Spin Coating: A Guide to Theory and Techniques

Introduction to Spin Coating
Spin coating is one of the most common techniques for applying thin films to substrates. It is used in a wide variety of industries and technology sectors. The advantage of spin coating is its ability to quickly and easily produce very uniform films, ranging from a few nanometres to a few microns in thickness.

The use of spin coating in organic electronics and nanotechnology is widespread and has built upon many of the techniques used in other semiconductor industries. It also has some differences due to the relatively thin films and high uniformity required for effective device preparation, as well as the need for self-assembly and organisation to occur during the casting process.

In this guide we aim to introduce general spin coating concepts and also describe some of the specific techniques useful in organic electronics and nanotechnology.

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Spin Coating General Theory
Spin coating generally involves the application of a thin film (a few nm to a few um) evenly across the surface of a substrate by coating (casting) a solution of the desired material in a solvent (an “ink”) while it is rotating.

![Diagram of spin coating process](image)

Figure 1: Example of spin coating a small molecule in solution using a static dispense.

- First the substrate is coated in the ink containing the molecules dissolved in a solvent (1).
- Then the substrate is rotated at high speed and the majority of the ink is flung off the side (2).
- Airflow then dries the majority of the solvent, leaving a plasticised film (3) - before the film fully dries to just leave the molecules on the surface (4).
The rotation of the substrate at high speed (usually >10 rotations per second = 600 rpm) means that the centripetal force combined with the surface tension of the solution pulls the liquid coating into an even covering. During this time the solvent then evaporates to leave the desired material on the substrate in an even covering.

Spin Coating Applications

Spin coating applications can vary greatly. The technique can be used to coat small substrates (from a few mm square) or flat panel TVs which might be a metre or more in diameter. It is used for coating substrates with everything from photoresists, insulators, organic semiconductors, synthetic metals, nanomaterials, metal and metal oxide precursors, transparent conductive oxides, and many more materials. In short, it is ubiquitous throughout the semiconductor and nanotechnology R&D/Industrial sectors.

Advantages and Disadvantages of Spin Coating

The advantages of spin coating are the simplicity and relative ease with which a process can be set up, coupled with the thin and uniform coating that can be achieved. Due to the ability to have high spin speeds the high airflow leads to fast drying times, which in turn results in high consistency at both macroscopic and nano length scales.

The disadvantage of spin coating is that it is an inherently batch (single substrate) process and therefore has a relatively low throughput compared to roll-to-roll processes. The fast drying times can also lead to lower performance for some particular nano-technologies (small molecule OFETs for example), which require time to self-assemble and/or crystallise. Finally, the actual material usage in a spin coating process is typically very low (at around 10% or less), with the rest being flung off the side and wasted. Whilst this is not usually an issue for research environments, it is clearly wasteful for manufacturing.

Despite these drawbacks, spin coating is usually the starting point and benchmark for most academic and industrial processes that require a thin and uniform coating.

Special Requirements for Spin Coating Nanoparticles

In many areas of organic electronics and nanotechnology, the casting and drying stages of an ink are an integral part of the technology, and is where all the “action” happens. We often refer affectionately to our own area as “the science of paint drying”, and in all of the examples below, part or all of the key process happens during the drying of the ink, which is what makes the control of this critical.

- π-π stacking/crystallisation of a small molecule or polymers
- self-assembly of a block-copolymer
- phase separation of a polymer-fullerene blend
- aggregation/assembly of nanoparticles and colloids

In short, this means that when spin coating nanoparticles for OE/nano applications, the properties of the film don’t just depend upon its physical characteristics (thickness, uniformity) but also very strongly upon the processing (drying time and conditions). This compares with many more general spin coating processes such as applying a photoresist where the end result is broadly independent of the exact application route. For this reason there are a wider variety of techniques that are often used in organic electronics and nanotech - especially in a research environment.

In particular, for industrial processes spin coating would generally only be recommended at speeds of >1000 rpm to ensure the best uniformity. However in OE/nanotech, spin speeds down to 200 rpm might be used slow down the drying process and allow additional time for self-assembly. An industrial process engineer probably wouldn’t consider this to be spin coating at all but this sort of “pseudo-spinning” can be a powerful tool to investigate order and self-assembly.

![Figure 2: Drop casting slowly without rotation is a good way to provide highly ordered films at the nanoscale but at the expense of uniformity across the substrate.](image)

- A small molecule in a solvent is first dispensed across the substrate and as the solvent begins to evaporate this produces internal currents (1).
- The droplet shrinks in size with the internal currents depositing molecules at the receding edges (2).
- By slowing down the evaporation rate it is possible to have highly ordered films produced at the edges (3).
- However, the coating across the surface is usually high uneven with a typical “coffee-staining” effect (4).

By spin coating at very low speeds it is possible to get a combination of the high levels of nanoscale order produced by drop casting with the uniformity of spin coating.

https://www.ossila.com/pages/spin-coating

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Other issues in research environments are the requirement to coat often very small substrates, the desire to use in difficult spaces such as gloveboxes, and the wish to keep services (vacuum, compressed air or nitrogen) to a minimum. The ability to cope with chlorinated or aggressive solvents while being low-maintenance is also of beneficial for many applications. As such, this guide details a full range of spin coating techniques and issues that might be encountered in a typical research lab.

For most applications the most important consideration is the thickness of the film that is produced during spin coating.

Spin Coating Thickness Equation

In general, the thickness of a spin coated film is proportional to the inverse of the spin speed squared as in the below equation where \( t \) is the thickness and \( \omega \) is the angular velocity:

\[
t \propto \frac{1}{\sqrt{\omega}}
\]

Equation 1: Spin coating thickness equation.

This means that a film that is spun at four times the speed will be half as thick. A spin curve can also be calculated from this equation such as the below.

![Example spin curve for a solution.](image-url)

The exact thickness of a film will depend upon the material concentration and solvent evaporation rate (which in turn depends upon the solvent viscosity, vapour pressure, temperature and local humidity) and so for this reason spin thickness curves for new inks are most commonly determined empirically. Typically a test film is spin coated and the thickness measured either by ellipsometry or surface profilometry (Dektak). From this one or more datapoint(s) the spin thickness curve can be calculated - usually with a good degree of accuracy. The spin speed can then be adjusted to give the desired film thickness.

Spin Speed

The range of spin speeds available is important as it defines the range of thicknesses that can be achieved from a given solution. In general, spin coating can produce uniform films relatively easily from about 1000 rpm upwards, but with care and attention good film quality can be achieved down to around 500 or 600 rpm in most cases (and even lower in some cases). Most common spin coaters will also reach a maximum speed of 6000 to 8000 rpm (although specialist coaters may go to 12000 rpm or higher). As such, a normal range of working spin coating rpm might span a factor of ten (from say 600 rpm to 6000 rpm) which in turn means a maximum variation in film thickness of around a factor \( \sqrt{10} \approx 3.2 \).

For example, a solution which gives a film thickness of 10 nm at 6000 rpm will give a thickness of around 32 nm at 600 rpm and if a thicker film is required then the solution concentration would need to be adjusted. In the reverse scenario, if a solution gives a thickness of 100 nm at 600 rpm then the minimum thickness that can be achieved without diluting the solution will be 32 nm (100 x 3.2).

This dependence upon the square root of spin speed is both an advantage and a disadvantage. The disadvantage is that it means that the range of thicknesses that can be achieved from a given solution spans a relatively narrow range (around a factor of 3-4). On the other hand the advantage is that it allows precise control of film thickness within this range.

The maximum thickness that can be produced from a given material/solvent combination also depends upon the maximum concentration that the material can be dissolved in the solvent. For high solubility materials (100 mg/ml or higher) then thicknesses of >1 \( \mu \)m can be achieved. Meanwhile for some low solubility conjugated polymers (a few mg/ml) the maximum thickness might be limited to 20 nm or so.

At low concentrations the thickness of a film is approximately linearly dependent upon the concentration of the material in the ink, however as concentrations increase this will affect the viscosity of the ink and thus a non-linear relationship will develop.

Spin Coater (http://www.ossila.com/products/spin-coater) - Price and Specification
Spin Coating Duration

For most standard spin coating techniques the objective is to keep the substrate spinning until the film is fully dry. As such this will mainly depend upon the boiling point and vapour pressure of the solvent that is used but also on the ambient conditions (temperature and humidity) that the spin coating is performed in. For most solvents (such as the list below) a spin coating duration of 30 seconds is usually more than adequate and is therefore recommended as a starting point for most processes.

**Table 1:** Common solvents for which 30 seconds spin duration is usually adequate and those for which longer durations are required

<table>
<thead>
<tr>
<th>30 seconds usually adequate</th>
<th>Longer spin speeds required</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>Dichlorobenzene</td>
</tr>
<tr>
<td>IPA</td>
<td>Trichlorobenzene</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Diodooctane</td>
</tr>
<tr>
<td>Methanol</td>
<td>Octanethiol</td>
</tr>
<tr>
<td>Acetone</td>
<td>Glycerol</td>
</tr>
<tr>
<td>Butanone</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
</tr>
<tr>
<td>Xylene</td>
<td></td>
</tr>
<tr>
<td>Chloroform</td>
<td></td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td></td>
</tr>
</tbody>
</table>

For higher boiling point (and/or lower vapour pressure) solvents, drying may take considerably longer (up to ten minutes in some cases) and therefore these solvents are most commonly used either as additives or with additional drying steps (covered in later sections).

Probably the most important aspect to consider is the spin coating method used to dispense the solution - either a static dispense or a dynamic dispense.

In a static dispense the solution is placed upon the substrate while it is stationary and usually the entire substrate is covered in the solution before rotation begins. The spin coater is then started and brought up to required speed as fast as possible.

In a dynamic dispense the substrate is first started spinning and allowed to reach the desired spin speed before the solution is dispensed into the centre of the substrate. The centripetal force then rapidly pulls the solution from the middle of the substrate across the entire area before it dries.

Normally a pipette or pipettor ([https://www.ossila.com/products/micropipette-variable-volume](https://www.ossila.com/products/micropipette-variable-volume)) of some description is used to dispense a known volume of liquid on the surface.

Choosing a Spin Coating Method

In general, a dynamic dispense is preferred as it is a more controlled process that gives better substrate-to-substrate variation. This is because the solvent has less time to evaporate before the start of spinning and the ramp speed and dispense time is less critical (so long as the substrate has been allowed time to reach the desired rpm). A dynamic dispense also uses less ink in general although this does depend upon the wetting properties of the surface.

The disadvantage of a dynamic dispense is that it becomes increasingly difficult to get compete substrate coverage when using either low spin speeds below 1000 rpm or very viscous solutions. This is because there is insufficient centripetal force to pull the liquid across the surface, and the lower rotation speed also means that there is increased chance that the ink will be dispensed before the substrate has completed a full rotation (at 600 rpm the substrate is rotating once every 0.1 seconds, commensurate with a fast pipette drop). As such, we generally recommend using a static dispense at 500 rpm or below with either technique a possibility in the region between 500 - 1000 rpm.

Dynamic Dispense Spin Coating Technique

For the majority of spin coating above 1000 rpm we use a dynamic dispense as standard unless there are any special circumstances or difficulties.

Normally we would use a pipettor ([https://www.ossila.com/products/micropipette-variable-volume](https://www.ossila.com/products/micropipette-variable-volume)) to dispense a known amount of solution each time - usually 20 μl for most common substrates/inks on our standard sized (20 x 15 mm) substrates or around 100 μl for our 50 x 50 mm substrates. However, if there is a problem with wetting then increasing the volume may help.

The below image links to our video page which shows an example of dynamic dispense spin coating of PEDOT:PSS.
In order to get a high quality and consistent thin film the below points must be observed:

- The substrate should have reached its desired rotational speed before the dispense happens (usually only a few seconds).
- The ink should be deposited as close to the centre of the substrate as possible otherwise you may end up with a gap in the middle.
- The ink should be deposited in one quick and smooth action.
- The ink should be deposited in one and only one drop in order to prevent multiple coats.
- There should not be any bubbles blown onto the surface from the pipette.
- The pipette tip (https://www.ossila.com/products/pipette-tips) should never touch the rotating substrate.

It’s also worth noting that for spin coating we also use a pipettor in a non-standard way. Normally when pipetting a solution the pipette would be used to the second stop so that additional solution is sucked up into the tip and then discarded afterwards. However, this leads to a higher chance of additional drops or bubbles being cast onto the surface. As such, we only use pipettors to the first stop when spin coating.

The above points will help to provide the best possible film uniformity for a particular substrate. However, what we often find in a research environment is that for new users in particular (but also for experienced users) the variation between substrates is usually greater than the variation across a substrate. While often this is a small effect it can be an important consideration - especially for statistical results.

Figure 4: Example of statistical data in a typical lab environment for devices with multiple devices on each substrate. In a research environment there are usually a few poor pixels but the typical spread in device performance between devices can be small compared to the spread between substrates.

As such, to get the best possible consistency between substrates there is a critical “practise factor”. This refers to the fact that once an action (or combination of actions) has been done many times it is committed to “muscle memory” which means that it is done automatically with little or no conscious effort. This generally means that the dispense happens more consistently and precisely which has a knock on effect for the film quality.
As spin speeds decrease below 1000 rpm or with very viscous solutions it becomes increasingly difficult to get a high quality film. Therefore if possible we would generally recommend the reformulation of an ink (increased concentration or change in solvent) to allow spin coating above this speed. However, there are a great many situations in nanotechnology where this is either not desirable or not possible. For example, better crystallisation will happen at low speeds and some materials just don’t have sufficient solubility to reach the desired thickness at 1000 rpm.

A dynamic dispense can be achieved at speeds all the way down to around 500 rpm, however it becomes more difficult to get complete substrate coverage and so more ink is required (using a 50 μl dispense rather than 20 μl will help with coverage but at the expense of greater material wastage). As such we would generally consider the cut-off point to be around 700 rpm, below which the static dispense spin coating method starts to give better film quality.

When using a static dispense it is usual to coat the entire substrate (or at least all of the active part of the substrate) before starting the spin coating. However, this is itself can cause several issues. The first is that unless the substrate surface gives particularly good wetting for the ink (i.e. the ink likes to spread out across the surface) then it is usually necessary to use the pipette tip (https://www.ossila.com/products/pipette-tips) to “pull” the ink across the surface. However, it is of course very important for the pipette tip never to touch the surface of the substrate in the active areas as this can change the surface properties and/or damage any other layers present.

By carefully placing the pipette tip close to the surface such that it touches the edge of the ink droplet, it is possible to move the ink around the surface without touching it. Alternatively, if the edges of the substrate are not critical then the pipette tip can be moved around the edge of the substrate to pull the meniscus around. A third alternative is just to add more and more ink until the substrate is fully covered - however this is in general not recommended as it may take up to a ml of solution in extreme cases for this to happen. The below videos show all three of these techniques being used for static dispense spin coating.

This image links to our video demonstrating the static dispense spin coating method without touching the edge of the substrate.

This image links to our video page which demonstrates the static dispense spin coating method, including how to touch the substrate edges (inactive area) to spread the ink.
Finally, in some cases it is desirable to statically dispense a viscous solution and ensure that it coats right to the very edge of the substrate (for example spin coating PMMA as a gate insulator for our prefabricated ITO OFET substrates). In this case it is not easy to use the pipette tip to pull the meniscus to the edge without touching it due to the viscosity of the ink and the relatively low wettability.

Instead we use a different spin coating method where the pipette tip is angled at 45 degrees to the substrate and moved along the far edge of the substrate. This creates an effective technique to coat the PMMA right to the very edge of the substrate without touching it.

However, one of the main issues for a static dispense is that the solvent in the ink has some time to evaporate before the spin coating process begins. For low vapour pressure solvents such as water this is not too much of an issue, however for high vapour pressure solvents such as chloroform (around 10x higher than water) it can be critical and the time between depositing the solution and the start of spinning can make a big difference to both film thickness and film quality. **This is the primary reason why a static dispense gives lower substrate-to-substrate film uniformity and why a dynamic dispense is recommended if possible.**

### Automated Dispensing

For certain situations manual dispensing of solutions during spin coating may not be appropriate, these include:

- Specific timing needed for the dispensing of solutions.
- Specific dispense rate of the solution during spin coating.
- Dispensing of multiple layers being too repetitive and time consuming.
- Time between multiple dispenses is too short to perform manually.
In these situations the dispensing of the solution needs to be automated, this can be done through the use of a programmable syringe pump (products/syringe-pump). Syringe pumps work by displacing a volume of liquid at a specified rate at a given time, these values can be controlled to extremely high degrees of accuracies. Rates of dispense can vary from as low as 0.1 nl/s to as high as 10 ml/s, while the timing of the dispense can be controlled to within 10 ms allowing for a level of control that is not possible with manual solution dispensing.

The Ossila Syringe pump is an example of an automated dispenser, the system can be used to finely control the dispensing of two different solutions at once.

Syringe pumps are especially effective when dealing with dispensing multiple solutions, some examples of situations where multiple solutions are required are:

- **Multilayered Structures** - Structures that require alternating multilayer coatings, such as distributed Bragg reflectors (DBR's), can be fabricated rapidly and reproducibly when using an automated dispenser.
- **Improved Substrate Wetting** - Some situations require the washing of the substrate with a solvent before the dispensing of the solution to improve the wetting on the substrate, by timing the dispensing of the solution so that it occurs just as the solvent is evaporating the wetting can be dramatically improved.
- **Surface Washing** - The washing of the top surface of a deposited layer where the surface of a dry or a semi-dry film can be washed with a solvent in order to alter the properties of the upper surface and improve morphological structure. This can be done when depositing PEDOT:PSS, the post deposition washing with solvents such as methanol or DMSO can significantly improve the conductivity of the film.
- **Quenching of Deposited Films** - Quenching of films is done by flooding the drying film with an anti-solvent causing the material in solution to rapidly precipitate. Syringe pumps excel in these situations as you can not only time when the quenching occurs but also the rate at which it happens something that is impossible to do accurately during manual deposition.
Enable automated dispensing with the Ossila Syringe Pump

- Controllable Dispense Rates
- Accurate Timing
- Dual Syringes for Two Solutions

View Now ➤ [products/syringe-pump]

Ultra-low Spin Speeds and Covered Drying

As mentioned above, spin coating below around 1000 rpm the uniformity of films begins to be affected and below about 500 rpm this can cause significant issues. However, it is still possible to process films at speeds even lower than this and still get good results - albeit at the expense of consistency.

In some cases we have even tried spinning films at speeds of 120 rpm. While this can not really be described as spin coating it does still provide a significant increase in uniformity over drop casting because there is still some centripetal force. It also ensures that there are no effects due to the substrates being on a slight slope (getting a substrate sufficiently flat that an ink droplet does not move and dries evenly over the course of 5-10 minutes is difficult without a goniometer).

![Film uniformity at 1000 rpm (left) and 300 rpm (right).](image)

However, when spinning at ultra low speeds it's also important to consider the edge bead removal ([pages/spin-coating#two-step-spin-coating-and-edge-corner-bead-removal](https://www.ossila.com/pages/spin-coating#two-step-spin-coating-and-edge-corner-bead-removal)) which is described below.

As described in previous sections, often we want a slow drying film to allow for self organisation to occur but if we reduce the spin speed then we get non-uniform films. On the other hand if we change the solvent to something with a high boiling point we often end up with a thinner film (the ink has more time to migrate to the edge of the substrate before drying) and we often also end up with poor surface wetting (higher boiling point generally means higher intermolecular interactions and therefore more surface tension).

Spin Coating with Solvent Blends
A good way to optimise spin coating uniformity is to mix two solvents together; using a major component of something that evaporates relatively quickly and a minor component of something that is relatively slow to evaporate. By using this combination it is often possible to get the best of both worlds: during the spin coating process the major component evaporates quickly to give good coverage and a uniform thick film, and the remaining minor component still leaves enough plasticity for the molecules to self-organise before the film is completely dry.

<table>
<thead>
<tr>
<th>Solvent A</th>
<th>Solvent B</th>
<th>Mixture of A + B</th>
</tr>
</thead>
</table>

![Figure 5: Example of solvent blends.](image)

- **Solvent A**: If a low boiling point solvent (high evaporation rate) is used then coating can be achieved more easily but an amorphous (disorganised) film is produced.
- **Solvent B**: If a high boiling point (slow evaporation rate) solvent is used then coating is harder because the ink has time to dewet and is flung off the edge of the substrate leaving no coating.
- **Mixture of A & B**: If a mixture of solvents is used with a majority of low boiling point (fast evaporation rate) with minority of high boiling point (slow evaporation rate) then coating can still be achieved because the fast evaporating solvent is removed quickly leaving a plasticised film that is less likely to dewet but also gives the molecules time to organise themselves.

An example of this which works to good effect is the spin coating of P3HT for OFETs. Spin coating from pure chlorobenzene will give worse performance than spin coating from trichlorobenzene. However, spin coating from trichlorobenzene gives poor wetting and a very rough surface. By spin coating from a solution of 98% chlorobenzene and 2% trichlorobenzene the wetting is significantly improved and the performance remains almost as good.

**Two Step Spin Coating and Edge / Corner Bead Removal**

When spin coating with viscous or high boiling point solvents such as trichlorobenzene at very low spin speeds (below 500 rpm), the middle of the substrate often dries significantly quicker than the edge of the substrate. While the middle might be dry within a few seconds, in some cases the edge of the substrate may take minutes to dry. While the edges of the substrate are often designed not to contain any active/critical components, if the spin coater stops then the edge/corner bead may spread back towards the middle which can ruin the film quality.

The above image links to our video page demonstrating poor spin coating uniformity caused by the movement of corner beads back into the middle of the substrate as a result of the spin coater stopping before the edges of the substrate are dry.

https://www.ossila.com/pages/spin-coating
There are essentially two ways to remove the edge/corner beads. The first and more preferable way is to use a two-step spin, with the first step programmed to give the desired film thickness and sufficient time for the ink to dry over the majority of the substrate, and a second step at maximum rpm to fling off the corner beads and dry the remainder of the substrate.

![Video](pages/video-edge-bead-removal-using-two-stage-spin-coating)

This image links to our video page demonstrating how to use a two step spin to prevent corner beads from forming and affecting the film quality.

In most cases a two stage spin is the easier and preferable way to remove edge beads to improve spin coating uniformity. However there are some occasions where the second stage (high speed) spin is not desirable, for example if you want to remove the substrate from the spin coater while it is still slightly wet for further processing such as a methanol wash, vacuum dry or even slower drying in a solvent saturated atmosphere. In these cases a second but more delicate technique can be used to remove edge beads where by a fine cotton bud is used to absorb the excess solution while it is still spinning.

![Video](pages/video-edge-bead-removal-during-spin-coating-using-manual-technique)

The image links to our video page demonstrating the removal of corner beads with a cotton bud while spinning. This is a tricky technique and takes a little practise to master, but can be very effective.

The key is to avoid knocking the substrate off the chuck and also not to damage the active area on the substrate. For effective corner bead removal via cotton bud follow the below points:

- Approach the substrate very slowly.
- Steady your hand by resting it on the lid and use the centre-hole in the lid to steady and guide the cotton bud in.
- Try not to touch the actual substrate; hold the tip of the cotton bud a fraction above the substrate so that it is in contact with only the edge bead but not the substrate.
- “Feel” the cotton bud like a divining rod; even the most gentle touch of the cotton bud onto the substrate will produce a vibration which you should be able to feel.
- Watch the cotton bud closely; many organic and nanotech inks are coloured so you should be able to see when the cotton bud is close enough to absorb the ink.
- Try to keep the cotton bud as close to the edge of the substrate as possible.
Visible Assessment of Drying and Film Uniformity

Learn to trust your eyes - they are the primary tool and first line of analysis for almost all device engineering.

Microscopy by optical, electron, AFM or STM techniques will obviously give you a better and more quantitative assessment of nanostructure. Dektak or ellipsometry can provide better thickness and roughness calculations. However all of these techniques are slow, may damage the sample and/or introduce additional delays or variables to a process that can be critically dependent upon timings. They are not suitable for assessing every pixel on every substrate at every stage of a process - at least in an R&D environment.

The eyes are a highly sensitive and very versatile optical recognition system capable of discerning small differences quickly and effectively. With training and the correct lighting you can quite easily spot a 5 nm variation in film thickness just by looking at the colour. As such, inspecting a substrate visually before and after each step is critical for understanding and improving variation and performance:

- Does the film look uniform?
- Is the colour (thickness) as it should be?
- Does the surface have a glass-like, smooth-matt or rough-matt finish?
- Are there any aggregates on the surface?
- Are the any pin-holes or comet streaks?

In addition, with the correct lighting it is also possible to assess whether a spin coated layer is dry while the substrate is still spinning. In some cases (such as for many conjugated polymers) this is relatively easy because the film changes colour as it dries. In other cases it will be more difficult as there is no obvious colour change.

However, as a film dries it generally reduces in thickness from a wet layer of a few tens-hundreds of microns to a dry layer of a few tens-hundreds of nanometres. During this time the film thickness is of the order of a few wavelengths of visible light which means that the reflectance properties will be interference based and highly non-linear. As such, even for a nominally transparent material in a transparent solvent the apparent colour will change as the film decreases in thickness and once the film stops changing colour it is predominantly dry (note that residual solvent is another issue and can be very hard to remove).

This image links to our video page demonstration of the film changing colour during spin coating as the solvent dries. In this example P3HT in TCB was spun on silicon.

This image links to our video page demonstrating the interference effects observed during the drying stages of spin coating. When the substrate stops changing colour it is a good indication that it has predominantly dried. Here, TCB is spun onto silicon in this example.
Spin Cleaning and Wash Steps

Spin coating can also be used to clean substrates, however our experience of this is that in general it produces relatively poor results compared to sonic bath based cleaning and is slow compared to cleaning a batch of substrates at a time. It also often results in large volumes of solvents being used in the spin coater, which can be a problem if these steps are performed in an environment where that solvent needs to be removed (for example a laminar flow).

However, there are times when spin cleaning and wash steps can be very useful, for example HMDS and certain other surface modification treatments benefit from a spin-wash. Meanwhile, spin coating a semi-orthogonal solvent can also be used to remove certain additives.

When spin washing we generally use a dynamic dispense of a medium volume of solvent (50 µl for the standard 20 x 15 mm substrates) and may wash several times. Beware of the fact though that this will create significant solvent vapour that can affect the drying dynamics of subsequent films if the solvent is not removed first (usually by wiping excess solvent from the inside of the spin coater with a clean-room tissue).

Avoiding a Hole in Middle of Film

A common spin coating defect for beginners is to see a hole in the middle of the substrate with no coating on it such as in the image below.

![Hole in Middle of Film](image)

This is typically cause by the ink not being dispensed in the middle of the substrate. Since the centripetal force will always make the ink flow to the edge of the substrate the middle will not get coated. By dispensing the ink closer to the centre of the substrate this should be eliminated. Note that by using the edge of the centre-hole in the lid to guide the pipette it can be positioned more accurately.

Avoiding Vacuum Warping of Substrate

Many spin coaters use vacuums to hold the substrates in place. Not only does this often cause problems for spin coater maintenance (the vacuum is often trying to suck in the ink and solvents) but it can also warp the substrates slightly which causes uniformity problems. The extent of the problem will depend upon the thickness of the substrate, the strength of the vacuum and the size of the vacuum aperture. The image below demonstrates the effects of vacuum warpage on film uniformity.

![Vacuum Warping](image)

The mechanical stiffness of a substrate is proportional to the cube of its thickness so a 1.1 mm thick substrate will be eight times stiffer than the equivalent 0.55 mm substrate. In general we have found that substrate warping becomes an issue for substrates of less than around 1 mm in thickness and the effects are worse at low speed (where there is less centripetal force).

The effects of vacuum warpage are one of the primary reasons why we developed the Vacuum free Spin Coater (/products/spin-coater). Firstly, we found that in order to improve the uniformity of the films we had to eliminate the vacuum and so designed specialist chucks (/products/spin-coater-chucks) to place on top our old spin coaters to eliminate the vacuum and hold the substrates in place mechanically. This technique worked brilliantly, but eventually we also got fed up with the vacuum pumps forever needing servicing and we decided to simply design a better spin coater (/products/spin-coater) which has since become one of our most popular pieces of lab equipment.

The below points will also help to alleviate the problem of vacuum warpage:

- Use thicker substrates
- Use higher spin speeds
- Mount the substrate on a thick carrier plate before spin coating.

Spin Coating Low Viscosity Solvents
When spin coating viscosity of a solvent can have a major impact on film quality. Certain solvents which are prevalent in research fields for historical or other reasons have very low viscosities which can provide significant issues. Examples of this kind of solvent include chloroform and acetone and there are two primary issues here:

- The solution dripping out of the pipette before it is supposed to and
- The film drying before an even wet-layer has been produced, which creates swirls in the substrate.

With regards to the ink dropping out of the pipette before it is supposed to, the first thing to do is to use the smallest size pipette tip (https://www.ossila.com/products/pipette-tips) that is available as it will have a smaller diameter aperture at the end and reduce dripping. It also helps to pipette the minimum amount of ink required for coating as that will reduce the effect of the weight compared to the surface tension (10 µl of solution will weigh half as much as 20 µl but the surface tension remains the same).

If the solvent is halogenated (such as chloroform) then it can also help to leave the pipette tip in the ink for a few seconds before removing it. The reason for this is that most pipette tips are made of polypropylene which will not dissolve in halogenated solvents but will swell slightly which will reduce the effective diameter of the aperture.

This image links to our video page demonstrating a pipette used to draw up 20 µl of chloroform which then drips out of the end. However, after immersion for 10 more seconds the chloroform no longer drips out.

This technique does not work for non-halogenated solvents such as acetone as they will not swell the polypropylene. As such an alternative is to tilt the pipettor at an angle to reduce the weight to surface tension ratio, returning the pipettor to vertical only just before dispensing the solvent. Care must be taken not to tilt the pipettor to the extent that solvent will enter the pipettor and damage it.

Ambient Conditions and Changes in Drying Time

For many organic electronics and nanotech applications the drying time and film properties are intimately linked and for this reason the ambient conditions can sometimes have significant effects. A professional cleanroom will usually have a relatively well controlled temperature and humidity and a glovebox is usually a pure nitrogen atmosphere. However, research labs are often not so well controlled and while this may not make much of a difference in most cases there are some extreme examples that can affect consistency and result in spin coating defects.

Here in the UK the ambient humidity in summer can swing quite dramatically from less than 20% to nearly 100% depending upon the weather. On times of very high humidity, typically during a rainstorm, we have noticed that films spun from aqueous solutions are still wet after the normal 30 second spin duration and this can have a significant effect on device performance. As such, although the majority of our work is done in temperature/humidity controlled environments we still keep a close eye on the ambient conditions and usually place a thermometer/hygrometer next to the spin coater.

If coating multiple large substrates with large volumes of solvent (100 µl or more) then it is also possible for the solvent to start pooling in the basin of the spin coater, which can also have the same effect as to increase the ambient vapour pressure and increase drying times. A simple solution to this is to wipe dry the spin coater basin after every spin if large volumes of solvent are used.

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Incomplete Coating of Substrate

The wetting of an ink onto a substrate is generally characterised by the contact angle of the liquid onto the surface. A low contact angle means good wettability (the ink likes to spread across the substrate) while a high contact angle means poor wettability (the ink likes to ball up).
Figure 6: A high contact angle means poor wettability while a low contact angle means high wettability. A drop of water on a lotus leaf is a good example of poor wetting while the alcohol in wine helps wetting and leads to the “legs”. In general a 90 degree contact angle is considered the cut-off between wetting and dewetting but can still lead to difficulty coating.

The contact angle will depend upon the surface tension of the liquid and the surface energy of the substrate. A liquid with a high surface tension wants to ball up more than a liquid with a low surface tension. Meanwhile, a substrate with a high surface energy is more likely to attract the ink as it will result in an overall lower energy state.

Some ink / substrate combinations will coat very nicely with the ink wanting to spread across the surface while in other cases it will want to ball up. In extreme cases this can mean that it is simply not possible to coat an ink onto a surface. More commonly it is simply difficult to wet a surface and this often results in partial coating of the substrate.

The first and simplest solution to this problem is simply to deposit more ink - for example for our standard 20 x 15 mm substrates we might increase the dispense volume on the pipettor (https://www.os silica.com/products/micropipette-variable-volume) from 20 to 50 or even 100 µL. Increasing the temperature of the ink and dispensing warm or hot can also help by reducing the surface tension and increase the evaporation rate so that there is less time for the ink to dewet from the surface.

However, if the above options don’t work then it is usually necessary to either change the solvent in the ink to something with a lower surface tension or to treat the substrate in some way such as by a UV/ozone or oxygen plasma to increase surface energy (note that this is often not desirable for organic based transistors where a low surface energy is key to high performance).

Common Spin Coating Defects: Pin Holes & Comet Streaks

The physical and chemical cleanliness of a substrate is critical for high quality films regardless of the application method. For spin coating the effect of dust and particulate matter is usually to cause pin holes and comet streaks, however this can also be caused by particles in the ink described in the below section.

To remove dust and particulate matter we generally recommend the use of an electronic grade detergent such as Hellmanex III (/products/hellmanex-iii). However, it's also important to remove any residues on the surface for which a semi-polar solvent such as acetone/IPA is helpful. Finally, it is usually worth chemically preparing a substrate before applying the first layer by using either a basic NaOH solution or an oxygen plasma/UV Ozone to produce "-OH" terminations which are excellent for most coating processes. As such, we use the below standard cleaning routine for most substrates. Where possible we use a solution-based NaOH process for providing "-OH" surface terminations for ease and simplicity but in the case of silicon this will wreck the surface so we use an oxygen plasma treatment instead.

Once a substrate is clean we then usually store it in a clean environment (often in DI water) to avoid dust and other contaminants. This is important as even though dust can be blown off a substrate it often leads to a change in surface energy where the dust particle was placed which can lead to pin-holes on the surface such as the below example.

Figure 7: The effect of dust on surface wetting

Aggregation and Filtration
For many OE/nanotech inks there is the possibility of aggregates or crystallites forming in solution prior to deposition of even during the spin coating process. This can lead to comet streaks or large lumps of aggregation left on the surface.

Generally, heating and stirring a solution will help to dissolve the active materials and then cooling and filtering will remove any aggregates and undissolved material and this can often have significant effects on device performance. In the below examples we show the improvement in device performance for both OFETS and OPVs after a solution has been filtered.

![Graph showing PCE (%) for different filter makes](image)

**Figure 8: Effect of filtration on P3HT:PCBM OPV performance.**

However, for many materials an ink solution may not be stable and will re-form aggregates or crystallites over time, such as the below examples of P3HT fibrils, PCBM crystallites and F8BT aggregates, all of which will form if an ink is left standing for long times (hours to days).

<table>
<thead>
<tr>
<th>PCB crystallites under an optical microscope</th>
<th>P3HT aggregates in a thin film via AFM</th>
<th>F8BT aggregation in a working OLED pixel</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Image of PCB crystallites" /></td>
<td><img src="image" alt="Image of P3HT aggregates" /></td>
<td><img src="image" alt="Image of F8BT aggregation" /></td>
</tr>
</tbody>
</table>

> **Figure 9: Aggregates of different materials and the approximate timescales required. In all cases the solutions were filtered prior to storage.**

In some cases it’s possible to re-dissolve these particles by re-heating/stirring and often it’s worth filtering a second time after the solution has cooled. However, in some cases, such as for PCBM, the energy of crystallisation is significant and therefore it’s very difficult, if not impossible (depending on the solvent) to re-dissolve them, therefore fresh solutions should be used each time.

However, before filtering any solution it is always worth considering the size of any solutes relative to the filter pore size; while polymers, PCBM, and small nanoparticles (<20 nm or so) can all be filtered without problems, larger nanoparticles or graphene flakes have a large chance of being caught in the filter and totally removed from the solution (leaving just solvent).

**Conclusions**

Spin coating is an incredibly effective and important technique for thin film and organic research and with a little practise it can be utilised to produce high quality, uniform films.

As mentioned earlier, we use our own vacuum free Spin Coater in our labs which we find reduces the possibility of substrate warping, helps to improve film quality and requires far less space in a lab and glovebox than standard vacuum spin coaters.

The Personal Spin Coater is powerful and versatile, with speed ranging from 100 rpm to 6000 rpm and 100 programs each with up to 100 steps. For more information visit our Spin Coater page or get in touch with us to discuss your questions with our technical support team.
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