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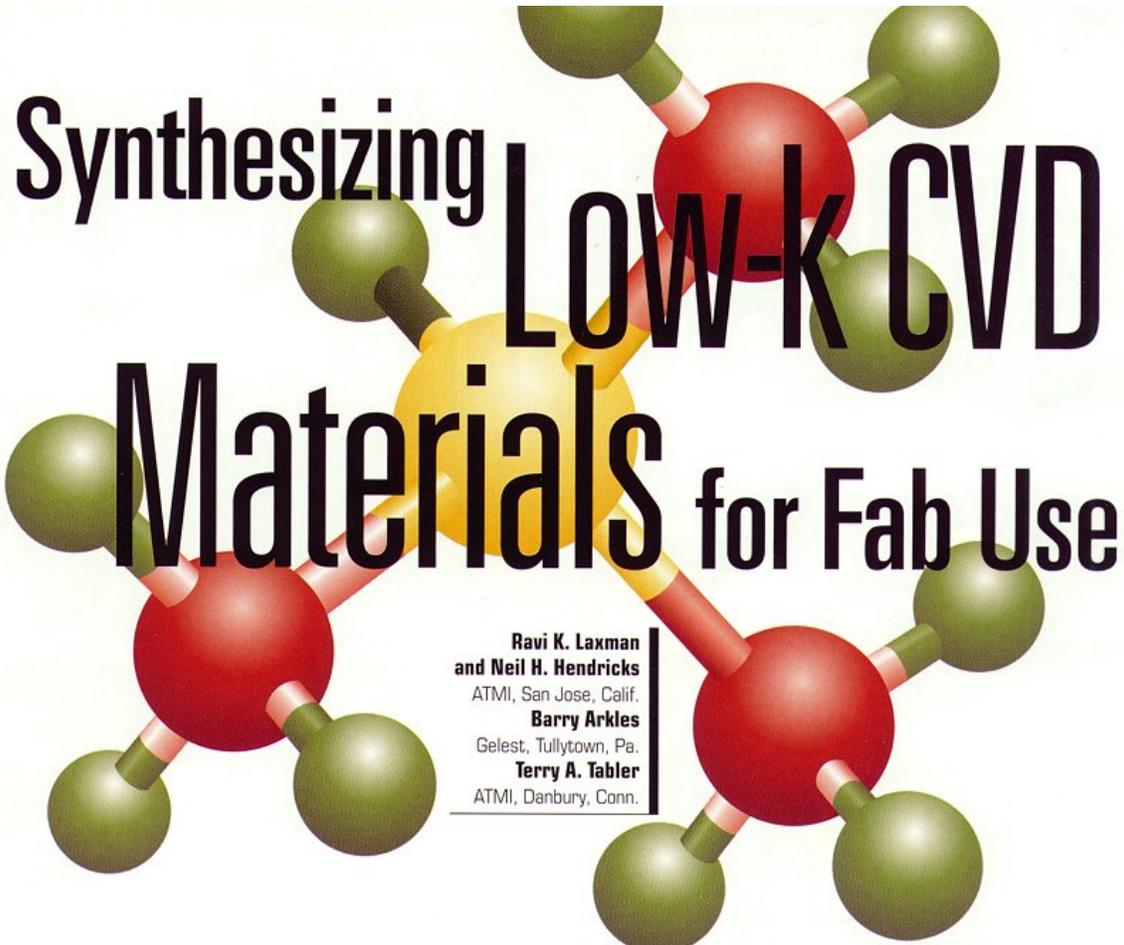
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Synthesizing Low-k CVD Materials for Fab Use

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Several major OEMs and their customers are developing processes to fabricate low-k CVD films with dielectric constants as low as 2.5. The seemingly simple addition of methyl groups to silicon dioxide to form a film with lower dielectric constant, k , is actually not so simple when you consider the synthesis of the gas or liquid precursor. For instance, trimethylsilane (3MS), probably the most widely integrated low-k CVD candidate at the 0.13 μm node, requires a multi-step synthetic process. Its preparation is more complex than that of tetraethylorthosilicate (TEOS), the “baseline” CVD dielectric precursor chemical,^{1,2} but it is more straightforward than the synthesis of low-k spin-on dielectrics, polymers that incorporate a much higher degree of molecular engineering. The following describes the various synthesis processes for several CVD low-k precursors, and shows how a novel delivery system can solve troubling chemical handling and transportation issues associated with 3MS delivery.

The OSG structure

When intermetal spacings in advanced IC interconnects become smaller than $\sim 0.18 \mu\text{m}$, low-k

dielectric insulators are needed to minimize RC delays and power consumption. Many researchers have described motivations for integrating low-k intermetal dielectric (IMD) as a replacement for CVD-deposited SiO_2 .³⁻⁸ Among many low-k candidates, however, only a few materials have shown all the required properties needed for integration into high-volume manufacturing processes.⁹ Unfortunately, the most promising precursors, alkyl and alkoxy silanes, do not currently have large-scale electronic or other industrial uses. For this and other reasons, the chemical synthesis of the precursors used to deposit low-k films constitutes an important set of technologies that directly impact the development

At a Glance

Development and process integration of CVD-deposited organosilicate glass (OSG) materials is underway for 0.13 μm device fabrication. Relative to TEOS, OSG precursors — including trimethylsilane (3MS) and tetramethylsilane (4MS) — are more complex to synthesize. This article presents synthesis routes for 3MS, 4MS and other low-k CVD precursors, and proposes a novel method for handling and delivering 3MS to the tool.

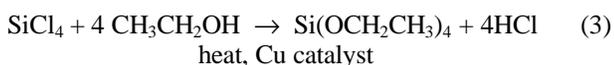
In today's typical CVD low-k films, 10%-25% of the silicon atoms are substituted with organic groups, typically methyl, CH₃. Incorporation of these groups strongly affects the key properties of the resulting film.

and manufacture of advanced ICs with copper damascene interconnects. Several companies are developing low-k CVD films using a variety of carbon-containing precursors. The resulting organosilicate glass (OSG) films, also called carbon-doped oxides, have a composition of Si_wC_xO_yH_z. The implementation of CVD low-k technology can benefit from a study of the differences between these organosilicon CVD precursors (with their silicon-carbon bonds) and TEOS.

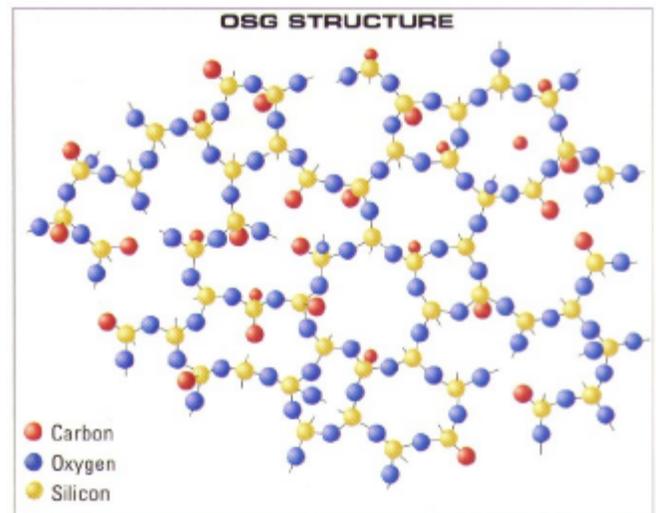
The organic groups in OSGs invariably take the form of tetravalent silicon with a wide range of alkyl and alkoxy substitutions. In these films, the silicon-oxygen network seen in glass is occasionally interrupted, in a more or less homogeneous fashion, by the presence of organic, typically methyl (CH₃) groups. Hydride (H) substitution at silicon can also be present. The film's lower dielectric constant, k, is due to these changes to the SiO₂ network and the reduced density of the OSG film relative to SiO₂. In tropical CVD low-k films, 10% to 25% of the silicon atoms are substituted with organic groups. A graphical representation (Figure) shows the differences in chemical bonding between amorphous SiO₂ and amorphous OSG (Si:C = 4:1). Incorporation of methyl or other groups has a significant effect on the key physical, thermal and chemical properties of the resulting film.⁹

TEOS synthesis

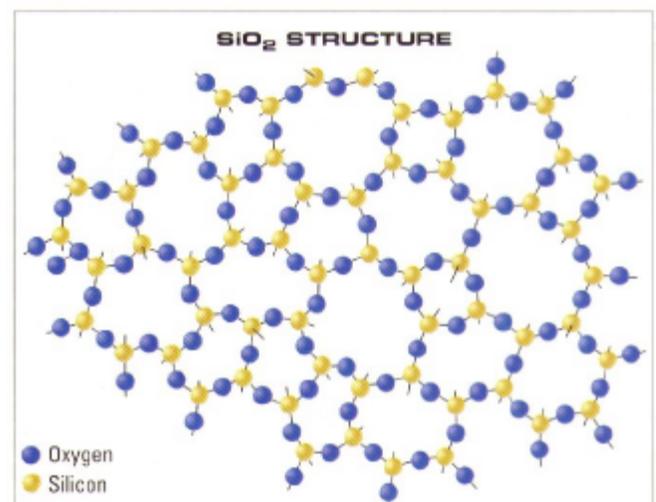
TEOS is an important industrial chemical used as a binder for cement casting, in high-temperature zinc-rich paints, in fabrics, and in a wide range of industrial films and coatings such as plastic optics. In fact, electronics applications constitute less than 5% of the world's TEOS production. The industrial route to TEOS takes place in three steps by reacting: silica with graphite to make silicon metal; silicon metal with chlorine to make silicon tetrachloride; and SiCl₄ with ethanol to make TEOS:¹⁰



In device manufacturing, TEOS provides lower deposition and oxide formation temperatures as well as more conformal coatings than silane (SiH₄).^{11,12} As a result, TEOS has replaced silane in many oxide CVD processes. In principal, the above reactions could be used to manufacture semiconductor-grade TEOS. However, the necessary removal of traces of chloride is problematic and expensive. Instead, chlorine-free TEOS¹³ is manufactured according to:



Graphical representations of the difference in chemical bonding structure between SiO₂ (above) and organosilicate glass with a Si:C of 4:1 (below).



Property	Trimethylcyclo-trisiloxane	Tetramethylcyclo-tetrasiloxane (TMCTS)	Tetramethylsilane (4MS)	Trimethylsilane (3MS)	Dimethylsilane (2MS)	Methylsilane (1MS)
CAS No.	541-05-9	556-67-2	75-76-3	993-07-7	1111-74-6	992-94-9
Molecular weight (g)	222.46	296.62	88.23	74.2	60.17	46.14
Melting point	64°C	17°C	-99°C	-136°C	-150°C	-157°C
Boiling point	134°C	175°C	26.6°C	6.7°C	-20°C	-57°C
Flash point	35°C	51°C	-27°C	<-20°C	<-40°C	<-40°C
Hazardous Materials Information System Codes						
— Health	1	1	1	2	3	3
— Flammability	3	3	4	4	4	4
— Reactivity	0	0	0	1	1	3
Autoignition temperature	n/a	400°C	450°C	310°C	230°C	130°C

Alkyl silanes & siloxanes

OSG films require silicon-carbon bonds, of which no known examples exist in nature. The silicon-oxygen structure in TEOS, by contrast, is common in nature—more than 27% of Earth's crust is silicon, all reacted with oxygen.

OSG films can be prepared from both substituted silanes and siloxanes. As shown in the forthcoming reactions, the industry uses fundamentally different synthetic processes for low-k OSG precursors than those used for TEOS.

The substituted silanes are most commonly alkylated silicon derivatives (molecules) wherein one to four of the hydrogen atoms have been replaced with an organic group—typically, but not necessarily, a methyl (CH₃) group. As shown through the series of chemical reactions that follow, the ubiquitous presence of the methyl group in organosilicon chemistry can ultimately be traced to the availability of methanol from very large-scale petroleum processes.

Siloxanes are silicon derivatives that have Si-O-Si linkages. As is the case with alkylated silanes, the methyl group is the most common organic substituent in siloxanes. Hydrogen substitution on silicon (Si-H) is often present and plays an important role in both types of OSG precursors.

The chemistry of organically substituted silicon has been comprehensively researched.^{1,2} The Table lists several key properties of representative OSG precursors.

The industry knows and has investigated all the alkylated (methylated) derivatives of silane (SiH₄)

for use in CVD low-k film deposition. These include methylsilane (CH₃)SiH₃, dimethylsilane (CH₃)₂SiH₂, trimethylsilane (CH₃)₃SiH and tetramethylsilane (CH₃)₄Si. While all of these methylated silanes are in principle useful in the deposition of CVD low-k films, trimethylsilane (3MS) and tetramethylsilane (4MS) are the derivatives that have received the most attention.

Trimethylsilane, 3MS

Trimethylsilane's most significant industrial use is in the semiconductor industry. Companies are using 3MS to deposit both low-k OSG films (k<3.0) and low-k barrier films (k~5) as a replacement for silicon nitride (k~7). Fabricators use a multi-step synthetic route based on dimethylchlorosilane (CH₃)₂Si(H)(Cl) to make 3MS. This route is problematic and rather expensive because dimethylchlorosilane is itself acquired as a very minor component resulting from the reaction of methyl chloride with silicon:



where (CH₃)SiCl₃, (CH₃)₂SiCl₂ and (CH₃)₃SiCl are the primary products. Thus, the desired dimethylchlorosilane must be distilled from the reaction mixture using large, specialized distillation towers.

Then the trimethylsilane is prepared via the methylation of dimethylchlorosilane using the Grignard methylating reagent derived from methyl chloride. The synthesis of methyl chloride (which is also a reactant in reaction 5) starts with methanol

The industry uses fundamentally different synthetic processes for low-k OSG precursors than those used for TEOS.

It is important to remove all traces of MgCl_2 and other sources of chloride for use in low-k semiconductor processes.

(CH_3OH). Methanol forms the basis for most organically substituted silicon chemicals, and is synthesized from petroleum byproducts in large process chemical volumes. Methyl chloride is converted to the required Grignard reagent through:

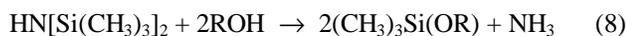


Finally, combination of the Grignard reagent with dimethylchlorosilane yields trimethylsilane:

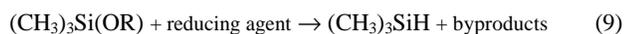


Reaction 7 is carried out under quite high-dilution conditions, typically in tetrahydrofuran (THF), to optimize yield. This in turn adds cost and complexity. Finally, it is important to remove all traces of MgCl_2 and other sources of chloride for use in low-k semiconductor processes.

By analogy to the use of a chloride-free process in the synthesis of TEOS, one can use a second approach to 3MS that employs a chloride-free chemistry developed by Gelest. In the first step, Gelest treats hexamethyldisilazane (HMDS) with an alcohol to form an alkoxy derivative, also called a silicon ester:



Then they directly reduce the ester to 3MS according to:

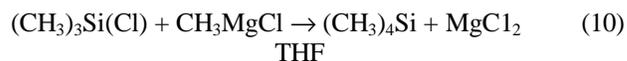


This method features high yield and overall purity, and it results in a chloride-free 3MS product. Disadvantages include the relatively high cost of both the silicon ester and suitable reducing agents.

Tetramethylsilane, 4MS

Tetramethylsilane has historically been used as an internal standard in nuclear magnetic resonance (NMR) spectroscopy. Thus it had a minor application, largely as a research chemical, prior to its introduction as a CVD low-k precursor. In recent investigations into the environmental abatement of 4MS in the CVD low-k process, ATMI demonstrated that the chemical is more kinetically stable, and thus more resistant to decomposition, than other

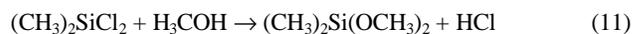
alkylated silanes. We can synthesize tetramethylsilane through the methylation of trimethylchlorosilane:



Because trimethylchlorosilane is a product of reaction 5, one can prepare 4MS using a route similar to the traditional synthesis of 3MS. In both preparations, the fabricator must take great care to remove traces of chloride and other impurities.

Dimethyldimethoxysilane

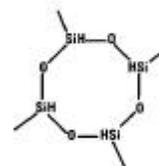
Siloxanes, both acyclic and cyclic, can be used in the fabrication of OSG films. We show examples of both, starting with dimethyldimethoxysilane, $(\text{CH}_3)_2\text{Si}(\text{OCH}_3)_2$. Its use in CVD film fabrication has been described.¹⁴ Dimethyldi-methoxysilane is prepared through the reaction of dimethyldichlorosilane (from reaction 5) with methanol:



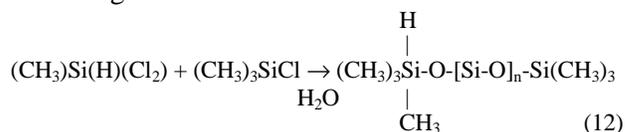
As with other precursors, one must remove all traces of chloride from the dimethyldimethoxysilane. Unfortunately, highly toxic methanol is released when the CVD low-k precursor is used.

TMCTS

The cyclic 1,3,5,7-tetramethylcyclotetrasiloxane (TMCTS) may also be used as a low-k CVD precursor:¹⁵⁻¹⁷

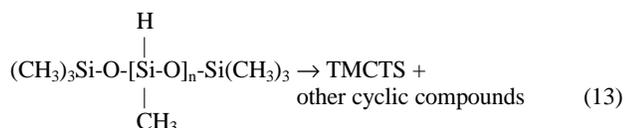


TMCTS is prepared through hydrolysis of methyldichlorosilane to firstly form a linear siloxane polymer that is end-capped with trimethylsilyl groups (derived from trimethylchlorosilane) according to:



Sub-atmospheric delivery of 3MS to the CVD tool is safe and cost-effective.

The linear siloxane polymer is subsequently “backtracked” to form a combination of cyclic siloxanes, predominantly 6-, 8- and 10-membered rings:



The company then distills the product to separate the TMCTS from other products of the depolymerization.

OSG packaging, storage, delivery

As with most traditional CVD materials, the new low-k precursors are either gases (e.g., methylsilane and dimethylsilane) or liquids—including tetramethylsilane (4MS) and alkoxy-substituted silanes and siloxanes. As such, the majority of these low-k precursors are amenable, with only slight modification, to the chemical packaging and CVD delivery equipment utilized with traditional CVD dielectric precursors. However, the physical properties of one important CVD low-k precursor, trimethylsilane, introduce significant challenges to chemical transport and delivery in the fab environment.

Trimethylsilane is a highly flammable, liquefied compressed gas with a relatively low vapor pressure of ~8 psig at 21°C, and a boiling point of 6.7°C. CVD low-k processes require flow rates as high as 2.0 slpm per chamber or greater. While personnel can transport 3MS through the fab as a liquid (like TEOS), adsorption of inert “push gases” would result. Conversely, the use of traditional, positive pressure, gas phase distribution methods creates conditions that support the liquefaction (condensation) of 3MS in distribution tubing. Furthermore, 3MS’s relatively low vapor pressure and high heat of vaporization (5.8 kcal/mole) readily cause the source vessel to drop below atmospheric pressure, generating flow perturbations. These fluctuations can cause mass flow controller errors and contribute to CVD tool downtime.

Since neither traditional liquid nor conventional gas delivery schemes appeared suitable for 3MS, ATMI developed an approach using a “sub-atmospheric fab-wide storage and delivery system.”¹⁸ The delivery system incorporates an integral vacuum actuated cylinder¹⁹ for the fab-wide 3MS source. The system further uses an adsorbent-based, sub-atmospheric, point-of-use reservoir²⁰ for local storage and immediate availability of 3MS and a sub-atmospheric gas control system.²¹ The user avoids condensation problems by withdrawing the 3MS directly from the source vessel outlet as a sub-atmospheric vapor. By positioning the sub-atmospheric 3MS reservoir at or near the CVD tool, 3MS flow perturbations are eliminated. Finally, in addition to providing an uninterrupted supply of 3MS to multiple CVD tools, the 3MS delivery system increases safety by removing liquefied compressed gas cylinders and change-outs from the sub-fab. This dramatically reduces the capital and installation costs of the delivery system.

Conclusions

At the 0.13 μm device generation, leading-edge companies are beginning to incorporate low-k dielectric films in their copper damascene interconnect structures. From the standpoint of complexity, the synthesis, purification and handling of a low-k CVD precursor is more difficult to prepare than TEOS, but is considerably less complex than spin-on low-k polymeric films. These new CVD low-k films are being prepared using a wide range of organically substituted silicon-based chemicals. We showed the various synthesis techniques, noting the advantages and disadvantages associated with each route. To handle and deliver 3MS, ATMI developed a chemical storage and delivery system that helps move 3MS into the production fab environment. •

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