Get Wet

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[Intro.]

This photo is to present the non-uniform defects happened in spin coating process. Spin coating is a procedure used to apply uniform thin film to flat surface. For semiconductor industry, it is widely used to deposit layers of photoresist about 1 micron thickness for lithography and later process. A non-uniform coating can be observed in color differences caused by interference on the thin film as Figure 1.

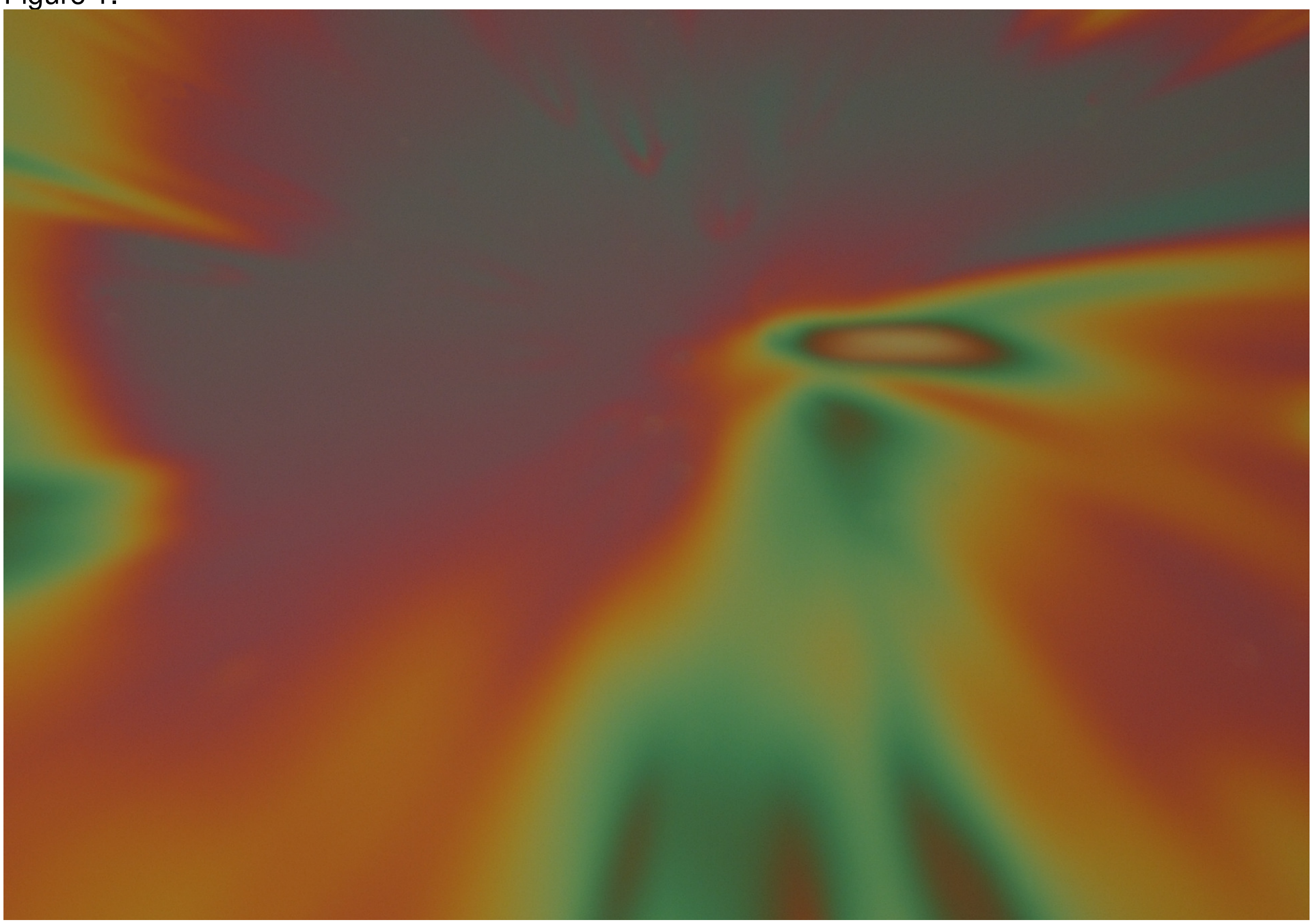


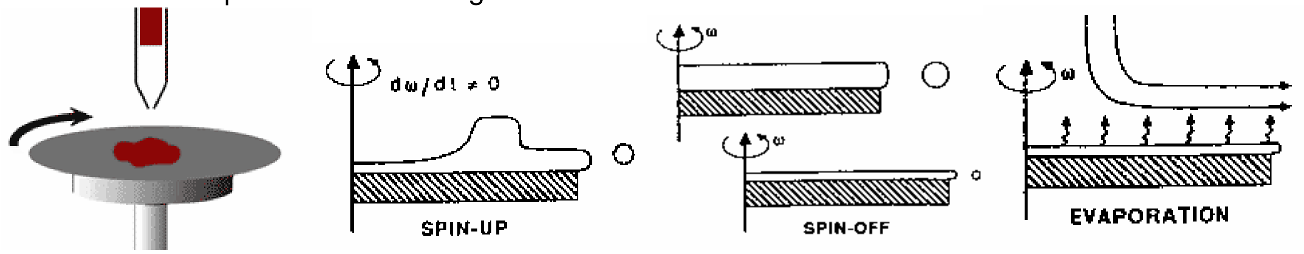
Figure 1 A non-uniform coating on silicon wafer shows iridescent colors.

[Sample preparation]

A typical spin process consists of a dispense step in which the resin fluid is deposited onto the substrate surface, a high speed spin step to thin the fluid, and a drying step to eliminate excess solvents from the resulting film. This sample is pre-cleaned by nitrogen air blow, spraying acetone and then iso-propane for ~ 30 seconds while spinning at 6000 RPM. After pre-clean, a static dispense is used to apply resin fluid (Shipley SPR 660) on a 3 inch diameter silicon wafer (1,0,0) followed by a 40 seconds spinning in 2200 RPM. After spin coating, the wafer is heated in 95 degree Celsius and then 105 degree Celsius for 1 minute to evaporate the solvent. The nominal thickness of photoresist coated is measured as 1.2 microns.

[Spin coating physics]

In general, there are four distinct stages to the spin coating, fluid dispense, spin-up, stable fluid outflow, and finally evaporation dominated drying as shown in figures below. The first stage is the deposition of the coating fluid onto the wafer or substrate. The second stage is when the substrate is accelerated up to its final, desired, rotation speed. The third stage is when the substrate is spinning at a constant rate and fluid viscous forces dominate fluid thinning behavior. The fourth stage is when the substrate is spinning at a constant rate and solvent evaporation dominates the coating thinning behavior. Stage 3 (stable fluid outflow) and Stage 4 (evaporation controlled) are the two stages that have the most impact on final coating thickness.



Fluid dispense **Spin up** **Stable fluid outflow** **Evaporation drying**

A spin coating model was published by Emslie, Bonner, and Peck [J. Appl. Phys. 29 (1958) 858-862] assuming that a Newtonian non-volatile flow has reached a stable condition where the centrifugal and viscous forces are just in balance (as shown in stage 3). When the centrifugal and viscous forces are in balance, the governing equation and film thickness as a function of material can be shown

$$\mu \frac{\partial^2 v_r}{\partial z^2} = -\rho\omega^2 r$$

μ = fluid viscosity

ρ = fluid density

ω = rotationspeed

$$\frac{H}{H_0} = \frac{1}{\sqrt{1 + \frac{4\rho\omega^2}{3\mu} H_0^2 t}}$$

where H is the thickness of the film, H_0 is its initial thickness, and t is the spinning time. Note that at long times, the film thickness is independent of its initial thickness.

At longer times, solvent evaporation becomes an important contribution. Meyerhofer was the first to estimate the effect of this on final coating thickness [J. Appl. Phys. 49 (1978) 3993-3997]. A quite reasonable approximation is that evaporation is a constant throughout spinning (where "e" is the evaporation rate [ml/s/cm^2] in the following), as long as the rotation rate is held constant

$$\frac{dh}{dt} = -2K h^3 - e$$

Setting the transition point at the condition where the evaporation rate and the viscous flow rate became equal. The final coating thickness, h_f, is predicted to be:

$$h_f = c_o \left(\frac{e}{2(1-c_o)K} \right)^{\frac{1}{3}}$$

where c_o is the solids concentration in the solution.

In fact, both the volatility of the solvent and non-Newtonian fluid flow are important in actual spin coating operations. Indeed, these effects are coupled because the solvent diffusivity and solution viscosity are functions of the concentration of polymer. Flack et al. [J. Appl. Phys., 56, 1199 (1984)] and Britten and Thomas [J. Appl. Phys. 71 (1992) 972-979] have provided a more detailed analysis which includes these effects. It should be noted that this results when airflow above the spinning substrate is laminar.

For this particular sample, assuming μ=1.2E-3 N s/ m^2, ρ=1.1 kg/ m^3, Re<500 (for open channel laminar flow), highest velocity is 5852 m/s (2200 RPM in 3 inch diameter wafer), we conclude with less than 90E-3 meter film thickness in stable thinning process, we can have laminar flow (For this case, its 1.2E-6 meter in thickness).

[Physics of thin film color variation]

The reflection and absorption of light on photoresist on highly polished silicon wafer produces a dark red color shown in the photo, however, thin film thickness variance produces iridescent colors (like rainbow) caused by interference.

Thomas Young in 1801 described thin film interference colors as the interaction of light waves reflected from the top surface of a thin film with those which penetrate the film and are reflected from the back surface of the film. As shown in Figure 2, Light incident on a transparent thin film produces two reflected beams: one from the front and one from the back surface. These two beams can interfere with each other to enhance or reduce the light intensity. Interference is the result of optic waves impinging on one another. Constructive interference occurs when the waves are nearly in phase, or when their 'peaks' combine; destructive interference occurs when the waves are nearly 90° out of phase, or when the 'peaks' cancel out the 'troughs' of the waves.

The path length differences (often called phase difference) of integral wavelengths or half-wavelengths required producing reinforcement or cancellation depends on the thin film material and the boundaries. If the thin film is tapered then the path lengths will differ across the film and will vary from integral to half-wavelengths across the film. This produces a series of parallel fringes on a tapered film. A representative film thickness is 500 nm or 0.5 microns for interference effects in visible light. If the films are much thicker, the iridescence vanishes.

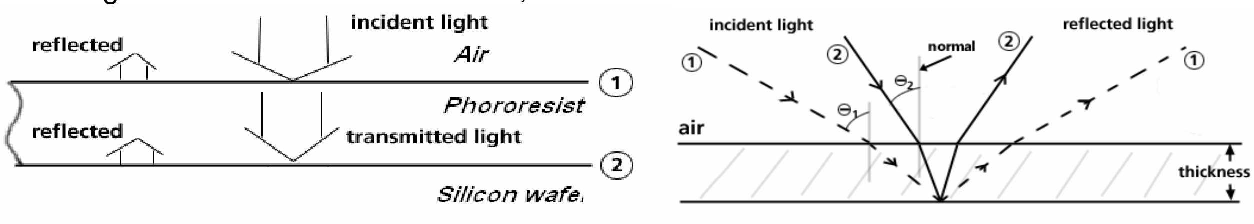


Figure 2 Light incident to transparent thin film and the path difference of light.

The isolated interference color island shown in the photo has orientation corresponds the direction of major fluid flow. Their occurrence is thought to a result of mix from surface wetting during spin coating and photoresist surface tension effect during evaporation.

The film thickness can be affected by the surface wetting level during spin coating. If the wafer surface is not well cleaned to be neither perfectly hydrophobic nor hydrophilic as in this case, film thickness variation could happen. During hot plate baking, the early evaporation of light solvents can cause an enrichment of water and/or other less volatile species in the surface layer. IF, the surface tension of this layer is larger than the starting solution (and what still exists at deeper levels), then instability exists where the higher surface tension actually draws material in at regular intervals and the spaces in-between are more able to evaporate, and surface relief develops.

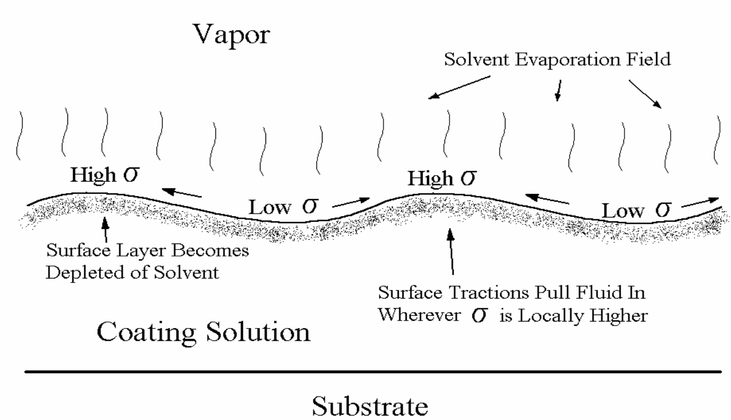


Figure 4 Surface tension happening in evaporation

[Photographic technique]

Size of the field of view: 2 inch x 1.5 inch (H x W); *Distance from object to lens*: ~ 2 inch; *Lens focal length and other lens specs*: [ISO 100] [exposure 2 sec] [Focal length 135 mm] [Max Aperture value 5.0] [No flash]; *Type of camera*: Nikon D80 with 18-135 mm Nikker lens, 10 mega pixels, pixel resolution X/Y=1944/1356; *Photoshop processing*: None; *Filming environment control:* The camera is taking 45 degree angle toward the surface of target and under dimming ambient light to avoid reflections from silicon wafers.

[Discussions]

As mentioned, this sample is pre-treated by nitrogen air blow, spraying acetone and then iso-propane for ~ 30 seconds while spinning at 6000 RPM. This process helps to clean the major particles and organics on the wafer. However, it cannot be create a perfectly clean and perfectly hydrophobic or hydrophilic surface for spin coating. Based on the physics above, a better cleaning process to eliminate surface wetting difference is one of the important factor to have a uniform coating.

[Reference]

1. J. Appl. Phys. 29 (1958) 858-862
2. J. Appl. Phys. 49 (1978) 3993-3997