Evaporation Effect on Thickness Distribution for Spin-Coated Films on Rectangular and Circular Substrates

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Abstract: Spin-coating is widely applied in the field of thin-film fabrication due to its simplicity and high film uniformity. To prepare thin films on rectangular substrates by spin-coating, the simulation and experimental methods were used to study the characteristics of the film thickness in this work. The two-phase flow simulations of spin-coating on a rectangular substrate and circular substrate were carried out with the volume of fluid (VOF) method. The simulation results showed that the airflow field and the substrate geometry had little effect on the evolution of spin-coated film thickness. However, in the experimental results, there was a significant difference in the thickness of the spin-coated film on the rectangular substrate and the circular substrate. According to further study, the solvent evaporation that was neglected in the simulation was the dominant factor of the differences. In addition, it was concluded that the non-uniform evaporation caused by the surface tension and edge accumulation in the later spin-coating stage was the main reason for the film accumulation of the windward area on the rectangular substrate. This work is useful to obtain a deeper understanding of the thin-film formation mechanism of spin-coating.

Keywords: spin-coating; rectangular substrate; film thickness distribution; two-phase flow; solvent evaporation

1. Introduction

The thin film on the workpiece surface is essential for ensuring and improving the performance of devices such as integrated circuits, laser equipment, and display devices [1]. The spin-coating method is currently the most widely used film-forming technology, with the advantage of high reliability and a simple operation. The demand for film preparation is no longer limited to the traditional circular substrate, and there is increasing demand for uniform film formation on a rectangular substrate. For example, the gratings that are widely used in laser devices are rectangular and uniform resin films are required to ensure the accuracy of lithography. Additionally, in the Organic Light-Emitting Diode (OLED) display technology, the preparation of a uniform organic electroluminescent layer on the rectangular substrate is important for a high-quality display [2–5]. Therefore, the film thickness distribution prepared by spin-coating needs to be further studied to meet the increasing demand for films with high uniformity.

Spin-coated film thickness has been widely discussed since the 1950s. Emslie et al. proposed an analytical model to predict the film thickness based on the balance between shear force and centrifugal force of Newtonian fluid [6]. Based on Emslie’s model, Acrivos et al. added fluid rheological properties to the model to analyze the film thickness of the non-Newtonian power-law fluid [7]. To simulate the real spin-coating process, Meyerhofer et al. considered the effect of solvent evaporation in the model, and this was the first attempt to consider the mass transfer in the model to estimate the film thickness [8,9]. Due to the complexity of the analytical model of the spin-coating process, researchers were more inclined to establish an empirical model according to the high number of experimental
results. Spanglar et al. considered the initial viscosity of the solution in the spin-coating process and predicted the film thickness with the help of an empirical model [10]. Chen and Lawrence et al. took parameters such as solvent evaporation and solute diffusion coefficient into account to make the empirical model more accurate [11,12]. There were also some numerical simulation studies on the spin-coating process, but due to the limitation of the maximum aspect ratio \((h/R \gg 1, h: \text{film thickness}, R: \text{radius of the substrate})\) of the spin-coating process, most researchers simplified the spin-coating process into a one-dimensional or two-dimensional axisymmetric model to make it easier to obtain the film distribution [13,14]. However, the axisymmetric model is not accurate enough to investigate the spin-coating process on asymmetric substrate.

Furthermore, researchers also focused on the film thickness distribution characteristics. Bornside et al. combined the numerical simulation and experimental methods to study the influence of gas flow in the spin-coating process on the radial thickness of films [15]. Kozuka and Shiratori et al. studied the fringe characteristics during the spin-coating process [16,17]. In their model, the effects of centrifugal force and effects on the film thickness were considered. Shiratori et al. explained the mechanism of the double-peaked edge-bead effect by combining analytical model and experiments [18]. According to their results, the solutocapillary flow, caused by the solvent evaporation, is the dominant physics for the double-peak formation. Arscott et al. established a theoretical model of edge-bead effect reflux flattening [19]. It was found that the changing physical properties of the spin-coated viscous liquid place limitations on the ultimate achievable practical planarization of the film. There are also some studies on the preparation of thin films by spin-coating on rectangular substrates. Carcano and Luurtsema et al. studied the film prepared by spin-coating on the rectangular substrate [20,21]. Most of the studies proposed axisymmetric models to analyze the effect of centrifugal force, solution viscosity and solvent evaporation on film thickness distribution for the spin-coating process. However, for the asymmetric substrate, the features of liquid accumulation and increasing local air velocity that make the film uniform in the corner region of the substrate are poorly investigated. The quantified impacts of solvent evaporation, shear force and Bernoulli effect are unclear, and further study is needed.

Most of the studies on the film thickness distribution of the spin-coating process are carried out for the infinite plate or circular substrate, without considering the influence of the geometry of the substrate. In this work, the process of spin-coating on the rectangular substrate is studied to explore the influence of substrate geometry on the evolution and distribution of the film thickness. Two-phase flow numerical simulation models are established on circular and rectangular substrates and the effects of substrate shape on the film thickness evolution and distribution are analyzed. In addition, the difference between spin-coating films on two kinds of substrates is compared through experiments, and the film thickness evolution and film thickness distribution of the spin-coating process on rectangular substrates are explained.

2. Numerical Simulation and Experiment

2.1. Simulation Model and Conditions

In this paper, a multiphase flow model is used to simulate the spin-coating process. The geometric model and meshing of the spin-coating process are shown in Figure 1a. In the simulation, a gradient meshing method was used to ensure that the mesh size near the substrate is small enough, and that there were enough meshing layers in the liquid film to represent the characteristics of the flow field at the final stage of spin-coating. The parameters representing the mesh quality are also listed in Figure 1a. Skewness was defined as the difference between the shape of the cell and the shape of an equilateral cell of equivalent volume. The maximum skewness for a triangular/tetrahedral mesh in most flows should be kept below 0.95, with an average value that is significantly lower. Orthogonal quality is also generally used to assess the mesh shape quality, as the skewness of mesh structures, as 0 is worst and 1 is the best. As displayed in Figure 1a,
the skewness and orthogonal quality of the two models met the requirements and showed good convergence in the calculation. The grid independence and convergence test were carried out to prove the accuracy of the model. In addition, for simulation of the spin-coating process on the rectangular substrate, the shape of the whole calculation area was rectangular (Figure 1a) to avoid large mesh distortion, which made the calculation difficult to converge. The boundary conditions used in the simulation and some feature sizes are indicated in Figure 1b. The substrate height was set as 500 µm. The radius of the circular substrate was 10 mm and the size of the rectangular substrate was 24 mm × 15 mm. The coating fluid was set as a Newtonian fluid, with a constant liquid viscosity. The coating fluid density was 950 kg/m³, the dynamic viscosity was 1.86 kg/(m·s), and the surface tension was 0.0212 N/m. It was assumed that the coating fluid and substrate were surrounded by gas (air) at room temperature (15 °C) and ambient pressure (1.01 MPa). The gas density was 1.225 kg/m³, and its dynamic viscosity was 1.79×10⁻³ kg/(m·s). The gravitational acceleration is −9.81 m/s² in the z-direction. Any evaporation that might have influenced viscosity and surface tension is ignored during the thin-film-spreading process. The main simulation parameters adopted in this paper are listed in Table 1.

Figure 1. Numerical simulation detail of spin-coating process. (a) Geometric model and meshing; (b) Boundary conditions and characteristic dimensions.
Table 1. Parameters used in the simulation cases.

| Simulation Parameters | Units       | Value          |
|-----------------------|-------------|----------------|
| number of phases      | –           | 2              |
| solution density      | kg/m³       | 950            |
| solution viscosity    | kg/(m·s)    | 1.86           |
| mesh motion rotational speed | rad/s | 104.8         |
| operating pressure    | Pa          | 101,325        |
| operating density     | kg/m³       | 1.225          |
| surface tension coeff | n/m         | 0.0215         |
| contact angle         | °           | 15             |
| time step size        | s           | 0.0001         |
| number of time step   | –           | 60,000         |
| initial liquid film thickness | µm | 700           |

2.2. Volume of Fluid Method

The VOF two-phase flow model is used to simulate the spin-coating process [22,23], and mainly explores the spreading of liquid film and the evolution of film thickness in spin-coating progress. The VOF model is usually used to simulate a variety of different immiscible fluids and can better simulate the free interface between two phases. The fraction of the fluid volume occupied by liquid or gas in a grid is used to calculate the position and movement of the free surfaces, which are the boundary surfaces between the two fluids. In each control volume, the sum of the volume fraction ratios of all phases is 1, and all phases shared the same variables and physical properties. In this way, the variables and their attributes in any given unit would appear in three states (the volume fraction of phase in the unit body was denoted as \(a_i\)): the cell is empty \((a_i = 0)\); the cell is full of one phase \((volume\ fraction\ ratio\ a_i = 1)\); the cell is filled with multiphase \((0 < a_i < 1)\).

Tracking the interface between phases is accomplished by solving the continuity equation for the volume fraction of one phase or multiple phases. For phase \(i\), the equation is as follows:

\[
\frac{\partial a_i}{\partial t} + \vec{v} \cdot \nabla a_i = \frac{S_{a_i}}{\rho_i}
\]

(1)

The quality source term at the right end of Equation (1) is 0 of the default. The main phase volume fraction is calculated based on \(\sum_{i=1}^{n} a_i\). \(\vec{v}\) is velocity vector, \(S_{a_i}\) is mass source, \(\rho_i\) is density of each phase.

The governing equation in computational-fluid-dynamics(CFD) is

\[
\frac{1}{\rho} \frac{\partial \rho}{\partial t} + \nabla \cdot \vec{v} = 0
\]

(2)

\[
\frac{\partial \vec{v}}{\partial t} + (\vec{v} \cdot \nabla) \vec{v} = -\frac{1}{\rho} \nabla p + \vec{f} + \mu \nabla^2 \vec{v}
\]

(3)

In the VOF model, properties such as density, viscosity, and velocity field in the equation are shared in each phase. Taking the density property in two-phase flow as an example, the density in each unit is

\[
\rho = a_2 \rho_2 + (1 - a_2) \rho_1
\]

(4)

and other properties, such as viscosity, are also calculated in this way.

The choice of laminar flow or turbulent flow model in the simulation process is judged by the Reynolds number

\[
Re = \frac{\rho v L}{\mu}
\]

(5)

where \(\rho\) is the density of the solution, \(v\) is the characteristic velocity of the flow field, \(L\) is the characteristic length of the flow field, and \(\mu\) is the hydrodynamic viscosity coefficient.
In the spin-coating process simulated in this paper, the thickness of the liquid film is in the micron dimension, the rotating speed is 1000 rpm, and the flow field velocity is small, so a laminar flow model is adopted in this simulation.

2.3. Experimental Setup

The spin-coating process can be divided into three stages, as shown in Figure 2: deposition, spin-off, and drying. In this experiment, the solution is dropped on the substrate when the substrate is still. The spin-off process is the main stage of liquid film thinning, and solution radial spreading and solvent evaporation are the two main reasons for liquid film thinning.

Rzj-304-10 positive photoresist (Suzhou Ruihong Electronic Chemicals Co. Ltd., Suzhou, China) was deposited on rectangular (120 mm × 80 mm × 0.625 mm) and circular substrates (6 inch surface polishing silicon wafer), as shown in Figure 2, and the spin-coating experiment was carried out on the KW-4B (Institute of Microelectronics, Chinese Academy of Sciences, Beijing, China) spin coater. The film thickness was measured with the OEM-MAP (Ellitop Scientific Co., Ltd., Beijing, China), as shown in Figure 3a. The probe of the measuring instrument was fixed on a two-coordinate moving platform, which can be moved to any position in the plane. The measurement schematic diagram of the thin film on the substrate with two shapes is shown in Figure 3b, and the red dot is the selected scanning measurement point. The central region of the film on the rectangular substrate was measured by equal intervals (8 mm in length and 5 mm in width). More points were measured in the edge region to describe the characteristics of the film on the edge of the substrate with an interval of (1 mm). For the circular substrate, the ring-scanning measurement method was adopted, and the measurement radius increased by 10 mm each time. Additionally, more points were measured with an interval of (1 mm) at the film edge to obtain the thickness distribution characteristics of the film edge.
3. Results and Discussion

3.1. Validation of the Numerical Simulation Model

To verify the validity of the numerical simulation of the 3D spin-coating process, the time-varying process of the film thickness on the two shapes of the substrate obtained by numerical simulation was compared with the results of the analytical model proposed by Emslie [6]. The analytical model established by Emslie simplified the spin-coating process. Firstly, the spin-coating process is regarded as an infinite horizontal plane, so there is no radial component of gravity. The liquid is considered a Newtonian fluid, which means the viscosity of the fluid remains constant. In the cylindrical coordinate system, the balance between viscous force and centrifugal force in unit volume is established:

$$-\eta \frac{\partial^2 v}{\partial z^2} = \rho \omega^2 r$$

where $\eta$ is the dynamic viscosity of the solution, $v$ is the radial flow rate, $z$ is the height, $\rho$ is the density of the solution, $\omega$ is the rotating speed, and $r$ is the radial position.

The boundary condition is $z = 0, v = 0$; $z = h, \frac{\partial v}{\partial z} = 0$, and the solution of Equation (6) is

$$v = \frac{1}{\eta} \left( -\frac{1}{2} \rho \omega^2 r z^2 + \rho \omega^2 rhz \right)$$

The radial flow per unit circumference length is,

$$q = \int_0^h v \, dz = \frac{\rho \omega^2 rh^3}{3\eta}$$
The combined continuity equation is

\[ \frac{\partial h}{\partial t} = -\frac{\partial (rq)}{\partial r} \]  

(9)

The partial differential equation of film thickness \( h \) concerning radial position \( r \) and time \( t \) is obtained by

\[ \frac{\partial h}{\partial t} = -K \frac{1}{r} \frac{\partial (r^2h^3)}{\partial r} \]  

(10)

where \( K = \frac{\rho \omega^2}{3\eta} \).

If the film thickness \( h \) changes only for time \( t \), the particular solution is:

\[ h = \frac{h_0}{(1 + 4Kh_0^2t)^{\frac{1}{2}}} \]  

(11)

The film thickness \( h \) is a function of time \( t \) and radial position \( r \), so there is the following full differential equation,

\[ \frac{\partial h}{\partial t} = \frac{\partial h}{\partial t} + \frac{\partial h}{\partial r} \frac{dr}{dt} \]  

(12)

According to Equations (10) and (12), the solution should be

\[ h = \frac{h_0}{(1 + 4Kh_0^2t)^{\frac{1}{2}}} \]  

(13)

\[ r = r_0 \left( 1 + 4Kh_0^2t \right)^{\frac{3}{4}} \]  

(14)

Equation (13) is the time-varying solution obtained under the assumption that the film thickness is independent of the radial position. Emslie [6] also numerically calculated the general solution, and the result showed that the film thickness tended to change with time at any radial position.

The comparison of the film thickness time-variation rule between the numerical simulation and analytical solution with the same parameters were shown in Figure 4. The average value of film thickness of the central region excluded the edge bead region. The results showed that the numerical simulation agreed well with the analytical prediction results. Therefore, the numerical simulation model is considered accurate enough to calculate the film-thinning process.

**Figure 4.** Comparison of results of numerical simulation and analytical model. (*\( h_{c0} \): average film thickness of the central region on the circular substrate in the simulation. *\( h_{r0} \): average film thickness of the central region on the rectangular substrate in the simulation).
3.2. Evolution of Film Thickness in the Central Region

The influence of substrate shape film thickness in the central region of spin-coated films was studied. In the theoretical model proposed by Emslie, the film was supposed to be spin-coated on an infinite plate, and the influence of substrate geometry on the evolution of film thickness was not discussed. In this paper, the VOF model was used to establish a three-dimensional spin-coating numerical simulation model, and the influence of substrate shape on the evolution of film thickness in the spin-coating process was studied.

Different from the analytical model, the two-phase flow model was used in the numerical simulation to simulate the interaction between air and liquid. According to the results displayed in Figure 4, the film thickness at different moments of the VOF model and the analytical model was compared. It can be concluded that when the solvent evaporation was ignored, the effect of the airflow on the film thickness thinning process during the spin-coating was very small. In addition, under the simulated conditions adopted in this paper (evaporation is not considered), the difference in film thickness between the rectangular substrate and circular substrate at each timepoint in the progress of spin-coating was very small \( (h_{r0} - h_{c0})/h_{c0} \leq 2\% \), and the evolution rule of film thickness was almost the same. According to the simulation results, it could be concluded that the shape of the substrate had little effect on the evolution of the film thickness during the spin-coating process without considering the solvent evaporation.

To verify the influence of substrate shape on the evolution of film thickness, spin-coating experiments were carried out on rectangular and circular substrates at different rotating speeds 1000, 2000, 3000, 4000 and 5000 rpm. Three groups of experiments were conducted, and the results of the final film thickness at each rotational speed were shown in Figure 5. The average film thickness of the central region was taken as the actual film thickness at this rotating speed, and the standard deviation of each set of data was taken as the error bar. Table 2 showed the results that the film thickness on the rectangular substrate was larger than that of the circular substrate at all speeds. The difference in film thickness ranged from about 5% to 15% and it tended to increase with the rotating speed. This result was inconsistent with the conclusion that the evolution of the film thickness was independent of the shape of the substrate. Compared with the numerical simulation, there was solvent evaporation during the whole spin-coating experiment. Therefore, the solvent evaporation was supposed to be the dominant factor that affects the film thickness of substrates in different shapes, and further experiments were designed to clarify this conjecture.

![Figure 5. Comparison of experimental results on circular rectangular plates at different rotating speeds.](image-url)
Table 2. Film thickness under different conditions.

| Speed (rpm) | Group A: Free Evaporation | Group B: Evaporation Inhibition |
|-------------|---------------------------|--------------------------------|
|             | Difference ($h_r - h_c$)  | Ratio ($\frac{h_r - h_c}{h_c}$) | Difference ($h_r - h_c$)  | Ratio ($\frac{h_r - h_c}{h_c}$) |
| 1000        | 93.5 nm                    | 6.63%                          | 28.2 nm                    | 2.16%                          |
| 2000        | 53.4 nm                    | 5.34%                          | 41.7 nm                    | 4.74%                          |
| 3000        | 77.5 nm                    | 9.55%                          | 34.1 nm                    | 4.58%                          |
| 4000        | 47.3 nm                    | 6.75%                          | 30.6 nm                    | 5.24%                          |
| 5000        | 90.7 nm                    | 14.7%                          | 44.3 nm                    | 7.98%                          |

(*$h_c$: average film thickness of the central region on the circular substrate in the experiment. *$h_r$: average film thickness of the central region on the rectangular substrate in the experiment*).

Enough solvent was arranged in the spin coater chamber and the other parameters were the same as mentioned previously. The spin coater chamber was sealed and kept still for 30 min to ensure the sufficient evaporation. It was supposed that the solvent evaporation was efficiently suppressed during the whole spin-coating process.

The film thickness results were obtained under different experimental conditions of solvent evaporation, as presented in Figure 6. In general, the film thickness of rectangular substrate was larger than that of the circular substrate, which was caused by the different evaporation rates at the edge region. It was supposed that the evaporation rate at the edge region of rectangular substrate was larger than that of circular substrate. The film at the edge region was dried faster, and the liquid in the center region was impeded, which resulted in larger film thickness. The solvent could evaporate freely for Group A, but the solvent evaporation was suppressed for Group B with the help of the arrangement of abundant solvent around the substrate. At all rotation speeds, whether on a rectangular or circular substrate, the film thickness of group B was in the range of from 100 to 200 nm, which was smaller than that of group A. At the beginning of the spin-coating process, the radial outflow induced by centrifugal force was the dominant factor in the film thinning. Then, solvent evaporation became the leading factor when the film was thinned to a thinner thickness. At this stage, the concentration of gaseous solvent in the chamber could inhibit the solvent evaporation, which would result in a decrease in viscosity. The low viscosity of the solution would enhance the effect of the radial outflow, and more liquid was driven out of the substrate under the same centrifugal force, which would lead to the thinner film. Based on the results in Table 2, the difference in the thickness of the film on the circular and rectangular substrate was significantly reduced, from 50–100 to 25–45 nm, under the condition of abundant solvent arrangement in the chamber. The difference ratio ($\frac{(h_r - h_c)}{h_c}$) was also significantly reduced under the same experimental conditions.

Figure 6. Comparison between solvent evaporation experiment and original experiment results.
It was noted that even in the evaporation inhibition experiment, the difference in film thickness between the rectangular substrate and the circular substrate still existed, and the difference ratio increased with the increase in rotation speed. On the one hand, this was because the thickness of the film decreased with the increasing rotation speed. On the other hand, the experimental conditions could not ensure that the concentration of gaseous solvent in the spin-coating chamber was in a saturated state, and the evaporation rate of the solvent kept decreasing. In addition, the large rotating speed increased the air velocity on the surface of the film and promoted evaporation to a certain extent.

3.3. Distribution Characteristics of Film Thickness

The numerical simulation results of the spin-coating process on the substrates of two shapes were analyzed. The film thickness distribution was displayed in Figure 7, and the same color bar was used to make the image clearer. The free interface of the liquid phase showed chaotic micro-features, in the form of irregular bumps and depressions. These micro-features were regarded as the random and disordered development of the two-phase interface. Except for the edge region, the film thickness distributions of the two shapes of substrates are similar. The film thickness of the central area on both substrates is reduced from about 700 to about 150 µm. For the edge region, the width of the edge bead region was about 1 mm and the height of the edge bead was about 250 µm on both circular and rectangular substrates.

The velocity characteristics of the airflow at 150 µm above the film was displayed in Figure 8. The black frame inside is the rectangular substrate in the size of 24 mm × 15 mm. Within the inner black frame (above the substrate), the relative velocity of air gradually increased to 0.1 m/s, along with the radial position. The direction of airflow near the liquid film was approximately circular. Compared with Figure 7a, it was concluded that the film’s distribution characteristics were not affected by the airflow field above the film. Therefore, the shear and wind resistance of airflow had little influence on film thickness and film thickness distribution with the conditions used in numerical simulation.

The experiment was carried out under the condition of multiple groups of rotating speeds, and the results were shown in Figure 9. At a low rotating speed (1000–3000 rpm), the thickness of the film on the circular substrate decreased slightly along the radial direction (neglecting the edge bead effect), but this phenomenon became less obvious when the rotational speed was greater than 4000 rpm. Figure 9d shows the film profile at the position of y = 0 on the circular substrate and rectangular substrate. Under a low rotating speed (taking 1000 rpm as an example), the film thickness of the center region of the circular

Figure 7. Final film thickness distribution in the spin-coating simulation process: (a) Numerical simulation of the thickness distribution of the coating film on the rectangular substrate; (b) Numerical simulation of the thickness distribution of the coating film on the circular substrate.
substrate decreased from 1354.2 to 1287.4 nm at the edge, and the film thickness on the rectangular substrate decreased from 1530.8 to 1422.2 nm at the edge. However, under a high rotating speed (5000 rpm), the decrease in film thickness along the radial direction was no longer obvious.

![Velocity vector](image)

**Figure 8.** Velocity vector (relative velocity) of airflow above the film (The black, bold box is the substrate region.).

At a low rotating speed, the liquid film on the substrate was driven by a smaller centrifugal force. The liquid film near the center region flowed more slowly because of the smaller centrifugal force. Before the film was completely driven from the central region, the thin film at the edge of the substrate started to dry and this would impede the outflow of the liquid film from the central region. At this moment, the solvent kept evaporating, and finally, the film thickness decreased gradually along the radial direction. As for the spin-coating process at a higher rotating speed, a large amount of solution in the central region was driven out along the radial direction before the solution viscosity, which was induced by the solvent evaporation with a higher rotating speed, changed. For rectangular substrate, local low pressure near the edge caused by the Bernoulli effect resulted in the faster evaporation of the solvent. This would also impede the outflow of the liquid in the central region of the substrate. Therefore, the film thickness also gradually decreased along the radial direction.

Besides the radial film thickness characteristics, the film corner accumulation characteristics of the windward area on the rectangular substrate were more noticeable. According to the results, the corner accumulation characteristics are related to the airflow field. The experimental results did not agree well with the numerical simulation results. One of the reasons for this difference was that the solvent evaporation process was ignored in the numerical simulation work. The airflow action in the numerical simulation was not strong enough to have a significant influence on the film thickness distribution compared with the internal viscous force of the solution. Therefore, the uneven evaporation of the solvent was the dominant factor for the windward area of the rectangular substrate. The accumulation of the solution at the edge of the substrate and the relative vacuum promoted by the accumulation were the main reasons for the uneven evaporation of the solvent on the rectangular substrate.
Figure 9. Film thickness distribution on rectangular and circular substrates: (a) Film thickness distribution at 1000 rpm; (b) Film thickness distribution at 3000 rpm; (c) Film thickness distribution at 5000 rpm; (d) Film thickness curve of circular (left) and rectangular (right) substrate at y = 0.
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In Figure 10, the velocity vector distributions of the film at 0.5 and 6 s were presented. The solution flowed along the edge at the later stage \( (t = 6 \text{ s}) \). However, both the radial flow rate of the solution and the centrifugal force were large in the early stage of the spin-coating process. The surface tension was small compared with the centrifugal force and had no significant effect on the film-spreading process. In the later stage of the spin-coating process, the radial outflow velocity of the liquid film decreased, and the mass of the film, as well as the centrifugal force, was very small. Therefore, the surface tension of the convex liquid surface at the edge could not be ignored at that stage.

According to the Young-Laplace equation:

\[
\Delta P = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right)
\]

where \( \Delta P \) is the pressure difference between the inside and outside of the liquid film, \( \gamma \) is the surface tension coefficient, and \( R_1 \) and \( R_2 \) are the principal radii of curvature of the film interface.

One of the best-known types of thickness unevenness is the “Edge Bead”, which appears as a thick ridge along the periphery of the substrate. The surface tension force schematic inside the “Edge Bead” is shown in Figure 11. The projection of the surface
tension force on the horizontal plane was perpendicular to the geometric edge of the substrate, which counteracted part of the centrifugal force. For this reason, the liquid film on the rectangular substrate flew along the edge and intensified the accumulation of solution at the edge of the substrate. The Bernoulli effect on the surface of the liquid film was promoted by the accumulation of the solution on the edge of the rectangular substrate, and the mechanism of the Bernoulli effect was explained in Figure 12.

Figure 10. Velocity vector of the film at different spin-coating moments: (a) Internal velocity vector of liquid after spin-coating for 0.5 s; (b) Internal velocity vector of liquid after spin-coating for 6 s.

Figure 11. Force analysis of the film free surface: (a) Section view; (b) Top view.

Figure 12. Explanation of Bernoulli effect mechanism.
According to Bernoulli’s equation:

\[
P_0 + \frac{1}{2} \rho V_0^2 + \rho g Z_0 = P_{\text{top}} + \frac{1}{2} \rho V_{\text{top}}^2 + \rho g Z_{\text{top}}
\]  

(16)

where \( P \) is the pressure, \( \rho \) is the density of air, \( Z \) is the height, and \( g \) is the acceleration of gravity. When the air streamline splits and flows through different paths, there will be differences in velocity. When the edge beads formed at the edge of the substrate, the airflow over the liquid film had a longer path, and the flow speed was relatively large. According to Equation (16), the pressure \( P_{\text{top}} \) above the liquid film is less than \( P_0 \), forming a relative vacuum and promoting the evaporation of the solvent. Therefore, a prominent edge-stacking feature of thin films is generated on rectangular substrates. Based on the above analysis, the differences in film geometry are mainly caused by the solvent nonuniform evaporation and the Bernoulli effect at the edge region.

4. Conclusions

The VOF method is used to simulate the two-phase flow of the spin-coating process, and the evolution and distribution of the film thickness on the rectangular and circular substrates are studied. The effects of substrate shape on the coating film geometry are discussed numerically and experimentally.

- Based on the results of VOF method, the shape of the substrate had little effect on the evolution of the film thickness during the spin-coating process without considering the solvent evaporation.
- When solvent evaporation exists in the coating process, the non-axisymmetric shape of the substrate leads to a high flow speed near the boundary, which is the dominant factor affecting the film thickness distribution.
- At the later stage of the spin-coating process, the film accumulation at the edge of the rectangular substrate is subjected to surface tension, which could not be neglected compared with the centrifugal force. The accumulation of liquid film on the edge promotes the Bernoulli effect, and the uneven solvent evaporation is the reason for the formation of film accumulation characteristics in the windward area. The better control of solvent evaporation is found to be effective in improving the film’s uniformity.

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References

1. Sahu, N.; Parija, B.; Panigrahi, S. Fundamental understanding and modeling of spin coating process: A review. Indian J. Phys. 2009, 83, 493–502. [CrossRef]
2. Kanamori, Y.; Roy, E.; Chen, Y. Antireflection sub-wavelength gratings fabricated by spin-coating replication. Microelectron. Eng. 2005, 78, 287–293. [CrossRef]
3. Yang, J.P.; Jin, Y.D.; Heremans, P.L. White light emission from a single layer organic light emitting diode fabricated by spincoating. Phys. Lett. 2000, 325, 251–256. [CrossRef]
4. Norrman, K.; Ghanbali-Siahkali, A.; Larsen, N.B. 6 Studies of spin-coated polymer films. J. Annu. Rep. Sect. C (Phys. Chem.) 2005, 101, 174–201. [CrossRef]
5. Jiang, P.; McFarland, M.J. Large-scale fabrication of wafer-size colloidal crystals, macroporous polymers and nanocomposites by spin-coating. *J. Am. Chem. Soc.* **2004**, *126*, 13778–13786. [CrossRef] [PubMed]

6. Emslie, A.G.; Bonner, F.T.; Peck, L.G. Flow of a viscous liquid on a rotating disk. *J. Appl. Phys.* **1958**, *29*, 858–862. [CrossRef]

7. Acrivos, A.; Shah, M.J.; Petersen, E.E. On the flow of a non-Newtonian liquid on a rotating disk. *J. Appl. Phys.* **1960**, *31*, 963–968. [CrossRef]

8. Meyerhofer, D. Characteristics of resist films produced by spinning. *J. Appl. Phys.* **1978**, *49*, 3993–3997. [CrossRef]

9. Rehg, T.J.; Higgins, G. Spin coating of colloidal suspensions. *AIChE J.* **1992**, *38*, 489–501. [CrossRef]

10. Spangler, L.L.; Torkelson, J.M.; Royal, J.S. Influence of solvent and molecular weight on thickness and surface topography of spin-coated polymer films. *Polym. Eng. Sci.* **1990**, *30*, 644–653. [CrossRef]

11. Chen, B.T. Investigation of the solvent-evaporation effect on spin coating of thin films. *Polym. Eng. Sci.* **1983**, *23*, 399–403. [CrossRef]

12. Lawrence, C.J. The mechanics of spin coating of polymer films. *Phys. Fluids* **1988**, *31*, 2786–2795. [CrossRef]

13. Ohara, T.; Matsumoto, Y.; Ohashi, H. Resist film formation in spin coating. In Proceedings of the Intersociety Conference on Thermal Phenomena in Electronic Systems, Austin, TX, USA, 5–8 February 1992; pp. 281–288.

14. Bornside, D.E.; Macosko, C.W.; Scriven, L.E. Spin coating: One-dimensional model. *J. Appl. Phys.* **1989**, *66*, 5185–5193. [CrossRef]

15. Bornside, D.E.; Brownm, R.A.; Ackmann, P.W. The effects of gas phase convection on mass transfer in spin coating. *J. Appl. Phys.* **1993**, *73*, 585–600. [CrossRef]

16. Kozuka, H. Radiative striations in spin-coating films. In *Handbook of Sol-Gel Science and Technology*; Springer International Publishing: Osaka, Japan, 2016; Volume 12, pp. 313–332.

17. Shiratori, S.; Kato, D.; Sugasawa, K. Spatio-temporal thickness variation and transient Marangoni number in striations during spin coating. *Int. J. Heat Mass Transfer.* **2020**, *154*, 119678. [CrossRef]

18. Shiratori, S.; Kubokawa, T. Double-peaked edge-bead in drying film of solvent-resin mixtures. *Phys. Fluids* **2015**, *27*, 102105. [CrossRef]

19. Arscott, S. The limits of edge bead planarization and surface levelling in spin-coated liquid films. *J. Micromech. Microeng.* **2020**, *30*, 025003. [CrossRef]

20. Carcano, G.; Ceriani, M.; Soglio, F. Spin coating with high viscosity photoresist on square substrates—Applications in the thin film hybrid microwave integrated circuit field. In *Microelectronics International*; MCB UP Ltd.: Bradford, UK, 1993; Volume 10, pp. 12–20.

21. Luurtsema, G.A. Spin Coating for Rectangular Substrates. Master’s Thesis, University of California, Berkeley, CA, USA, 11 July 1997.

22. Gao, D.; Morley, N.B.; Dhir, V. Numerical simulation of wavy falling film flow using VOF method. *J. Comput. Phys.* **2003**, *192*, 624–642. [CrossRef]

23. Prosperetti, A. Navier-Stokes numerical algorithms for free-surface flow computations: An overview. In *Drop-Surface Interactions*; Springer: Berlin/Heidelberg, Germany, 2002; pp. 237–257. [CrossRef]