Spin-On Inter-Metal Dielectric Materials: Hydrogensilsesquioxane versus Methylsiloxane

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Abstract
As technology races forward, older technology nodes are often the benefactors of new and more efficient technology. One case where this has not occurred is with spin-on inter-metal dielectric (IMD) materials. Methylsiloxane spin-on glass (SOG) has been a mainstay for IMD applications for the past 15 years: Availability, history, and lack of alternative options being the driving factors for its continued use. Hydrogensilsesquioxane (HSQ) spin-on dielectrics are providing new alternatives for the replacement of older SOG materials. This paper provides a comparative review of these materials, their uses, their extendibility, and their costs.

Introduction
Spin-on glass materials have been a mainstay as an inter-metal dielectric in semiconductor devices for more than 15 years. Starting with the use of silicate materials, SOG use migrated towards methylsiloxanes in the 1980’s to provide increased cracking resistance and minor improvements in dielectric constant. The initial industry drive for low-\(k\) materials in the 1990’s led to the introduction of silsesquioxanes to provide further speed enhancements for high-end devices.

Both of these materials continue in widespread use today, however, some confusion continues to exist around differences in these materials and their uses. Provided here is a comparative review of the two most common versions of these materials: methylsiloxane and hydrosilsesquioxane.

A brief review of the material chemistries will provide a base for better understanding technical differences between the products.

Processing flow overviews for methylsiloxane and hydrogensilsesquioxane products reveal that multiple opportunities exist for process-step reduction or elimination. These opportunities will be discussed, providing users with potential insights into improvements that may be applicable to their facilities.

A technical review, highlighting key film property differences and their impact to users, will then be provided. Technical limitations, with respect to product extendibility, will also be discussed.

Finally, taking into account technical impacts, processing differences, and product extendibility, a cost-of-ownership scenario will directly compare the cost-effectiveness of the two product families.

\[ \text{Material Chemistries and Manufacturing} \]

There are multiple manufacturing routes for methylsiloxane and HSQ materials [1], however, the most common route is a hydrolysies reaction: Methylsiloxane production involving the hydrolysis of tetraethylorthosilicate (TEOS), methyltriethoxysilane, and dimethyldioethoxysilane [2]; Whereas, HSQ involves the hydrolysis of trichlorosilane. Acid catalysts are also generally used in both processes. Common reactions for these processes can be summarized as follows:

\[
\text{Si(OEt)}_4 + \left[ \text{Me}_2\text{Si(OEt)}_2 + \text{MeSi(OEt)}_3 \right] + H^+ \xrightarrow{ROH} \text{methylsiloxane}
\]

\[
\text{HSiCl}_3 \xrightarrow{H^+ \text{ROH}} \text{hydrogensilsesquioxane}
\]

The hydrolysis reactions in both cases result in a resin slurry. This slurry may then be subjected to further processing such as drying and molecular weight fractionation. The resulting powered resin is then dissolved in a suitable carrier-solvent system and filtered in a cleanroom environment to required particle specifications.

The chemical structures for these two materials (shown in Figures 1 and 2) reveal a number of differences from a strictly chemistry perspective:

- HSQ is composed of fully condensed species whereas methylsiloxane is composed of <20% condensed species. This incomplete condensation of the methylsiloxane resin will readily allow moisture absorption. A direct result of the moisture absorption is increased silanol content in the...
As indicated above, methylsiloxane resins can be expected to have significantly higher silanol content than their HSQ counterparts. Silonal is known to have deleterious effects on final film properties such as dielectric constant, via outgassing, and film cracking threshold [3,4]. Additionally, silonal can reduce material shelf life and limit maximum solids content in solution due to its volatility and destabilizing effects on the resin.

The Si-H functionality present in HSQ materials presents an increased challenge in waste management and solvent compatibility as compared to the methylsiloxane’s organic groups. The presence of the inorganic HSQ in a largely organic material based fabrication facility means that additional considerations must be given to waste segregation and safety.

Inter-Metal Dielectric Process Flow

Basic processing steps for both materials consist of spin-coat deposition, soft-bake, and cure. Spin coating of both materials is carried out via standard, commercially available spin-tracks. Deposition recipes may require some optimization for each given application, however, are relatively simple and well characterized. General processing times for the deposition operation is less than one minute per wafer.

The bake processes—carried out to remove carrier solvents and soften materials for optimal flow across the topology—will vary slightly for each material. General bake temperatures are in the range of $80^\circ - 350^\circ \text{C}$. This process is most often performed on hotplates integrated with the coating track. Most processes include hotplate bakes of not more than one minute each and are carried out in an air or inert-blanketed environment.

The curing process for the materials is carried out in a quartz-tube furnace—generally under inert atmosphere. Processing times vary from 30 – 60 minutes in a temperature range of $350^\circ - 425^\circ \text{C}$. The curing process provides polymer cross-linking to provide mechanical integrity and film stability during subsequent processes.

While these basic process steps are very similar for the methylsiloxane and HSQ, consideration of a broader process flow shows some unique process differences that are directly attributable to the chemical composition differences discussed earlier. The comparative process flow view (provided in Figure 3) shows two key differences associated with these materials during routine processes.

The first key difference in the complete process flows is a frequent need for multiple methylsiloxane deposition/cure iterations to achieve desired thickness. The limitations in solids loading, discussed earlier, leads to a significantly lower single-coat thickness being achievable for the methylsiloxane materials. An increase in carbon content of the methylsiloxane is a possible route to increasing the thickness threshold for the material; however, this route leads to a degradation of the film’s adhesion and steam resistance properties [5].

A second, and possibly most significant, key difference is the widespread use of etchback processing with

![Figure 2: Basic chemical structure of methylsiloxane materials.](image)

![Figure 3: Process flow comparison for hydrogensilsesquioxane and methylsiloxane films for inter-metal dielectric applications.](image)
methylsiloxane films; whereas, the HSQ films are typically implemented in a non-etchback scheme. The etchback process removes the methylsiloxane from regions where vias will be opened in later process steps, leaving the SOG to fill only low-lying features. This removal is necessary as a means to avoid poisoned-vias—leading to high via contact resistance or electrical opens—caused by water emission from any methylsiloxane exposed in the via sidewalls during metallization processes [3,4].

In general, non-etchback processes are preferred due to the decreased process complexity, lowered costs, and lower occurrence of etch-related particles/defects.

Finally, additional minor process differences may apply depending on the individual implementation of the methylsiloxane material. Some of those possible (shown in Figure 3) include: Film hold or queue prior to multiple depositions and bakeout processing prior to metal deposition if any siloxane film remains exposed.

**Film Properties**

Final films prepared from the HSQ and methylsiloxane materials show a few key differences important to IMD applications – Table 1 summarizes these properties for films cured at 425°C.

<table>
<thead>
<tr>
<th></th>
<th>Methylsiloxane</th>
<th>Hydrogensilsesquioxane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max. single-coat thickness (nm)</td>
<td>500</td>
<td>1,200</td>
</tr>
<tr>
<td>Tensile Stress (MPa)</td>
<td>120</td>
<td>75</td>
</tr>
<tr>
<td>Dielectric Constant @ 1 MHz</td>
<td>3.8</td>
<td>2.9</td>
</tr>
<tr>
<td>R.I. @ 632 nm</td>
<td>1.40</td>
<td>1.38</td>
</tr>
<tr>
<td>Modulus of Elasticity (GPa)</td>
<td>17</td>
<td>6</td>
</tr>
<tr>
<td>Minimum Gap-fill Capability (nm)</td>
<td>300</td>
<td>&lt;&lt; 50*</td>
</tr>
</tbody>
</table>

*Absolute minimum has not yet been established

Figure 4: Fourier Transform Infrared Spectroscopy (FTIR) spectra of as-spun hydrogensilsesquioxane and methylsiloxane films.

The cured polysilicate nature of the methylsiloxane means that its dielectric constant and refractive index properties will be similar to that of SiO₂: The small amount of remaining carbon in the structure lending to the slightly lower values (i.e., \(k = 3.8\) for methylsiloxane films versus 4.2 for SiO₂). HSQ films, by comparison, retain a more open cage-like structure leading to greater free space in the films and, subsequently, a lower dielectric constant of 2.9.

The cage like structure of the HSQ, however, also leads to a lower modulus of elasticity for these films when compared to methylsiloxane. The open structure creating a softer, less densified film by a factor of three.

Finally, gapfill capabilities of these two materials are known to be dramatically different. Methylsiloxane is generally limited to filling gaps greater than 300nm. The lower limit for HSQ, on the other hand, has not yet been reached; however, it is known to be capable of filling gaps below 50nm. Figure 5 provides one example of minimum gapfill for HSQ. This difference in gapfill capability for these materials has significant impacts on the material extendibility as discussed below.
Material Extendibility

The gapfill capabilities of the methylsiloxane materials limit its use in IMD applications to design rules greater than 350nm. HSQ, to date, has found use in IMD applications down to the 130nm technology nodes due to its superior gapfill ability. The broader technode applicability means increased lifetime for tool sets and fewer product requalification costs due to material and process changes associated with IMD.

Further supporting the broader technology node usage of the HSQ materials is the lower dielectric constant. The 3.8 dielectric constant of methylsiloxane films often fails to provide adequate interconnect performance beginning around the 350nm technology node. HSQ films provide a 15–25% improvement in inter-metal and intra-metal capacitance leading to significant improvements in device performance and speed.

Material versatility beyond IMD applications is also worth brief mention. Methylsiloxane and HSQ films may also be used in pre-metal dielectric (PMD) applications [6]. Both materials having a Si-O backbone structure allows for high temperature curing to remove functional groups and create SiO2 films.

Additionally, HSQ films are also used as a negative tone e-beam resist for nanoscale structures [7], and the high aspect-ratio gapfill capabilities of these materials are showing great promise for use in shallow trench isolation (STI) applications below 90nm [8,9].

Process Cost-of-Ownership

Based on the process flows described here, a cost-of-ownership (CoO) scenario can be determined. Modeling detailed here was performed using a commercially available software tool for semiconductor processes.

In order to provide a relative comparison of the methylsiloxane and HSQ materials and their respective processes, it is necessary to derive a baseline fabrication process to work from. The key parameters and values used for this modeling are detailed in Table 2.

The parameters detailed in Table 2 are a small portion of the overall model, however, they represent the key parameters that will change relative to the material and process differences discussed previously. A final note in considering the cost data and parameters presented here: this is intended as a generic model and the results a relative comparison—individual results for a given fabrication facility will vary depending on the integration process used, actual equipment and material costs, etc.

The baseline inter-metal dielectric process described here results a cost per good wafer out of USD $3.69. This value includes the deposition, bake, and cure of the two IMD layers necessary for a three level metal device. The result for the baseline etchback process is USD $1.43/wafer.

Starting from this baseline, the following key differences must be considered:

- **Multiple Coating Operations**: If multiple coats of methylsiloxane materials are used, the net effect is a reduction in throughput and increase in material usage. In the case of a double coating operation (modeled in this scenario) the throughput would be reduced to 25 wafers/hour and material usage increased to 6.5ml per IMD layer.
- **Hold Time in Process**: When a hold or queue time is employed within the methylsiloxane process, the effective throughput of the process is decreased. The addition of a one-hour hold time will reduce throughput for this process to 25 wafers/hour—this scenario will be used for modeling.
- **Etchback processing**: This is an additional process step used in many methylsiloxane applications. This process must be modeled separately and included in the overall cost per wafer to complete the IMD process.
- **Etchback Yields**: Etchback processes may often have small yield loss associated with the process due to micro-loading during etch and subsequent re-deposition of particles. A 0.025% yield loss will be
considered to provide a reference point in this model.

The effects of the process differences detailed above are provided in Figure 6. The baseline process of USD $3.69 per wafer is the cost of basic deposition, bake, and cure for both materials under consideration shown in the lower bars of the graph. Costs, in excess of this baseline, for each of process variations associated with methylsiloxane properties are shown in the upper bars.

As seen, addition of even simple changes can increase process costs by as much as 22%. Since the HSQ materials generally follow the baseline process, one must conclude that the methylsiloxane, if implemented with any variations from this basic flow, will have added costs. These costs may range from 22%, for the addition of a short hold time, to 75%, or more, if multiple coating operations or multiple process changes are employed.

Conclusions

Hydrogensilsesquioxane and methylsiloxane products have both found widespread use in inter-metal dielectric applications. In many senses, these materials display similar film properties and share common processing characteristics. All things considered, however, HSQ maintains several advantages with respect to processing simplicity, technology extendibility, and dielectric performance. Moreover, these advantages equate to possible cost savings opportunities for manufacturers of 75% or more per wafer.

References


![Figure 6: Process cost-of-ownership comparison for HSQ and methylsiloxane processes.](image)