The main difference seen was a narrower line with less head pressure especially with a smaller gap $G$. The head pressure has negligible effect on line width because the inertial force of the fluid ($H = 10$ mm) is very small compared to the lateral surface tension.

3.4. Tip outer diameter ($D_o$)

The inner ($D_i$) and outer ($D_o$) diameters of each capillary tube have excellent linear correlation as shown in Figure 2. For example, two representative tips with outer diameters of $D_o = 90$ and 200 μm (with corresponding $D_i = 56$ and 130 μm) were tested using different coating speed $V$ and gap $G$, see Figure 11. The results show that the capillary with the smallest $D_o$ gives the narrowest and thinnest line. However, the degree of wetting achieved by capillary tubes of different internal diameter $D_i$ is not the same. The feed rate through a narrow tube will be lower than that achieved by a wider capillary due to greater viscous loss. Also, the coating properties ($t$ and $w$) are less sensitive to $V$ in a smaller diameter $D_i$ because there is a relatively greater viscous force developed inside the capillary.

3.5. Measurement of electrical properties

After suitable drying and sintering, the electrical resistance ($R$) of patterned conducting circuits was measured, see Figure 12. With the exception of the line made with a gap $G$ of 10 μm, the resistances $R$ of lines made with different gaps were within the same range, and went up with an increase in coating speed $V$. The corresponding resistivity ($\rho$) can be calculated as follows,

$$\rho = R \times \left( \frac{A}{L} \right)$$  \hspace{1cm} (1)

the calculated resistivity for the coated lines was within the range of 6–12 $\mu\Omega$ cm, that of bulk silver is 1.6 $\mu\Omega$ cm.

4. Applications of the direct precision patterning system

4.1. Patterning feasibility test

Figure 13 shows a complicated two-dimensional pattern that was successfully produced with good repeatability, the lines were smooth, and the sharp corners were clean. The intersecting lines were well-defined and there were no disconnections or defects at the crossing points.
The coating was done using the workbench precision patterning system shown in the diagram in Figure 3(a). By setting different substrate temperatures and different coating speeds, different drying patterns could be obtained. It is worth noting that the HIL material dried almost as fast as it could be applied because it was relatively thin, especially in the heated environment used to avoid possible defects caused by partial wetting between the coating liquid and the substrate. Typical results for different coating velocity $V$ are shown in Figure 14. It should be noted that only the first and third rows of each specimen were coated with HIL material to make the comparison of coated and uncoated areas easy.

When the coating speed was low (see Figure 14(a)), the contact line between the coating liquid and the substrate was not smooth because the drying rate was lower than the liquid supply rate, and a non-uniform wavy pattern would form. Increasing the coating speed to more than 1.0 mm/s (Figure 14(b) and (c)), gave a good balance between the coating and drying rate and a uniform HIL film could be successfully generated on the substrate.

A similar result was achieved in the application of PEDOT: PSS as a HIL onto ITO film in an OLED fabrication process.

## 4.2. Direct coating on an OLED display

Capillary coating can also be applied in the display panel industry.[15] Figure 14 shows the glass substrate used in a coating and drying experiment. The microstructure was made by standard IC manufacturing technology, and special surface treatment was used to ensure the space between the HIL material and the barrier was not wettable. The size of each notch is 100 µm wide and 250 µm long, and the barrier height was 2 µm.
by capillary action. The liquid is replenished from a reservoir and no precise pressure control is needed during the coating process. In comparison to inkjet printing, which utilizes a spray of droplets to form the pattern, capillary coating can instantly ‘write’ any kind of arbitrary pattern. The advantages of the method include high precision and excellent material utilization in the production of a film that is uniformly thick and has very smooth edges. The effect of the control parameters, including coating velocity, the coating gap, liquid head pressure, and tip diameter, on the physical and electrical properties of the resulting coat were studied quantitatively in an elucidation of the mechanism.

The application of the device in three different fields: silver ink for circuits, a HIL on an OLED, and antibody reactions in a liquid layer, were successfully demonstrated to show the feasibility and superiority of this novel capillary coating method. A desktop device, similar to the one used in the experimental work, could be marketed as a compact precision patterning system for use in the laboratory, office, or even at home. The interface is intuitive and such a system would not be expensive. Complicated patterns could easily be generated using different exchangeable capillary coating modules. This kind of desktop precision coating system can be expected to lower the entry barrier for potential users in other fields where versatile coating is a requirement.

### 4.3. Direct coating for a biomedical application

The Western blot (WB) is widely used in biochemical research for such purposes as the determination of target proteins in cells and tissue and even for such procedures as the detection of HIV and Lyme disease in blood. However, this method requires large amounts of specific antibodies to probe the target antigens. In response to these issues, a thin-film direct coating (TDC) was introduced to Western Blotting (WB) for biomedical detection [16] and direct coating was used to lay down a very thin antibody containing film onto a test slide. This novel technique applies only few microliters of antibody film for a rapid interaction between the glutathione-S-transferase (GST) protein and antibody. The reaction occurs by diffusion within a very small volume in a short time. This procedure results in a remarkable improvement in efficiency of the technique and Tables 1 and 2 list comparisons with conventional WB. The thin coats of antibody-containing reactant were laid down as shown in Figure 15 using our desktop precision patterning system as shown in Figure 4(a). The amount of antibody used in this capillary coating method is three orders of magnitude smaller than needed for the slot coating method. The cost of reactants used can be reduced by 76% in comparison to traditional methods, see Table 1.

### 5. Conclusion

In this study a novel direct-writing process that uses capillary coating technology has been presented and a prototype desktop capillary coating device was designed and constructed. The technique utilizes a capillary tube filled with coating liquid which is drawn out onto the substrate by capillary action. The liquid is replenished from a reservoir and no precise pressure control is needed during the coating process. In comparison to inkjet printing, which utilizes a spray of droplets to form the pattern, capillary coating can instantly ‘write’ any kind of arbitrary pattern. The advantages of the method include high precision and excellent material utilization in the production of a film that is uniformly thick and has very smooth edges. The effect of the control parameters, including coating velocity, the coating gap, liquid head pressure, and tip diameter, on the physical and electrical properties of the resulting coat were studied quantitatively in an elucidation of the mechanism.

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### Terminology

- $A$: cross sectional area of coating film
- $D_i$: inner diameter of capillary tip


\[ D_o \] outer diameter of capillary tip
\[ G \] coating gap
\[ H \] head pressure (height of liquid column in the capillary)
\[ L \] line length
\[ t \] wet film thickness
\[ R \] electrical resistance
\[ V \] coating velocity (substrate moving velocity)
\[ w \] line width
\[ \mu \] viscosity of the coating fluid
\[ \rho \] electrical resistivity
\[ \sigma \] surface tension across the air–liquid interface

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