# Hexachlorodisilane as a Precursor in the LPCVD of Silicon Dioxide and Silicon Oxynitride Films

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## ABSTRACT

Films of silicon dioxide and silicon oxynitride were grown by LPCVD using gas-phase mixtures of $Si_2Cl_6$, $N_2O$, and $NH_3$ in the temperature range 550°-850°C. The activation energy for $SiO_2$ deposition was 29 kcal/mole. Under comparable pressure and temperature conditions, growth rates of $SiO_2$ from $Si_2Cl_6$ were at least three times higher than those obtained using $SiH_2Cl_2$ or $SiH_4$. The effect of temperature and reactant flow ratios on film composition, stress, refractive index, etch rate, and uniformity were studied, and these properties were found to be comparable to those in films deposited from $SiH_2Cl_2$ and $SiH_4$. The effect of $N_2O/NH_3$ ratio on physical properties was investigated for oxynitride films. The dependence of these properties on film composition was the same regardless of the CVD reactant mixture used. However, the $NH_3$ to oxidant ratio required to obtain a specific film composition was strongly influenced by the oxidant and silicon precursor used. Comparisons are made to the LPCVD systems: $SiH_2Cl_2$-$N_2O$-$NH_3$, $SiH_4$-NO-$NH_3$, and $SiH_4$-$CO_2$-$NH_3$.

We have recently reported on the use of hexachlorodisilane ($Si_2Cl_6$) in the chemical vapor deposition of polycrystalline and amorphous silicon (1) and silicon nitride (2). Hexachlorodisilane was selected as a possible safe and efficient alternative to silane and dichlorosilane, the currently preferred precursors in silicon and silicon nitride CVD. Since we found $Si_2Cl_6$ capable of producing high quality films of both Si and $Si_3N_4$ over a wide range of temperatures, an extension of the investigation to the deposition of $SiO_2$ and silicon oxynitride films would be clearly of interest. Although $SiO_2$ can be deposited at moderate temperatures with nonhazardous precursors such as tetraethoxysilane (TEOS) (3, 4) or diacetoxyditeriarybutoxysilane (DADBS) (5, 6), higher temperature depositions (>750°C), which lead to improved density, uniformity, and conformality, are still carried out using either $SiH_2Cl_2$-$N_2O$ (7-13) or $SiH_4$-$N_2O$ (8, 14, 15). Silicon oxynitride films are deposited almost exclusively from $SiH_2Cl_2$-$N_2O$-$NH_3$ (16-20) or $SiH_4$-$NH_3$-$CO_2$(NO) (21-24) gas mixtures. In contrast to $SiH_4$ and $SiH_2Cl_2$, $Si_2Cl_6$ is not known to autoignite under ambient conditions. It is a liquid with a vapor pressure that allows useful transport rates with minimal source temperature control and the vapor readily decomposes to provide films of silicon and silicon nitride down to 450°C.

## Experimental

The $SiO_2$ and oxynitride films were deposited in a tubular hot-wall reactor at temperatures from 550° to 850°C. The 1 in. diam (100) silicon substrates were placed horizontally on a quartz plate. Total pressure was maintained at 0.7 torr by an automatic throttle valve located downstream. Distilled $Si_2Cl_6$ was supplied by Cambridge Isotope Laboratories (Cambridge, Massachusetts), and contained less than 0.01% chlorosiloxane. $N_2$, $NH_3$, and $N_2O$ gases were all 99.999% pure. In $SiO_2$ film growth, the total flow of $N_2O + N_2$ was kept at 250 sccm with $N_2O$ between 50 and 250 sccm, while the flow of $Si_2Cl_6$ was varied between 2-11 sccm. This resulted in an $R = N_2O/Si_2Cl_6 = 5$-125. For the growth of silicon oxynitride, the flow of $Si_2Cl_6$ was either 2 or 10 sccm. The total flow of $NH_3 + N_2O$ was constant at 150 sccm, whereas $N_2$ was fixed at 100 sccm. The ratio $R' = (N_2O + NH_3)/Si_2Cl_6$ was therefore either 15 or 75, while $NH_3/N_2O$ varied from 2.0 to 0.07. The $Si_2Cl_6$ container was held at 5°C (1.2 torr vapor pressure) and flow was controlled by a needle valve. The 5°C temperature (6°C above the melting point) was chosen in order to obtain acceptable growth rates and still conserve the $Si_2Cl_6$ source material. The partial pressure of $Si_2Cl_6$ in the system ranged from 0.0055 torr (2 sccm) to 0.03 torr (11 sccm).

Film thickness and index of refraction were measured with a Gaertner ellipsometer equipped with a He-Ne laser. Auger electron spectroscopy was used for Si, N, O, and Cl analysis. Hydrogen content and Si-H and N-H bond distributions were determined with a Nicolet Model 5PC FTIR spectrometer. X-ray topography was used to measure film stress. Etch rates were measured by ellipsometry after room temperature etching in 100:1 $H_2O$:HF.

## Results and Discussion

*Silicon dioxide.*—The silicon dioxide growth rate as a function of temperature is shown in Fig. 1 for $R = 15$ and 75 over the temperature range 550°-850°C. No $SiO_2$ growth was observed below 550°C. Since growth of $Si_3N_4$ occurred as low as 450°C (2), the higher minimum growth temperature for $SiO_2$ must be due to lower reactivity of $N_2O$. The dashed lines are the observed temperature-dependent growth rates for $Si_3N_4$ (2) at $R = 15$ and 75 with an activation energy of 29.3 kcal/mole. It can be seen that the same activation energy applies to $SiO_2$ deposition between 600° and 750°C where the deposition is most likely surface reaction-controlled. The slope decreases above 750°C, suggesting the beginning of a mass transport-limited reaction. Similar growth rate saturation occurs at the same temperature in the $SiH_4$-$N_2O$ (15) and TEOS (4) systems. The 29.3 kcal/mole activation energy is comparable to the 33 kcal/mole re-

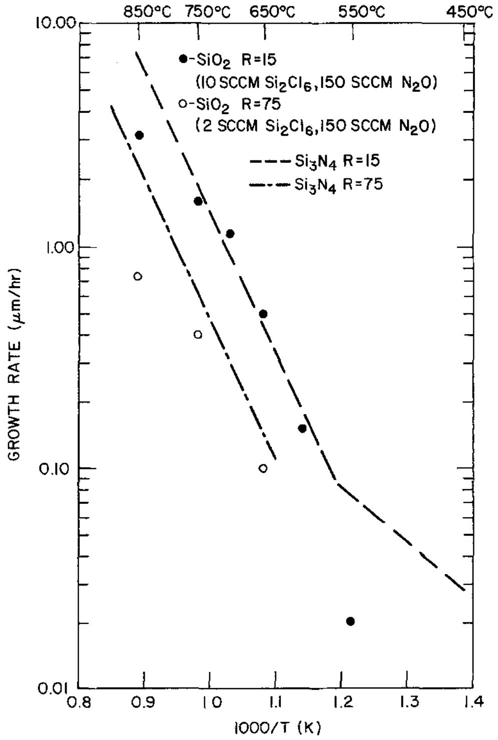

**Fig. 1. Growth rate of $SiO_2$ and $Si_3N_4$ as a function of substrate temperature at $R = 15$ and $R = 75$.**

ported for $SiH_4$-$N_2O$ (15), higher than the 12.0 kcal/mole found for $SiH_4$-$O_2$ (25), but lower than the 45-46 kcal/mole found for TEOS (3, 4) and $SiH_2Cl_2$-$N_2O$ (13).

The $SiO_2$ growth rates obtained using $R = 15$ vary from 3.2 μm/h at 850°C to 0.02 μm/h at 550°C. If the $Si_2Cl_6$ flow is decreased by 80% to 2 sccm ($R = 75$), the growth rate also decreases by 80% at all temperatures. A 67% drop in growth rate was observed for $Si_3N_4$ films under the same conditions (2). The effect on growth rate of changing $R$ by increasing $N_2O$ flow from 50 to 250 sccm (partial pressure 0.134-0.673 torr) while $Si_2Cl_6$ flow remains constant at 10 sccm (partial pressure 0.027 torr) is shown in Fig. 2 for 650° and 750°C. Comparable results for $Si_3N_4$ are given by the dashed lines. At both temperatures, the $SiO_2$ growth rate is directly proportional to the $N_2O$ flow. In contrast, $Si_3N_4$ growth at 650°C saturates for $NH_3$ flows having $R > 10$(2).

The growth rates obtained compare very favorably to all other moderate to high temperature CVD methods. Appreciable growth generally cannot be observed below 800°C in the $SiH_2Cl_2$-$N_2O$ system. The deposition rate at 900°C is only 0.3-0.7 μm/h at a total pressure of 0.6-0.8 torr and 0.08-0.09 torr $SiH_2Cl_2$ partial pressure (8, 10). In contrast, the $SiO_2$ growth rate from $Si_2Cl_6$-$N_2O$ at 850°C was 3.2 μm/h at a total pressure of 0.7 torr and $Si_2Cl_6$ partial pressure of only 0.03 torr. A similar comparison was noted in $Si_3N_4$ growth (2). Dichlorosilyene ($SiCl_2$), produced by homogeneous decomposition, has been singled out as the film growth precursor using chlorinated monosilanes (1). If this is the case, then the growth rate advantage of $Si_2Cl_6$ could be due to its considerably lower kinetic stability toward gas-phase decomposition into this intermediate. However, a growth rate advantage of $Si_2Cl_6$ also exists relative to $SiH_4$-$N_2O$(8, 15). In this system, growth rates between 0.15-0.30 μm/h have been observed at 850°C at 1.0 torr total pressure and 0.01-0.02 torr $SiH_4$ partial pressure. Deposition rates comparable to our results are obtained with TEOS(3) and DADBS(5), at 725° and 600°C, respectively, but much higher precursor partial pressures must be used (0.35 and 0.7 torr).

Auger (AES) analysis of films grown at 750°C ($R = 20$-100) and at 650°C ($R = 75$) showed the films to contain 30 atom percent (a/o) Si. Therefore, within the accuracy of AES (±3 a/o) the films appear to be somewhat oxygen-rich. As in the case of $Si_3N_4$, the $R$ values used to achieve this stoichiometry lie between those found for oxide growth from $SiH_2Cl_2$ and $SiH_4$. The chlorine content was 1.3 a/o for a film grown at 750°C using $R = 20$, whereas it was nondetectable (<0.2 a/o) for $R = 100$. At 650° and 750°C with $R = 75$, the Cl concentration was 0.5 a/o. Chlorine is therefore in the high $10^{19}$ atom/cm$^3$ range, about the same as reported for films grown from $SiH_2Cl_2$ at 800° (12) and 900°C (9). Chlorine seems to be uniformly distributed throughout the thickness of the film, within the accuracy of AES, with possibly a slight buildup at the Si/$SiO_2$ interface.

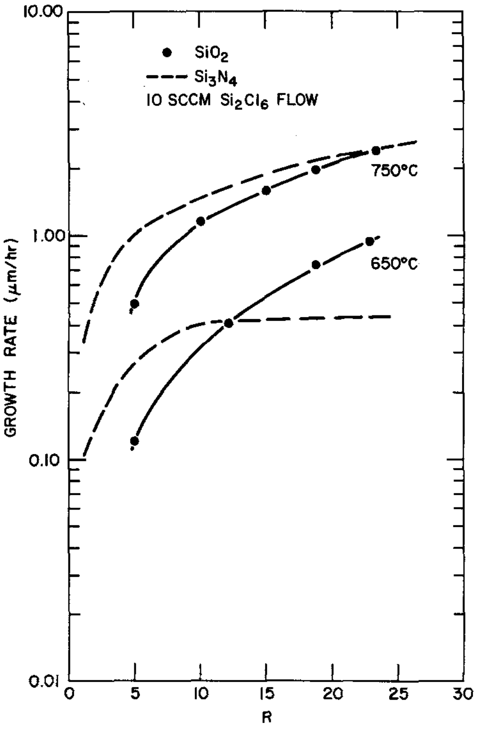

Fig. 2. Growth rate of $SiO_2$ and $Si_3N_4$ as a function of $R$($N_2O$/$Si_2Cl_6$ or $NH_3$/$Si_2Cl_6$).

**Table I. Stress and refractive index in silicon dioxide films**

| Growth temperature (°C) | $R$ | Stress ($10^9$ dynes/cm$^2$) | $n$ |
|---|---|---|---|
| 600 | 20 | −2.2 | 1.54 |
| 650 | 5 | −3.6 | 1.55 |
| 650 | 20 | −3.1 | |
| 650 | 75 | | 1.49 |
| 750 | 5 | −4.2 | 1.53 |
| 750 | 20 | −3.2 | 1.51 |
| 750 | 75 | −2.3 | 1.47 |
| 850 | all | | 1.47 |

Deposition under optimized flow and temperature conditions led to $SiO_2$ films with good thickness uniformity. For example, for 750°C and $R = 75$, films deposited on substrates placed in the 30 cm central zone of the reactor showed less than ±3.5% thickness variation. Comparison with other CVD systems is difficult without having data for $Si_2Cl_6$ for vertically mounted close-spaced wafers. Compositional uniformity was excellent. Figure 3 reveals Auger profiles of a 300Å $SiO_2$ film grown at 750°C with $R = 100$, and for comparison, a 240Å $Si_3N_4$ film grown from $Si_2Cl_6$ and $NH_3$ at the same temperature with $R = 60$. Table I provides film stress and index of refraction measurements. Stress in the oxide films was compressive. It increased with both increasing deposition temperature and decreasing $R$, and is very typical of $SiO_2$ films deposited by other methods at these temperatures (26). The higher index films in Table I are likely to be somewhat silicon-rich. Using the relationship given by Learn and Jackson (15), an index change from 1.47 to 1.53 would correspond to 2.5 a/o excess silicon.

*Silicon oxynitride.*—The growth rate plots for silicon oxynitride (SiON) deposited at temperatures between 650°-850°C ($R' = 15$ or 75) lie between the plots obtained for $Si_3N_4$ and $SiO_2$ shown in Fig. 1. The effect of the reactant flow ratio ($R'' = N_2O/(N_2O + NH_3)$) on the oxygen content ($O/(O + N)$) is shown in Fig. 4. It is evident that the reactivity of $NH_3$ is higher than that of $N_2O$, because $R'' = 0.85$ is required to achieve $O/(O + N) = 0.5$ in the film. The effect is even more pronounced with $SiH_2Cl_2$-$N_2O$-$NH_3$(18, 19) as shown in Fig. 4, where $R'' = 0.95$ for $O/(O + N) = 0.5$. At $O/(O + N) = 0.15$, the Si concentration in the film is 44 a/o

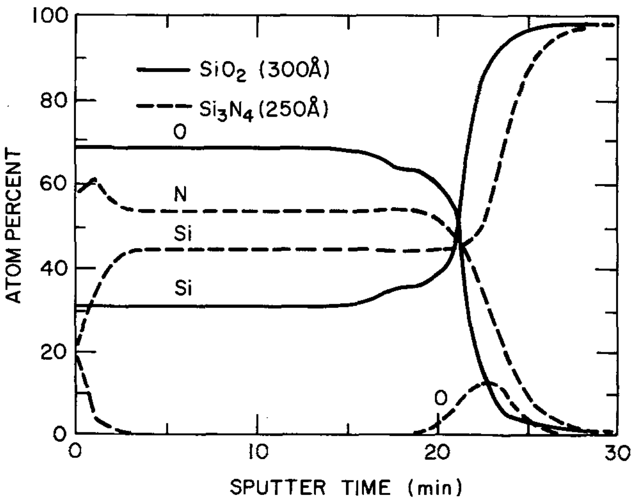

Fig. 3. Auger depth profile of $SiO_2$ and $Si_3N_4$ films deposited on Si substrates at 750°C with $R = 100$ and $R = 60$, respectively.

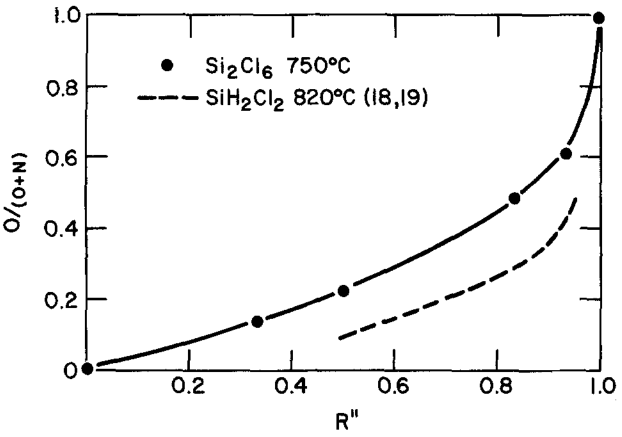

**Fig. 4. Effect of reactant flow ratio, $R''$, on SiON film composition in $Si_2Cl_6$ and $SiH_2Cl_2$ systems.**

typical of $Si_3N_4$. For $O/(O + N) \geq 0.23$, the Si content is 32-34 a/o, corresponding to $SiO_2$, but lower than expected for these intermediate compositions. Silicon deficiencies of a few a/o are common in LPCVD oxynitride films grown from both $SiH_2Cl_2$ and $SiH_4$ (16, 19, 24). For films grown at 750°C and $R' = 75$, the chlorine concentrations decreased rapidly from 1.0 a/o in films with $O/(O + N)) = 0.61$, to values below detectibility (<0.2 a/o) for oxygen contents below 0.42. A similar trend was reported for $SiH_2Cl_2$ grown films (18).

The effects of oxygen content $(O/(O + N))$ and $R''$ on film refractive indexes are depicted in Fig. 5 and 6, along with data for several other CVD systems (16, 19, 23, 24). Film indexes vary smoothly with composition regardless of the CVD system, as expected, but not with $R''$, where $R''$ may be considered here to be the oxidant/(oxidant + $NH_3$) ratio. The latter result simply reflects the effect of the relative reactivities of the precursors on film composition. The use of $SiH_2Cl_2$ results in a very low $N_2O$ reactivity, requiring $R'' = 0.95$ to grow a film with $n = 1.67$, an index corresponding to $O/(O + N) = 0.5$. Very low $NH_3$ reactivities are observed in the $SiH_4$-based methods. The use of $CO_2$ results in a film with $n = 1.67$ when $R'' = 0.23$, whereas $R'' = 0.05$ is required to achieve this index when NO is the oxidant. On the other hand a smooth variation of index with $R''$ over much of its range is observed using $Si_2Cl_6$, resulting in a minimum variation of composition with reactant flow fluctuation.

The FTIR spectra between 2000 and 3500 $cm^{-1}$ are shown in Fig. 7 for films of silicon nitride and SiON $(O/(O + N) \simeq 0.5)$ grown at 750°C. Using Lanford and Rand's method (27), the hydrogen concentration of both films was determined to be $\simeq 3.5 \times 10^{21}$ atoms/$cm^3$ (3.5-4 a/o), which is close to that found in films grown from $SiH_2Cl_2$(18). Differences in the hydrogen distributions are clearly observed for the two films. Previously, we found (2) that $Si_3N_4$ films grown at 750°C contained hydrogen in predominantly Si-H form; the distribution is 60% SiH and 40% N-H for the film shown in Fig. 7. The addition of oxygen to

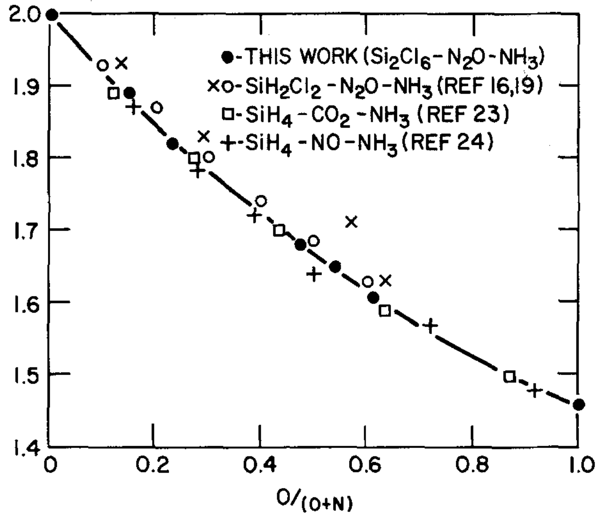

**Fig. 5. Effect of SiON film composition on index of refraction for several CVD systems.**

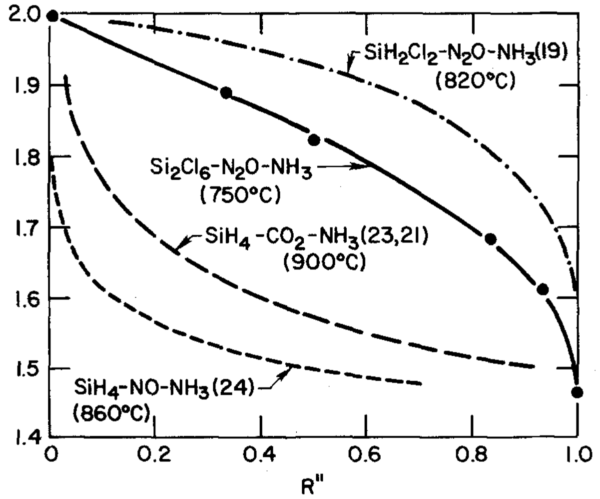

**Fig. 6. Effect of $R''$(oxidant/(oxidant + $NH_3$)) on SiON index of refraction for several CVD systems.**

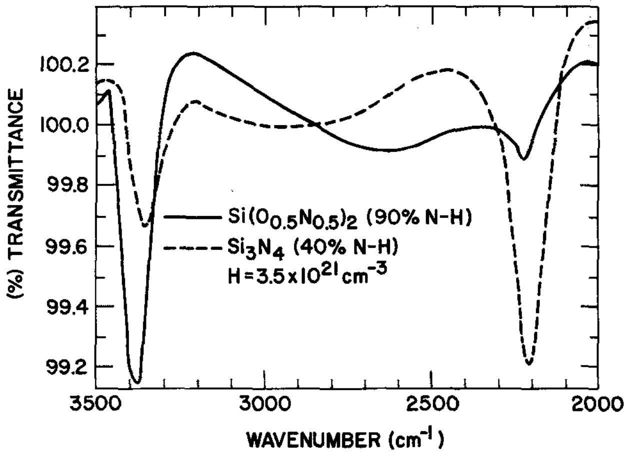

**Fig. 7. IR spectra from 2000-3500 $cm^{-1}$ for SiON and $Si_3N_4$ films with $3.5 \times 10^{21}$ $cm^{-3}$ hydrogen grown at 750°C.**

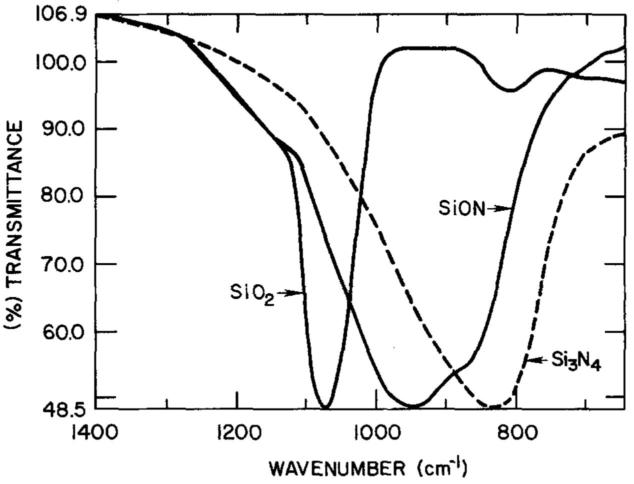

**Fig. 8. IR spectra from 650-1400 $cm^{-1}$ for SiON, $Si_3N_4$, and $SiO_2$ films grown at 750°C.**

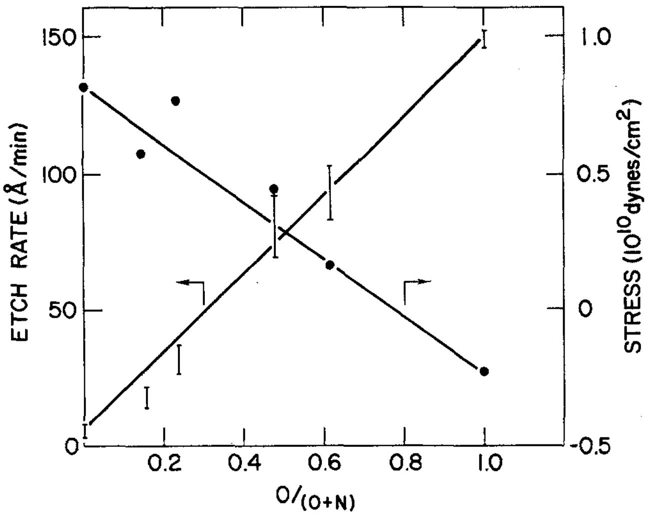

Fig. 9. SiON film stress and etch rate in 100:1 $H_2O$:HF as a function of film composition. All films were grown at 750°C with $R' = 75$.

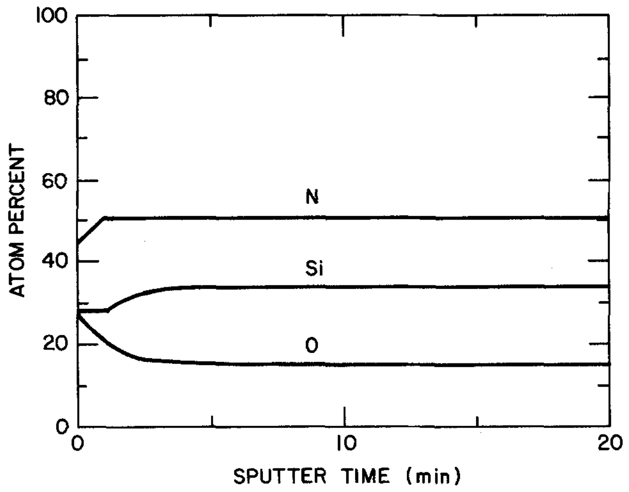

Fig. 10. Auger depth profile of top 300Å of SiON film grown at 750°C

produce SiON yields 90% N-H/10% Si-H, a distribution commonly observed in $Si_3N_4$ films grown from $SiH_2Cl_2$-$NH_3$ (28, 29). Figure 8 shows IR spectra between 700 and 1400 cm$^{-1}$ for 2000Å films of $SiO_2$, $Si_3N_4$, and SiON ($O/(O + N) \simeq 0.5$). All were grown at 750°C. The Si-O and Si-N stretching modes of the $SiO_2$ and $Si_3N_4$ films are at 1080 and 840 cm$^{-1}$, respectively. The broad peak from the SiON film is at 950 cm$^{-1}$, indicating a different bonding matrix, not a mixture of $SiO_2$ and $Si_3N_4$ clusters. Similar observations were made for films grown from $SiH_2Cl_2$ (16).

Film stress and etch rate for SiON as a function of film composition are shown in Fig. 9. All films were grown at 750°C with $R' = 75$. Stress displays a linear decrease with increasing oxygen concentration from $8.2 \times 10^9$ dynes/cm$^2$ ($Si_3N_4$) to $-2.3 \times 10^9$ dynes/cm$^2$ ($SiO_2$). Zero stress occurs for $O/(O + N) = 0.77$ at $R'' = 0.98$. In general, film stress decreased slightly with decreasing growth temperature. Film etch rates in 100:1 $H_2O$:HF increase linearly with increasing oxygen content from 5 to 150 Å/min as the composition changes from pure $Si_3N_4$ to $SiO_2$. The stress and etch rate data are very typical of films grown under comparable conditions by other methods (26).

Auger measurements indicate excellent compositional uniformity. The profile of the top 300Å layer of a 1000Å film grown at 750°C ($R'' = 0.5$) is shown in Fig. 10. The film composition is 34.5 a/o Si, 50.3 a/o N, 15.2 a/o O, and no detectable Cl. However, the wafer-to-wafer thickness uniformity varied considerably with the $N_2O/NH_3$ ratio. At 750°C and $R' = 75$, depletion effects were very strong at high $NH_3$ partial pressures. Increasing $N_2O$ partial pressure caused the thickness gradients to decrease. Thickness uniformity over the central 30 cm segment of the reactor was ±30% for $Si_3N_4$(2), whereas it is ±3.5% for $SiO_2$ under similar conditions, and lies intermediate for the oxynitride films. Depletion effects can be minimized or eliminated and thickness profiles improved by either increasing $Si_2Cl_6$ flow (decreasing $R'$) or lowering the deposition temperature.

## Conclusions

We have shown that high quality films of silicon dioxide and silicon oxynitride can be deposited by LPCVD using hexachlorodisilane as a precursor. Growth takes place at temperatures above 550°C. For $T > 750$°C, growth rates are greatly enhanced compared to monosilane and dichlorosilane, the precursors most commonly in use. The higher growth rate from $Si_2Cl_6$ is attributed to its lower kinetic stability and greater reactivity. Physical and chemical properties of the films are comparable to those obtained from other precursors at these temperatures. The higher growth rates and possibly greater safety margins associated with the use of $Si_2Cl_6$ make it an attractive alternative to silane and dichlorosilane in CVD processes for silicon and its insulators.

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# Chemical Vapor Deposition of Epitaxial Silicon from Silane at Low Temperatures

## I. Very Low Pressure Deposition

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ABSTRACT

The deposition of epitaxial silicon films at temperatures from 600°-800°C by both very low-pressure chemical vapor deposition (VLPCVD) and plasma-enhanced chemical vapor deposition (PECVD) has been examined. The VLPCVD deposition process is first order in silane partial pressure, zero order in hydrogen partial pressure, and exhibits a low, 8-12 kcal/mole, activation energy for temperatures from 700°-800°C with 1-15 mtorr silane and hydrogen. For temperatures below 700°C an activation energy of 40 kcal/mole is observed. The growth rate depends upon surface orientation, decreasing in the order (100), (111), polycrystalline, indicating surface processes are rate controlling. The low activation energy regime is associated with a process controlled by silane adsorption and decomposition on a sparsely covered silicon surface. The higher activation energy regime is thought to reflect growth under conditions of high surface coverage with silane fragments and the transition temperature is thought to be pressure dependent. Conditions for the deposition of device quality epitaxial silicon at low temperatures are defined and discussed. Plasma enhancement of the VLPCVD process is discussed in a companion paper.

This paper and a companion paper examine the epitaxial deposition process under very low-pressure chemical vapor deposition (VLPCVD) and plasma-enhanced chemical vapor deposition (PECVD) conditions, respectively. Previous PECVD epitaxy research has focused on the role of a plasma in enhancing the removal of native oxide and made independent analysis of deposition enhancement difficult. In this work we examine VLPCVD and PECVD growth processes subsequent to an optimized argon plasma sputter cleaning procedure (1, 2). Plasma enhancement for crystalline deposition operates as a parallel addition to an existing heterogeneous thermal deposition process. Thus it was necessary to first isolate the nature of the VLPCVD process in order to interpret or assess any enhancement processes. The ultimate goal of this research, however, was the development and implementation of a technologically useful process for the deposition of epitaxial silicon at low temperatures.

This paper (Part I) will discuss the experimental determination of reaction orders and apparent activation energies for the VLPCVD deposition process. These results are then compared with the literature to provide a consistent picture of the interaction of silane with silicon surfaces at low temperatures. Existing deposition models will be assessed to determine their validity and to propose directions for more comprehensive modeling of silicon deposition from silane. Conditions which lead to the deposition of device quality epitaxial silicon films suitable for bipolar device fabrication will also be presented. The second paper (Part II) will discuss plasma enhancement of the deposition process within the context of the thermal deposition model. It will be shown that, as implemented here, plasma enhancement of intrinsic deposition is relatively inefficient but does not introduce any observable degradation in film quality. This will set the stage for the more crucial application of plasma enhancement to the deposition of doped epitaxial films at low temperatures which will be discussed elsewhere (3, 4). Methods for increasing the efficiency will be discussed and suggestions for future PECVD implementations will also be provided.

### Intrinsic VLPCVD

Although silicon deposition from silane has been studied for over 20 years there is still a surprising lack of understanding of mechanistic details, particularly concerning surface-controlled deposition processes. Early research, carried out in atmospheric pressure systems employing surface temperatures in excess of 1000°C, typically exhibited significant gas-phase heating and silane decomposition. Deposition kinetics were generally determined by mass-transfer limitations and thus strongly coupled to the details of the reactor hydrodynamics. Modeling efforts focused on solution of the relevant mass and energy balances coupled with simplified treatment of the silane reaction network. These early models suffered from a lack of detail and thus were only able to reproduce or predict isolated features of the deposition systems and could not truly be considered predictive. Recent advances in the understanding of the basic gas-phase reaction network for homogeneous silane pyrolysis (5) and application of sophisticated hydrodynamic modeling have led to the development of detailed models for silicon deposition under conditions where gas-phase reaction and mass transport dominate the deposition kinetics (6-8). These models are quite general and are capable of predicting reactor behavior under a variety of experimental conditions provided a defined geometry is employed. A common feature of these models, however, is the lack of detail concerning the direct, heterogeneous decomposition of silane at silicon surfaces which must appear as a boundary condition in the numerical simulations.

As deposition pressures and temperatures are reduced to suppress homogeneous decomposition and improve deposition uniformity, the importance of these surface interactions increases relative to the homogeneous pyrolysis deposition pathway. Recently it was pointed out that overestimation of the rate of homogeneous silane pyrolysis under low pressure conditions has led to incorrect and misleading conclusions regarding the extent of gas-phase decomposition under low temperature, LPCVD conditions (9). As a result most silane deposition processes are completely controlled by surface chemistry which is, as yet, poorly understood and subject to considerable controversy. For the very low pressure conditions employed

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