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Fundamental understanding and modeling of spin coating process : A review

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Abstract : A mathematical model is derived to elucidate the dominant mechanism governing film formation. It leads to a relation between film thickness and film radius spreading with time. Inclusion of evaporation and shear stress was made with extension to non-Newtonian fluid. The advantages and disadvantages of this process with applications are reviewed.

Keywords : Spin coating, film thickness, shear stress, non-Newtonian fluids.

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1. Introduction

Spin coating is currently the predominant technique employed to produce uniform thin films of photosensitive organic materials with thickness of the order of micrometers and nanometers. The pioneering analysis of spin coating was performed more than fifty years ago by Emil *et al* [1] who considered the spreading of a thin axisymmetric film of Newtonian fluid on a planner substrate rotating with constant angular velocity. In many cases the coating material is polymeric and is applied in the form of a solution from which the solvent evaporates. Spin coating was first studied for coating of paint and pitch [2].

This process has been widely used in the manufacture of integrated circuits [3], optical mirrors, color television screens and magnetic disk for data storage [4]. Centrifugal force drives the liquid radial outward. The viscous force and surface tension causes a thin residual film to be retained on the flat substrate. The film thins by the combination of outward fluid flow and evaporation [5].

The spin coating can be broken down into several key stages : fluid dispense,

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spin-up, stable fluid out flow, and finally evaporation dominated drying [6]. Stage 3 (flow controlled) and stage 4 (evaporation controlled) are the two stages that have the most impact on final coating thickness. Clearly stage 3 and stage 4 describe the two processes that most be occurring simultaneously throughout all times (viscous flow and evaporation). However, at an engineering level the viscous flow effects dominates early on while the evaporation processes dominate later. Fluid flow on a flat spinning substrate is one of the most important physical processes involved in spin coating [7].

Several processing parameters involved in the spinning process are : dispense volume, final spin speed (*w*), final film thickness, solution viscosity, solution concentration (*c*), spin time, *etc*. Using different parameters film thickness and radius of spreading are calculated [8]. The film forming process is primarily driven by two independent parameters, viscosity and spin speed. The range of the film thickness easily achieved by spin coating is 1–200 micrometers [9–10].

2. Modeling of spin coating

Even though spin coating has been universally used in the semiconductor industry long before, hardly any theoretical study has been initiated. An accurate theory of spin coating would permit better design and control of the process in its various applications. Decades of industrial production have shown that the depositions of thin photoresists films, which constitute the main utilization of the spin coating process, are quasi-perfectly controlled. However, any progress in developing mathematical models should be probably more helpful in the case of heat resistant dielectric insulating films (polyamides or other materials). In contrast to the photoresists which are often low molecular weight materials dissolved in low boiling solvents at low concentration, polyimide precursors are high molecular weight polymers. These materials are supplied in organic solvents boiling at temperatures close to 200°C at concentration, levels (10–20%) where the non-Newtonian behaviors can not be neglected. This implies that spin analytical models will be based on sophisticated equation taking in consideration a number of physical parameters.

2.1. Key stages of spin coating :

The physics of spin coating can be effectively modeled by dividing the whole process into four stages sketched in Figure 1, which are deposition, spin-up, spin-off and evaporation of solvents. The first three are commonly sequential, but spin-off and evaporation usually overlap. Stage 3 (flow controlled) and stage 4 (evaporation controlled) are the two stages that have the most impact on final coating thickness.

Deposition :

During this stage, solution is allowed to fall on rotating substrates from microsyrings and the substrate is accelerated to the desired speed. Spreading of the

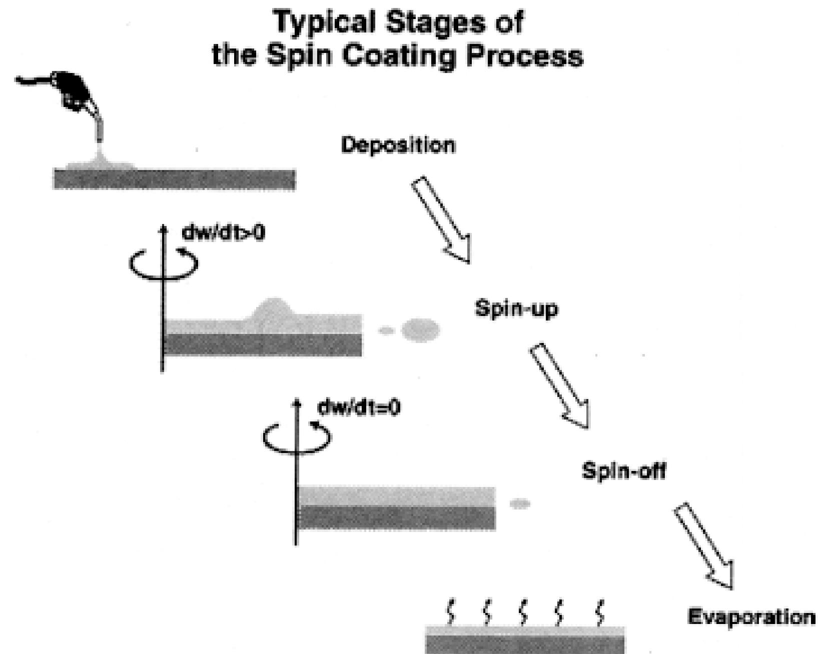

Figure 1. Key stages of spin coating process.

solution takes place due to centrifugal force and height is reduced to critical height. This is the stage of delivering an excess of the liquid to be coated to the surface of the substrate a portion of which's immediately covered or "wetted". In this stage liquid can be deposited in different ways (a) as a heavy rain that inundates the entire disk; (b) as a bolus at the center or around the perimeter of hole if the center has been cut out, the liquid then spreading over the rest of the disk, or (c) as a continuous stream at the center, or all the way around the inner perimeter, the liquid then flowing outward over the entire disk, or (d) as a continuous stream from an elevated delivery port that moves racially over the disk. No matter what way is used the amount of liquid deposited through excessive is limited and this stage ends when delivery ceases.

Spin-up :

The second stage is when the substrate is accelerated up to its final, desired, rotation speed. This stage is usually characterized by aggressive fluid expulsion from the wafer surface by the rotational motion. Because of the initial depth of fluid on the wafer surface, spiral vortices may briefly be present during this stage; these would form as a result of the twisting motion caused by the inertia that the top of the fluid layer exerts while the wafer below rotates faster and faster. Eventually, the fluid is thin enough to be completely co-rotating with the wafer and any evidence of fluid thickness differences is gone. Ultimately, the wafer reaches its desired speed and the fluid is thin enough that the viscous shear drag exactly balances the rotational accelerations.

Stable fluid outflow :

The third stage is when the substrate is spinning at a constant rate and fluid viscous forces dominate fluid thinning behavior. This stage is characterized by gradual fluid thinning. Fluid thinning is generally quite uniform, though with solutions containing volatile solvents; it is often possible to see interference colors "spinning off", and doing so progressively more slowly as the coating thickness is reduced. Edge effects are often seen because the fluid flows uniformly outward, but must form droplets at the edge to be flung off. Thus, depending on the surface tension, viscosity, rotation rate, *etc.*, there may be a small bead of coating thickness difference around the rim of the final wafer. Mathematical treatments of the flow behavior show that if the liquid exhibits Newtonian viscosity (*i.e.* is linear) and if the fluid thickness is initially uniform across the wafer (albeit rather thick), then the fluid thickness profile at any following time will also be uniform.

Evaporation :

When spin-off stage ends the film drying stage begins. During this stage centrifugal out flow stops and further shrinkage is due to solvent loss. This results in the formation of thin film on the substrate. The fourth stage is when the substrate is spinning at a constant rate and solvent evaporation dominates the coating thinning behavior. In this, the rate of evaporation depends on two factors (a) the difference in partial pressure (actually chemical potential) of each solvent species between the free surface of the liquid layer and the bulk of the gas flowing nearby. During the evaporation stage the suspended or dissolved solids may grow so concentrated at the liquid surface as to form a high viscosity, low diffusivity layer or solid skin.

2.2. Modeling the spin coating process :

Using cylindrical polar co-ordinates (r, θ, z) with origin at the center of rotation, z perpendicular to the plane, and the axes r and θ rotating with the plane with angular velocity ω, the balance between viscous and centrifugal forces per unit volume for Newtonian fluid is given by

$$-\eta\left(\frac{d^2\nu}{dz^2}\right) = \rho\omega^2 r \tag{1}$$

η = absolute viscosity

ρ = fluid density

ν = velocity in the direction of r.

Integrating with respective Z and using suitable boundary condition of zero shears at the free surface *i.e.* $\partial\nu/\partial z = 0$

at $z = h$ yields

$$V = \frac{1}{\eta}\left(-\frac{1}{2}\rho\,\overline{\omega}^2 rz^2 + \rho\,\overline{\omega}^2 rhz\right)$$

The radial flow q per unit length of the circumference is given by

$$q = \int_0^h \nu(z)dz = \left(\rho\omega^2 rh^2\right)\Big/3\eta. \tag{2}$$

The equation for continuity is given by

$$r\left(\frac{\partial h}{\partial t}\right) = -\frac{\partial(rq)}{\partial r}. \tag{3}$$

Use of eq. (2) in (3) yields

$$\frac{\partial h}{\partial t} = -K\left(\frac{1}{r}\right)\frac{\partial(r^2h^3)}{\partial r} \tag{4}$$

where $K = \rho\omega^2/3\eta$.

Before seeking general solution of eq. (4) let us consider the special solution, which depends only on time *t.*

Special solution :

$$\frac{\partial h}{\partial t} = -2Kh^3 + 3Krh^2\,\frac{\partial h}{\partial r}.$$

Since the film is uniform at the beginning, h is independent of r and hence $\partial h/\partial r = 0$ which gives

$$dh\big/dt = -2Kh^3 \text{ or } \frac{\partial h}{h^3} = -2K\partial t. \tag{5}$$

Integrating both sides between proper limits *i.e.* at t = 0, $h = h_0$ and at t, $h = h_t$, we get

$$h_t = h_0\Big/\left(1 + 4h_0^2Kt\right)^{1/2} = h_0\Big/\left[1 + 4h_0^2\rho\omega^2 t/3\eta\right]^{1/2}. \tag{6}$$

General solution :

Similarly from equation of continuity

$$r\left(\frac{\partial h}{\partial t}\right) = -\frac{\partial(rq)}{\partial r}$$

and the expression for $\partial h/\partial t$ is

$$\frac{\partial h}{\partial t} = -2Kh^3 + 3Krh^2 \frac{\partial h}{\partial r}.$$

Relating partial and total derivatives as under

$$\frac{dh}{dt} = \frac{\partial h}{\partial t} + \frac{\partial h}{\partial r}\frac{dr}{dt}.$$

we have

$$\frac{\partial h}{\partial t} = -2kh^3 \quad \text{and} \quad \frac{dr}{dt} = 3krh^2,$$

$$\frac{dr}{dt} = \frac{3kh_0^2 r}{1+4kh_0^2 t}$$

$$\Rightarrow \ln\left(\frac{r}{r_0}\right) = \frac{3}{4}\ln\left(1+4kh_0^2 t\right) = \ln\left(1+4kh_0^2 t\right)^{3/4}$$

$$\Rightarrow r = r_0\left(1+4kh_0^2 t\right)^{3/4}. \tag{7}$$

Taking Gaussian initial contour of the form

$$h_0 = ae^{-\alpha^2 r_0^2} \quad \text{or} \quad \frac{h_0}{a} = e^{-\alpha^2 r_0^2},$$

the exponential term is expected to flatten with increase in t.

For slowly falling initial contour of the form

$$h_0 = \frac{a}{\left(1+\alpha^2 r_0^2\right)^{3/4}},$$

the flattening due to the exponential is absent.

For Gaussian plus uniform initial contour of the form

$$\frac{h_0}{a} = e^{-\alpha^2 r_0^2}, \tag{8}$$

the exponential term will lead to flattening with increase in t.

Inclusion of evaporation :

Evaporation plays a very important role on final film thickness. Adding a constant evaporation term to the thinning rate we have

$$\frac{dh}{dt} = -2kh^3 - e \tag{9}$$

where e = evaporation rate [ml s^{-1} cm^{-1}]

Early stages are flow dominated and later stages are evaporation dominated.

At the transition point when evaporation rate and viscous flow rate become equal, evaporation depends on rotation rate (ω)

$$e = C\sqrt{\omega} \quad (C \text{ is constant}). \tag{10}$$

Let the final film thickness be h_f. Then taking cube-root and rearranging :

$$h = (2k)^{-1/3}\left(-\frac{dh}{dt}\right)^{1/3} - h_f\,. \tag{11}$$

This resembles equation of straight line

$y = mx + c.$

The flow constant is determined by the slope and the final film thickness is determined by the intercept.

The height of the fluid h could be separated into the height of the solid S and the height of the solvent L *i.e.*

$h = S + L.$

By expressing the concentration of the solid $C(t)$ as

$C(t) = S/(S + L),$

One can obtain from the equation of continuity

$$\frac{dS}{dt} = -C(t)\,\frac{2\omega^2 h^3}{3\vartheta}\,,$$

where ϑ is the kinetic viscosity (= η/ρ). Including the liquid evaporation rate ϕ, the change in liquid height can be expressed as

$$\frac{dL}{dt} = -\left[1 - C(t)\right]\frac{2\omega^2 h^3}{3\vartheta} - \phi. \tag{12}$$

The viscosities of these solutions have been reported to be the power law function of the concentration which can be written as

$$\vartheta = \vartheta_L + \vartheta_S C^{\gamma}(t) \tag{13}$$

where ϑ_L and ϑ_S are the viscosities of solvent and solid respectively and γ = 2.5. The final film height can be simplified to the form

$$h = \left[\frac{3C^3(t)\vartheta_0\phi}{2\left\{1 - C_0(t)\right\}\omega^2}\right]^{1/3} \quad \text{or} \quad h \propto \omega^{-2/3}\,. \tag{14}$$

Inclusion of shear stress and non-Newtonian condition :

In the simplest model of spin coating, which neglects effect of shear stress *i.e.* under no slip condition, the final film thickness $h(t)$ after time *t,* is related to the initial film thickness h_0 by the equation

$$h(t) = \frac{h_0}{\left(1 + 4kh_0^2 t\right)^{1/2}} .$$

In the dimensionless sense we have

$$H \sim \tau^{-1/2}$$

where $H = h(t)/h_0$ is the dimensionless film thickness and $\tau = (2\rho\omega^2 h_0^2/3\mu)t$ the dimensionless time.

For a large spinning disk, the air in contact must be exactly co-rotating. However, upper layers of air do not rotate at the same velocity (velocity gradient exists). Since air has finite viscosity, this causes a shearing stress at the interface during the initial stage and is more predominant during “skin formation” at the liquid surface. The film thickness is found to decrease more rapidly compared to the rate of thinning under partial vacuum conditions. Attempts have been made to include the effect of shearing stress in the mathematical modeling of spin coating in order to answer the question. This air flow generates a radically directed shearing force, whose shearing stress magnitude is given by

$$\tau_{rz} = \frac{1}{2}\omega^{3/2}\upsilon_{\text{air}}^{-1/2}\mu_{\text{air}} r .$$

Using suitable boundary condition to account for the shear stress imposed by external air flow and power law behavior of non-Newtonian fluid, the volumetric flow per unit circumference is given by

$$q = \int_0^h \nu_r dz = \frac{n}{2n+1}\left(\frac{\rho\omega^2 r}{k}\right)^{1/n} h^{\frac{2n+1}{n}} .$$

Using the equation of continuity and after some simplification one gets the solution of $h(t)$ in the form

$$\left(\beta + \frac{1}{H}\right)\Big/(\beta+1) = \exp\left[\frac{1}{\beta}\left(\frac{1}{H} - \frac{\tau}{\beta} - 1\right)\right]. \quad (15)$$

Similarly in the dimensionless sense we have

$$H \sim \tau^{-1}. \quad (16)$$

It is concluded that air shear stress increases the rate of thinning, to the extent

$H \sim \tau^{-1}$ for small *H*, rather than $H \sim \tau^{-1/2}$ as expected earlier *i.e.* without considering the effect of sheer stress.

3. Advantages

As evidenced by its maturity, spin coating has many advantages in coating operations with its biggest advantage being the absence of coupled process variables. Film thickness is easily changed by changing spin speed, or switching to a different viscosity photoresist. But among the alternative coating techniques, many have multiple coupled parameters, making coating control more complex.

Another advantage of spin coating is the ability of the film to get progressively more uniform as it thins, and if the film ever becomes completely uniform during the coating process, it will remain so for the duration of the process. It is low cost and fast operating system. The maturity of spin coating implies many of the issues involved in spin coating have been studied and a lot of information exists on the subject.

4. Disadvantages

The disadvantages of spin coating are few, but they are becoming more important as substrate size increases and photoresist costs rise. Large substrates can not be spun at a sufficiently high rate in order to allow the film to thin. The biggest disadvantage of spin coating is its lack of material efficiency. Typical spin coating processes utilize only 2–5% of the material dispensed onto the substrate, while the remaining 95–98% is flung off in to the coating bowl and disposed. Not only the prices of the photoresist increasing substantially, but disposal costs are increasing as well. If economically feasible manufacturing costs are to be maintained, a method for improving this material utilization is of primary importance, especially in the flat panel display area.

5. Applications

Spin coating has been used for several decades for the application of thin films. It is widely used in the manufacture of integrated circuits, optical mirrors, magnetic disk for data storage, device of solar cells, detectors, sensors, VLSI (very large scale integration), nano scale device (quantum dots, carbon nanotubes), DVD and CD ROM, photo resist for patterning wafers in microcircuit production, insulating layers for microcircuit fabrication such as polymers (where it can be used to create thin films with thickness below 10 nm), flat screen display coatings, antireflection coatings and conductive oxide *etc*.

6. Conclusions

From this review we conclude that one can understand the basic physics behind the spin coating process. A mathematical model to elucidate the dominant mechanism governing film formation and establish a the relationship between film thickness and

time is established. Inclusion of evaporation and shear stress was made with extension to non-Newtonian fluid. Advantages and disadvantages with some industrial applications are discussed.

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