Spin-On-Dielectrics: Planarity and Density Model Development

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June 21, 2003

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Background and Introduction

The idea of replacing chemical vapor deposition (CVD), plasma enhanced chemical vapor deposition (PECVD), and sputter oxide materials, among others, with a spin-on approach has been of interest in the Semiconductor industry for the last two decades. The basic technique draws from the planarizing nature of a liquid when applied to surface topography. The method was initially known as Spin-On-Glass (SOG) and has more recently taken on the more general acronym of Spin-On-Dielectric (SOD). The focus over the years has been to make the material as close to oxide (SiO₂) as possible after a cure step or series of cure steps in various ambient gases, temperatures and pressures. The work includes doped oxides such as phosphor-silicate-glass (PSG) because of important mobile cation gettering characteristics. The many works have addressed issues including, but not limited to, crack resistance, etch rate in both wet and dry etch chemistries, resistance to photo resist stripping conditions, film stress control, and particulate control. The ideal result, in many present day applications, would be to find a material that would match the materials character of densified or as-deposited CVD oxide. There are applications where matching the materials character of densified (often called “reflow” or “flow”) boro-phospho-silicate-glass (BPSG), phosphor-silicate-glass (PSG) or high-density plasma (HDP) oxide would be beneficial. There are two characteristics that are important for integration of SOD materials: prediction of planarity and prediction of material properties.

The first characteristic has not been addressed with rigor relative to the interaction between underlying topography and degree of local and global planarization. The general concepts are widely known in the industry but little has been done to provide models that guide the 2D-layout rules of semiconductor circuit design. Some relevant work has been done outside the industry. The process technology known as Chemical-Mechanical-Polishing (CMP) has conversely received focus in this area with many papers and Doctoral Theses, particularly at MIT, on the subject of modeling such interactions. Now that widely used SOD materials have been sufficiently refined and new materials developed, it is appropriate to develop models that will guide optimization of layout to facilitate optimum benefit from implementation of SOD materials in sub 100 nm semiconductor process technologies.

The second characteristic has been studied as a result of integration evaluations to replace or complement various CVD layers. Published works over the last few years have begun to recognize an effect that is unique to small features. Many works over the last two decades have
covered in great detail the bulk characteristics of SOD materials. The small feature effect is just now becoming a limiting factor in successful integration of SOD materials for certain applications.

This work reviews the details behind modeling the local and global planarization character of SOD materials in the context of underlying topography and how those results would be used to guide 2D-layout rules and define limitations in the 3D sense. The work also reviews the background and proposes potential modeling aspects of the small feature effect.
Discussion of Available Models: Planarity

The work by J.K. Chu et.al.\(^1\) provides insight to some of the integration issues associated with implementation of SOG materials. They report on an inter-metal application evaluation and selection process. They used the following categories: material stability, material consistency, film shrinkage, adhesion, vendor support, and ability to coat in the 1000 to 5000Å range. The basic requirement was to reduce the topography created by patterning of the first layer of aluminum metalization. With regards to planarization, they report, “The amount of SOG remaining in the device depends on the underlying metal aspect ratio and the initial CVD dielectric thickness”. It is this point that continues to motivate the development of robust spin-on planarization models. The use of SOG eliminates the so-called forbidden gap constraints of CVD oxides. They provide a relation for % planarization, \(\%P\), as a function of aspect ratio \(X/Y\) per Equation 1 and Figure 1.

\[\%P = \left[1 - \left(\frac{Z}{X}\frac{\theta}{90}\right)\right] \times 100\]

where: \(\theta\) = step coverage angle

\(X\) = step height
\(Y\) = step space
\(Z\) = dip from top of oxide to lowest SOG point

The workers did provide an initial figure of merit but did not provide parameters for material viscosity, bare wafer thickness and other factors related to how a liquid coats a surface with topography.
Vines and Gupta\textsuperscript{2}, in a joint work, report on inter-metal dielectric planarization using Allied Chemical Accuglass 204 and 105/305 materials. Both materials are siloxane polymers dissolved in alcohol/ketone based solvent systems. A 3 ml dispense volume was used for 100 mm wafers. The casting RPM was 3000 rpm. Casting refers to the portion of the spin sequence that sets the thickness on wafer without topography.

The researchers report that the Accuglass 105 forms a thinner layer on top of metal lines than the 305. The distinction between 105 and 305 is that 105 has a lower viscosity and is blended to achieve a lower thickness on a bare wafer for a given set of spin conditions. Though the technology had 1.2 um spaces between metal lines, the actual space for SOG fill was reduced by the initial PECVD oxide deposition. This is illustrated\textsuperscript{2} in Figure 2 by comparison of the space between metal lines, $Y$ and the space between the edges of the conformal CVD oxide $Y_1$.

![Figure 2: SOG on CVD Oxide Schematic](image)

Pei-Lin Pai and coworkers\textsuperscript{3} reported their findings as a result of detailed characterization of materials properties of polysiloxane. They point out that stress (tensile) can be attributed to film shrinkage. The equation for stress based on induced wafer curvature is given by Equation 2 (Stoney’s equation).

\textbf{Equation 2} \[ \sigma_t = \frac{E_s}{6(1-\nu_s)} \frac{t_f^2}{R t_f} \]

where:
- $\sigma_t (+) =$ tensile (concave on coated side)
- $\sigma_t (-) =$ compressive (convex on coated side)
- $t_f =$ film thickness
\[ R = \text{radius of curvature} \]
\[ v_s = \text{Poisson's ratio of Si (0.064)} \]
\[ t_w = \text{wafer thickness} \]
\[ E_s = \text{Young's modulus of Si [1.689E11 N/m}^2\text{ for (100)]} \]

Stress was collected as a function of heating to 600ºC and cooling back to room temperature. The methyl polysiloxane becomes more tensile during heating and then does not return to a lower level upon cooling. The film maintains the high tensile stress. The reference to stress is included because of its potential as a contributing mechanism in the explanation of the small feature effect.

The work of Naguib et. al\(^4\) examined the implementation of SOG in a 1.2 um design rule double metal process. They evaluated two silicate-type materials: Emulsitone silica film 209 and 210; Allied Chemical (now Honeywell Electronic Materials) 203. They also evaluated two versions of Allied Chemical’s siloxane material (204 and 208). The researchers proposed a metric of planarity as a function of the line-space pitch. The general idea is that a small gap (relative to the coat thickness) can be near 100 percent planar while larger features are only smoothed. At the time, the idea of global planarity was not seriously considered.

Morimoto and Grant\(^5\) reviewed results for a process that involved sacrificial etch back, 400ºC N\(_2\) cure before capping oxide deposition, and capping oxide deposition. They define planarity as the slope of the oxide surface between feature lines. They state that the spin characteristics are also affected by the organic content. Higher organic content gives better planarity for the same thickness. One specific example is that higher organic content materials form a local mounding of thick SOG on wide metal features. They report that 12 wt% is the optimum carbon content.

The changes in the material during heating and cure are described as solvent evaporation followed by evolution of water from polymerization of silanol (Si-OH) groups.

Planarization performance of a Tokyo Okha material was measured in work by Yen and Rao\(^6\) on a 1.2 um design rule double metal technology. The implementation used 3000 Å of PECVD oxide, 1500Å of SOG and 3000Å of capping PECVD oxide. The results of their work caused them to conclude, “coating behavior of the SOD depends not only on its viscosity but also on its composition.” They demonstrated use of a multi-step coating process to eliminate crack formation in valleys where the SOG reaches the greatest thickness. They define the degree of planarization as follows in Equation 3:

\[ \%\text{Planarity} = \left[ 1 - \frac{\text{Step after coat}}{\text{Step before coat}} \right] \times 100 \]
The %Planarity was found to have different ranges depending on step for the same spacing as shown in. The numeric order reflects the expected relation that for a given step height and coating thickness, the percent planarity will increase as the spacing decreases. This is one example of how useful a comprehensive model would be for definition of materials requirements and layout rules.

Table 1: Percent Planarity Results from Yen and Rao

<table>
<thead>
<tr>
<th>Step (um)</th>
<th>Spacing Range (um)</th>
<th>% Planarity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>8 to 1</td>
<td>70 to 90</td>
</tr>
<tr>
<td>1.1</td>
<td>8 to 1</td>
<td>50 to 70</td>
</tr>
</tbody>
</table>

One of the benchmark materials studies was by Nakano and Ohta\(^7\). They studied inorganic (silicate; silanol Si-OH) and organic (siloxane) SOD materials. Their evaluation was conducted using 5000 angstrom film thickness; hotplate bakes of 80ºC, 150ºC, and 230ºC (1 min each); final cure at 400ºC for 30 minutes in N\(_2\). Gap fill was successful down to 0.09 um for some of the SOG materials evaluated. Materials with molecular weights from 1200 to 14000 were evaluated. They propose that the solvent is the dominant factor for film quality and coating characteristics. Their analysis included very detailed NMR analysis of bond structure including conclusions about nearest neighbor atoms to silicon. For direct reference in simulations, their viscosity tables have been included.

Table 2: Table III\(^7\) For Viscosity from 2.44 to 5.33 mPa-s

<table>
<thead>
<tr>
<th>SOG</th>
<th>Main Solvent</th>
<th>Sub Solvent</th>
<th>Viscosity at 25ºC (mPa S)</th>
<th>Striation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Methanol</td>
<td>1-Propoxy-2-propanol</td>
<td>4.61</td>
<td>+</td>
</tr>
<tr>
<td>B</td>
<td>Methanol</td>
<td>1-Propoxy-2-propanol, water</td>
<td>5.22</td>
<td>+</td>
</tr>
<tr>
<td>C</td>
<td>Ethanol</td>
<td>Butyl acetate, Butanol</td>
<td>2.18</td>
<td>-</td>
</tr>
<tr>
<td>D</td>
<td>Methanol</td>
<td>1-Propoxy-2-propanol, water</td>
<td>4.79</td>
<td>++</td>
</tr>
<tr>
<td>E</td>
<td>Methanol</td>
<td>2-Propanol</td>
<td>2.44</td>
<td>-</td>
</tr>
<tr>
<td>F</td>
<td>Ethanol</td>
<td>2-Propanol, Acetone Butanol</td>
<td>2.54</td>
<td>-</td>
</tr>
<tr>
<td>G</td>
<td>Ethanol</td>
<td>2-Propanol, Acetone</td>
<td>3.15</td>
<td>+ or -</td>
</tr>
</tbody>
</table>
Table 3: Table IV\textsuperscript{7} for viscosity of solvents from 0.59 to 3.18 mPa-s

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Viscosity at 20\textdegree C (mPa - s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.59</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.22</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>2.41</td>
</tr>
<tr>
<td>Butanol</td>
<td>2.95</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.80</td>
</tr>
<tr>
<td>Butyl acetate</td>
<td>0.88</td>
</tr>
<tr>
<td>2-Methylpropyl acetate</td>
<td>0.88</td>
</tr>
<tr>
<td>1-Propoxy-2-propanol</td>
<td>3.18\textsuperscript{(1)}</td>
</tr>
</tbody>
</table>

(1) measured at 25\textdegree C

Note: For reference, 10 Poise = 1 Pa – sec, or 1 cP = 1 mPa-sec, where the units of mPa-sec are often used in other works.

After extensive study, the researchers provide the following broad conclusion:

“There appears to be no obvious relation between gap filling properties and the chemical compositions. Gap filling phenomena relate not only to a complex behavior of the surface tension and viscosity change of the solution as a function of its concentration and the spinning speed, but also interfacial tension between the solution and the under layer film.”

For material curing, researchers have reported use of electron-beam exposure to cure siloxane\textsuperscript{8,9}, MSQ\textsuperscript{10}, HSQ\textsuperscript{11}. Others\textsuperscript{12,13,14} have used thermal processing with a relatively new material, polysilazane or PZ-SOD.

Researchers\textsuperscript{15} at Dow Corning Corp. have recently (2002) reported on SOD applications for 0.10 um design rules and below. They point out that a material needs to simultaneously meet the requirements of: gap fill, thermal budget and wet etch resistance. They provide a specific example of the 600\textdegree C phase transformation of Ti-silicates as one thermal budget limitation. Their study of SEM cross-sections reveal the “corner-etch” patterns of HSQ (hydrogen silsesquioxane) after being etched with 200:1 HF for 90 seconds. The HSQ was steam annealed at 700 \textdegree C for 30 minutes. The “corner-etch” regions have been reported to function as a stress relief in large regions. From their study of cure as a function of aspect ratio of feature being filled they make the following observation: “The densification of spin on materials in the sub micron trenches is a complicated process.” They offer the following areas of discipline: fluid mechanics, chemical reactions, mass transfer, heat transfer and interfacial science. Though implied by the engineering and science fields mentioned, modeling mathematics and programming are certainly appropriate.
The pattern samples were coated with a thin nitride layer prior to application of the SOD material. A casting rpm of 2000 was used with a total spin time of 20 seconds. The researchers used EELS-STEM (Electron Energy Loss Spectroscopy in Scanning Tunneling Electron Microscope) to map density and composition along with HAADF-STEM (High Angle Annular Dark Field) imaging. The differing degrees of inelastic scattering were used to distinguish differences in density. They report much larger low-density regions for N₂ cured HSQ as compared to oxidatively cured films. They propose that, in narrow trenches, the densification of HSQ films is constrained by the capillary effect and surface skin formation. They go on to state that, “the initial shape and film height in the trenches are determined by the surface tension of the HSQ solution.” They also used Ultrasonic Force Microscopy (UFM) to assess film density differences. The results of the Dow Corning work support the hypothesis that the cure process has unique limitations as the aspect ratio is increased. However, aspect ratio alone may not be as important as the absolute value of the X term when aspect ratio is defined as Y over X. The point will be expanded in the proposal of work section.

Though not directly connected to SOD applications, research by Luoh and coworkers does reflect the importance of managing stress in STI architectures. They report on the use of RTP steam oxidation to grow the liner oxide and the sacrificial oxide prior to final gate oxidation. This is compared to a standard thermal oxidation prior to STI fill with HDP oxide. The work was done in the context of a 0.25 um design rule flash technology. The approach uses ISSG (In Situ Steam Generation) in which the H₂ and O₂ are reacted at the wafer surface. The OH, O radical and atomic O reaction with Si-Si and Si dangling and strained Si-O bond occurs at pressures below 20 Torr. The resulting oxide is reported to have lower corner stresses based on simulations. This may suggest that such an environment would lend itself to oxidative reaction of SOD materials in thin layers.

The review has now covered the period from 1986 to 2002. The selected works represent the nature of hundreds of papers covering materials and process implementations in the period. The next step is to cover some aspects of spin coating that relate to modeling planarization.
Modeling Spin-Coating Planarization

Stillwagon and Larson\textsuperscript{17} updated their two-stage flow/shrinkage model to account qualitatively for solvent evaporation. In the introduction, they point out the simple relation of the balance between capillary (i.e. surface tension) and centrifugal forces. The issue of solvent evaporation is included because of the effect on viscosity. The general idea then is to maintain capillary effects as long as possible because they drive leveling (i.e. planarization). The centrifugal forces drive the film to a uniform thickness. The prime example is the so-called casting step in the spin-coat sequence: The rpm selected sets the film thickness on a bare wafer, and in most cases, on large features (e.g. 1000 um). Their model is a good candidate as a starting point because it includes: density of fluid, surface tension of fluid to air, angular velocity of spinning substrate, feature width, feature depth and radial position from center. To first order, the only missing factors would be a term to describe the nature of the feature before and after the depression being filled. The work of Stillwagon and Larson is very detailed and will be studied and exercised to a great extent.

The following reviews the component details of the Stillwagon and Larson model. For the flow stage of the model, planarization is given as $P_1$. The value of $P_1$ is calculated based on fundamental lubrication analysis for features with high values of $w/d$. Where $w$ is the feature width and $d$ is the feature depth. In deep sub-micron semiconductor applications the concept of aspect ratio is given as the opposite relation $d/w$, or more commonly, $h/w$. In this case, $h$ is later used to refer to the coating film thickness so $d$ will be kept as the parameter representing the depth of the feature or step-height to be planarized. The lubrication analysis is based on a balance between capillary and centrifugal forces.

They give the following relation as Equation 4 to express this balance:

\[
\Omega^2_i = \frac{\rho \omega^2 w^3 r_o}{\gamma h_i}
\]

\(\Omega\) = dimensionless value  
\(\rho\) = density of the fluid (SOD Material of interest)  
\(\omega\) = angular velocity of the spinning substrate  
\(\gamma\) = surface tension against air
w = width of feature (at depth d)
h₁ = film thickness on flat featureless area (i.e. unpatterened substrate or very large area)
r₀ = radial distance of the feature from the center of the feature (this definition is not supported by any kind of schematic)

The model predictions are for trenches arranged in concentric rings. One can interpret this to mean that the estimates apply to the infinitesimal case where the flow is normal to the step to be planarized.

In the case of the common 200 mm wafer used in semiconductor applications, the two factors angular velocity and r₀ are inter-related in the sense that for a given RPM, the value of angular velocity changes with r₀. Hence, the model will need to comprehend the complete wafer condition. For example, in the controlled studies, individual features can be examined for fixed r₀ and variable omega. While for the whole wafer case, we must somehow comprehend the effects of omega changing with r₀. Research¹² has shown a difference in post-clean dimensional change as a result of differences in RPM (and hence angular velocity and centrifugal forces). In their case, higher RPM was correlated to higher wet chemical etch rates hole-type features. The value P₁ is then plotted against values of Ω₁ with different curves for various values of h₁/d for isolated trench-like features.

Stillwagon and Larson make reference to the work of Emslie et al. who provided the flow relation:

\[
H = \left[1 + \frac{4}{3} \left( \frac{\omega}{r_0} \right) T \right]^{-1/2}
\]

where \( H \equiv \frac{h}{h_f} \) and \( T \equiv \frac{t}{t_c} \)

From this, Stillwagon and Larson define \( t_c \) as centrifugal time. The value is given by

\[
t_c \equiv \frac{w \eta}{(h_f)^2 \rho \omega^2 r_0}
\]

where \( \eta \) is the material viscosity. The centrifugal time is defined as the time required for the local film profile over the feature to come to equilibrium with the centrifugal field given a fixed film thickness far from the feature. The other factor is called the spin-down time and is given by

\[
t_s \equiv \frac{t_c r_0}{w}
\]
The third time factor is the time $t_L$ required for leveling from capillary forces. In the absence of centrifugal forces, this, in general, describes the condition when the film becomes level. This idea assumes that there is sufficient material to fill the feature. That is, $h_f$ is greater than $d$.

$$t_L \equiv \frac{\eta \omega^4}{\gamma h_f^3} = t_L \Omega^2$$

In a prior work\(^4\), Stillwagon and Larson gave typical values for the variables. Those are reproduced for reference in Table 4.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Numeric Range</th>
<th>Unit of Measure</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$</td>
<td>1</td>
<td>g/ml</td>
</tr>
<tr>
<td>$\omega$</td>
<td>200-850 (2000-8000)</td>
<td>rad/sec (RPM)</td>
</tr>
<tr>
<td>$w$</td>
<td>1-200</td>
<td>um</td>
</tr>
<tr>
<td>$r_o$</td>
<td>1-10</td>
<td>cm</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>20-50</td>
<td>dyn/cm</td>
</tr>
<tr>
<td>$h_f$</td>
<td>0.5-2</td>
<td>um</td>
</tr>
</tbody>
</table>

$h_f$ is the film thickness far from the feature $d$, the feature depth, is stated to be typically 1 um

For present day semiconductor applications, angular velocity extends to 1000 RPM, $w$ extends down to below 0.1 um (100 nm), surface tension can be near 10, film thickness extends down to 0.2 um (200 nm) and $d$ can be in the range of 0.2 to 2 um.

Peurrung and Graves\(^5\) followed Stillwagon and Larson to develop a simulation to predict the effect of an isolated block that disturbs the path of flowing material. They also include the evaporation effect and specifically point out that drying does not effect the film shape until the fraction of solvent drops such that the viscosity is high enough to effectively freeze the film in position. If we follow their assumption that the fraction shrinkage is constant without regard to thickness, a perfectly planar (global or local) surface after coat will have depressions where the film is of greatest thickness. This would suggest that the only method to achieve even local planarity would be to use many coats. However, present day experience says that such planarity can be achieved even after high temperature curing of a single coating. Hence, the need for a model that comprehends not only the coat and dry parameters but also the scaling effects.
Hirasawa and coworkers\(^2\) studied the surface-tension driven flow of liquid (i.e. SOG) on a two-dimensional grooved substrate during the drying or shrinkage phase. Their modeling approach makes the assumption that spreading (i.e. flow) driven by centrifugal force occurs mainly in the first 2 to 3 seconds and the dry shrinking occurs in the following 10 seconds (approximately). Therefore, they treat the two effects separately. The equation for the surface tension force includes a term for the pressure of the surrounding gas. The report some useful empirical relations that will guide development of models that are fine-tuned for smaller ranges of conditions. It seems clear from the existing works that a universal planarization and cure model is not practical, though the idea is not completely absurd.

Control of evaporation during the spin process is covered by various U.S. Patents (circa 1997 to 2000) and reflects the general idea that slowing the evaporation process increases the length of time that surface tension driven forces can improve planarity. One example is by Fairchild Technologies Corp.\(^2\), they demonstrated improvements in local planarity of both large (up to 200 um) and small features with 0.7 um steps. The other example is by Silicon Valley Group\(^3\) to be discussed later.

Kucherenko and Leaver\(^2\) report on spin coating work in the integrated optics and micro-mechanics area. They model features in 2D from 0.6 um to as high as 6 um. Their simplifications and range of features will provide guidance in developing more fine tuned models for the range of features encountered in deep sub micron semiconductor processing.

Gurer and coworkers\(^3\) report on the closed cup approach to DUV lithography coatings and low-k SOD materials. Because of the cost of DUV chemicals, one driving force is to reduce the amount dispensed per wafer. They report the ability to reduce the amount from 2 cc to as low as 0.4 cc for a 200 mm wafer. With chemical costs in the thousands per liter, this is a very important achievement. Their model results indicate that it is possible to planarize large steps if the evaporation rate can be sufficiently slowed.

Haas and coworkers\(^4\) studied the source of striations that can form in SOD coatings. They point out that surface tension gradients can develop. These gradients cause high surface tension regions to draw material from low surface tension regions. It is likely that this is a key factor in
modeling the interactions relative to the position of a given feature from the center of the spinning wafer.

Osredkar\textsuperscript{25} reported on his work to study the limits of SOG planarization. He concludes that a planarization factor (i.e. fractional step reduction) of 0.9 may be achievable with multiple coat/cure steps in local but not global regions.

**Proposed Work for Global Planarity**

The next phase of the work is to take the details of published models and calculate results based on a group of HSQ, MSQ, polymer and polysilazane materials as applied to various step height features and coating and cure conditions. The first pass will only cover enough points to determine where the various approaches fail to predict the existing planarization and cure (i.e. densification) profiles as a function of radial location, w, d and the critical aspect ratio of d/w. Prior works have used the ratio w/d but for this work, the more relevant ratio is the inverse.

The initial results will guide development of new parameters that are beyond the typical constants or fitting parameters often employed. Yes, such parameters can often serve a noble purpose but are not appropriate for this exploratory work.

Initial data collection plan is to measure planarity and density for w from 80 nm to 800 nm, d from 250 nm to 400 nm and $r_o$ from 0 (i.e. $< 2$ mm) to 90 mm. The longer view is to extend to values of w from 8000 nm (8 microns) to 100s of microns.

An example of large feature planarity is shown in Figure 3. The plot is created from the stylus deflection signal of a surface profiler. The double-ended arrow shows the degree of planarity from the base plane achieved for spaces that are a factor of 30 smaller. Ten units in the Z-axis are equal to one unit in the X-axis.
Figure 3: Global Planarity for Large Features

The zoomed view in Figure 4 shows the symmetry of the space planarity. There is some evidence of standing wave formation. The results are from an initial test of a thick coat HSQ material using a dynamic dispense and casting spin with following dry step.

Figure 4: Global Planarity for Large Features - Zoomed View

Optical image showing the region of zoom in Figure 4. Fringe lines are consistent with the surface profile results.

Figure 5: Optical Image of Large Feature Sample
The preceding figures and associated observations provide a baseline for more detailed study of the factors that influence the planarization effect. The work is expected to proceed in an iterative fashion: collect data; make model; calculate outcomes; generate prediction for comparison to observations; refine the model and parameters; repeat. The desired outcome is to create a family of models that will guide development of new SOD materials, coat techniques, and layout/structural rules for future technology.

Some initial interpretation of the known models is provided here for various conditions to be evaluated. The first case examines the unit-less term $\Omega^2$ in the regime of surface tension from 10 to 20 dyn/cm and values of w from 0.1 to 5 microns. The full range is shown in Figure 6 while the sub-micron range is shown in Figure 7. The general relation reported in prior works predicts increased planarity for values of $\Omega^2$ below $10^{-2}$. The figures show the predicted effect of surface tension of the SOD in relation to the surface being coated. The inputs to $\Omega^2$ are SOD density (SOD in solvent), wafer angular velocity, trench width, radial position of trench (9 cm) and SOD surface tension.

![Figure 6: Calculated Omega^2 for expected condition](image-url)
Figure 7: Calculated $\Omega^2$ in sub-micron range
Proposed Work for Small Feature Effect

The small feature effect is defined as the case where a feature filled by SOD is sufficiently small that the material no longer maintains bulk properties. This condition may exist as soon as after solvent bake out or as late as the final cure, or reaction, to the desired bulk property. In this context, bulk property refers to that observed for a blanket layer coated on un-patterned sample or for a feature that is greater than 50 microns in X and Y.

Etch rate of blanket films in wet chemistry will be used to provide a measure of bulk film properties. The same materials used for blanket films will be applied to pattern samples with various values of w and d. The materials will be applied through a range of thickness values and then processed through various cure environments. The term cure will be used in reference to any condition that results in a change in the material. Hence, this can include simple steps such as hot plate nitrogen treatment up to steps that are more complex.

On example is when a typical SOD material is exposed to oxygen plasma. The effect is shown in Figure 8 and Figure 9. The first shows the porous appearance in the narrow trench region for a cross-section sample that is has not been exposed to any kind of decoration etch. The second photo show the effect of s short exposure to an HF based etch solution. The oxide structure is completely removed as indicated by the dark region.
A second example is for SOD material treated with a combination of steam ambient and oxygen ambient at temperatures above 800ºC. This example provides a direct comparison of a region that is smaller by near a factor of 4 in w but with the same value of d. The arrow in Figure 10 indicates the direction of decreasing material density or change in material character. It is pointed out in this manner because it will be subsequently shown by TEM image that density alone is not the driving factor to cause an increase in material removal rate in the etchant used for decoration. This vertical transition is not evident for the feature shown in Figure 11. When the feature size is on the order of 20 microns in X and Y (in the horizontal plane) optical measurements have shown that the material has the same wet etch rate (WER) as a blanket film of similar thickness. Blanket is a term used to refer to a uniform coating on an un-patterned wafer.

The effect shown in Figure 8 through Figure 11 is known in the semiconductor industry but is not well understood. To a certain extent, cost effective implementation is limited by the need to complete a single coat and then react the material to the desired characteristic. Though multi-step sequences can overcome much of this effect, they are not cost effective. Therefore, this work will focus on finding the limiting mechanisms for the case shown.

One factor must be diffusion of oxidizing species through the material and removal of gaseous by products. If this is a main effect, then the amount of material above the small feature should have
some influence on the etch rate. The two cases shown in Figure 12 support that simple diffusion may not be a primary factor for the model.

<table>
<thead>
<tr>
<th>Case A: SOD fills just to near the top of the trench feature.</th>
<th>Case B: SOD is approximately 40 to 50 percent of trench depth above the top of the trench.</th>
</tr>
</thead>
</table>

![17 CENTER](image1)

![13 CENTER](image2)

Figure 12: Thickness Effect of Densification Reaction

The photos shown in Figure 13 of the wider features support uniform etch rate through the complete depth without regard to amount of SOD material above the feature opening. It is also important to note that the curvature over the wide feature does not indicate that material shrinkage is different within the limitation of the SEM photo as metrology. For solvent-based materials (like photo chemicals) shrinkage is generally stated as a percentage. Therefore, if SOD was acting primarily with linear shrinkage, the radius of curvature should have decreased proportionate to the difference in thickness of region A compared to region B (right side of Figure 13).
Materials and Structures

There will be three general material categories, hydrogen silsesquioxane (HSQ), methyl silsesquioxane (MSQ) and polysilazane. Treatments for densification will include, but are not limited to, thermal treatments in various ambient gas environments, electron beam exposure, plasma exposure and various wet chemical exposures. The work is expected to include combinations as required.

All work will be completed using 200-mm silicon substrates with topography. Materials will be dispensed either automatically or by hand depending on the material being evaluated. Coated samples will all include a minimum amount of hot plate baking to reduce solvent levels prior to subsequent reaction steps.

Analytical Methods

FTIR will be used as a reference method to determine the bulk character of materials after reaction treatments. Optical methods will be used to determine film thickness changes and refractive index. SEM section samples will be used to determine the relative etch rate of material in narrow and wide features. WER of large area features and blanket films will be collected as a reference for correlation to small feature etching. Section samples will be etched in various wet chemical solutions for correlation to the blanket films. Auger (and others as made available) elemental mapping will be used to determine distribution of expected components.
Surface profiles (contact stylus and AFM) will be collected to determine degree of planarity. Optical measurements will be made to corroborate the surface profile measurements.

Next Steps

Define initial set of conditions for screening experiment and run samples using PZ, HSQ, and MSQ materials. Samples will be measured by surface profile and optical methods. The optical method is currently limited to larger features. Samples will then be processed through the appropriate densification step and measured again by surface profile and optical methods. Finally, samples will be cross-sectioned and etched with various chemistries to determine the nature of bonding and composition in small features compared to large features.
References:


