Chemical Vapor Deposition of Silicon Nitride and Oxynitride*

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1 Introduction

Stoichiometric silicon nitride (Si$_3$N$_4$) is used for chemical passivation and encapsulation of silicon bipolar and metal oxide semiconductor (MOS) devices, because of its extremely good barrier properties for water and sodium ion diffusion. Water causes device metallization to corrode, and sodium causes devices to become electrically unstable. Silicon nitride is also used as a mask for the selective oxidation of silicon, and as a strong dielectric in MNOS (metal-nitride-oxide-silicon) structures.

The use of ion implantation for the formation of active layers in GaAs MESFET devices (Figure 1) allows for control of the active layer thickness and doping density. Since implantation causes structural disorder, the crystal lattice of the GaAs must be subjected to a post implantation rapid thermal anneal step to repair the damage and to activate the implanted species. The required annealing temperature (> 800 °C) is higher than the temperature at which GaAs decomposes. Silicon nitride encapsulation is used to prevent such dissociation. Silicon nitride is also used for the final encapsulation of GaAs MESFET devices (Figure 1).

Figure 1: Schematic diagrams of a GaAs metal-semiconductor field effect transistor (MESFET). Adapted from A. R. Barron, in CVD of Nonmetals, Ed. W. S. Rees, Jr., Wiley, NY (1996).

The deposition of Si$_3$N$_4$ is a broadly practiced industrial process using either grown by low pressure CVD (LPCVD) or plasma enhanced CVD (PECVD) with comparable properties for the grown films (Table 1).

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Table 1: Summary of the properties of silicon nitride grown in typical commercial systems.

One of the disadvantages of Si$_3$N$_4$ is its high dielectric constant that may limit device speed at higher operating frequencies. It is hoped that silicon oxynitride (SiON) films will exhibit the best properties of Si$_3$N$_4$ and SiO$_2$, namely the passivation and mechanical properties of Si$_3$N$_4$ and the low dielectric constant and low stress of SiO$_2$.

A summary of some typical CVD systems for silicon nitride is given in Table 2.

<table>
<thead>
<tr>
<th>Silicon precursor</th>
<th>Nitrogen source</th>
<th>Carrier gas</th>
<th>CVD method</th>
<th>Deposition temp. (°C)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH$_4$</td>
<td>NH$_3$</td>
<td>N$_2$</td>
<td>APCVD</td>
<td>70 - 900</td>
<td></td>
</tr>
<tr>
<td>SiH$_4$</td>
<td>NH$_3$</td>
<td>Ar/N$_2$</td>
<td>PECVD</td>
<td>20 - 600</td>
<td>Commercial process</td>
</tr>
<tr>
<td>SiH$_4$</td>
<td>N$_2$</td>
<td>N$_2$</td>
<td>PECVD</td>
<td>70 - 300</td>
<td>Porous films</td>
</tr>
<tr>
<td>SiCl$_2$H$_2$</td>
<td>NH$_3$</td>
<td>N$_2$</td>
<td>LPCVD</td>
<td>700 - 900</td>
<td>Commercial process</td>
</tr>
<tr>
<td>Si$_2$Cl$_6$</td>
<td>NH$_3$</td>
<td>-</td>
<td>LPCVD</td>
<td>450 - 850</td>
<td></td>
</tr>
<tr>
<td>Et$_2$SiH$_2$</td>
<td>NH$_3$</td>
<td>-</td>
<td>LPCVD</td>
<td>650 - 725</td>
<td>C impurities</td>
</tr>
<tr>
<td>RSi(N$_3$)$_3$ (R = Et, tBu)</td>
<td>-</td>
<td>-</td>
<td>LPCVD</td>
<td>450 - 600</td>
<td>Danger precursor explosive</td>
</tr>
<tr>
<td>MeSiH(NH)$_n$</td>
<td>-</td>
<td>NH$_3$/H$_2$</td>
<td>APCVD</td>
<td>600 - 800</td>
<td>Significant C content</td>
</tr>
</tbody>
</table>

continued on next page
2 CVD of silicon nitride from hydrides and chlorides

The first commercial growth of silicon nitride was by the reaction of SiH4 and NH3 by either atmospheric pressure CVD (APCVD) or PECVD. Film growth using APCVD is slower and requires higher temperatures and so it has been generally supplanted by plasma growth, however, film quality for APCVD is higher due to the lower hydrogen content. While thermally grown films are close to stoichiometric, PECVD films have a composition in which the S/N ratio is observed to vary from 0.7 - 1.1. The non-stoichiometric nature of PECVD films is explained by the incorporation of significant hydrogen in the films (10 - 30%). PECVD of SiNx using SiH4/N2 leads to electronically leaky films due to the porous nature of the films, however, if an electron cyclotron resonance (ECR) plasma is employed, SiNx films of high quality may be deposited on ambient temperature substrates.

The more recent commercial methods for silicon nitride deposition involves LPCVD using SiCl2H2 as the silicon source in combination with NH3 at 700 - 900 °C. The reduced pressure of LPCVD has the advantages of high purity, low hydrogen content, stoichiometric films, with a high degree of uniformity, and a high wafer throughput. It is for these reasons that LPCVD is now the method of choice in commercial systems. A large excess of NH3 is therefore used in commercial systems to obtain stoichiometric films. Silicon nitride has also been prepared from SiCl4/NH3, SiBr4/NH3, and, more recently, Si2Cl6/NH3.

Silicon oxynitride (SiON) may be prepared by the use of any of the precursors used for silicon nitride with the addition of either N2O or NO as an oxygen source. The composition and properties of the SiOxNy films may be varied from SiO2-like to Si3N4-like by the variation of the reactant flow rates. SiCl2H2 gas plumbing to a LPCVD reactor must be thermally insulated to prevent condensation that would otherwise lead to hazy deposits on the film. The volatile by-products from CVD produce NH4Cl at the exhaust of the reaction tube, and in the plumbing and pumping system. It would be desirable, therefore, to find an alternative, chlorine-free silicon source with none of the toxicity or pyrophorocity problems associated with SiH4. It is for this reason that organosilicon compounds have been investigated.

3 CVD from organosilicon precursors

Diethylsilane, Et2SiH2, has shown promise as a replacement for SiH4 in the low temperature LPCVD of SiO2, and has been investigated as a source for SiNx and SiOxNy films. Deposition by LPCVD in the presence of NH3 produces SiNx films, in which the carbon contamination (4 - 9%) depends on the partial pressure of the Et2SiH2. The presence of carbon raises the refractive index (2.025 - 2.28) with respect to traditional LPCVD films (2.01). Mixtures of Et2SiH2, NH3, and N2O deposit SiOxNy films where the composition is controlled by the NH3:N2O ratio.

3.1 CVD from silicon-nitrogen compounds

The incorporation of carbon into silicon nitride films is a persistent problem of organosilicon precursors. Several studies have been aimed at developing single source precursors containing a Si-N bond rather than Si-C bonds. Polyzidosilanes, RnSi(N3)4-n, are low in carbon and hydrogen, reasonably volatile, and contain highly activated nitrogen, however, they represent a significant explosive hazard: they are explosive with an equivalent force to TNT. Films deposited using EtSi(N3)3 and (tBu)Si(N3)3 showed promise, despite the observation of oxygen and carbon. Pyrolytic studies on the azide precursors suggest that the primary
decomposition step is the loss of dinitrogen, which is followed by migration of the alkyl onto the remaining nitrogen, (1). The fact that neither the addition of \( \text{NH}_3 \) or \( \text{H}_2 \) influence the film deposition rate suggest that the intramolecular nitride formation process is fast, relative to reaction with \( \text{NH}_3 \), or hydrogenation.

\[
\begin{align*}
\text{N}_2\text{N} & \xrightarrow{\Delta} \text{N} \quad \text{N} \\
\text{N}_2 & \rightarrow \text{RN} \\
\end{align*}
\]

(1)

Carbon incorporation is also observed for the APCVD deposition from \( \text{Si(NMe}_2\text{)}_n\text{H}_{4-n} \) (\( n = 2 - 4 \)). However, using the Hoffman transamination reaction, deposition in the presence of \( \text{NH}_3 \) completely removed carbon incorporation into the stoichiometric \( \text{Si}_3\text{N}_4 \) film. From FTIR data, the hydrogen content was estimated to be 8 - 10 atom percent. While the \( \text{Si(NMe}_2\text{)}_n\text{H}_{4-n}/\text{NH}_3 \) system does not provide substantially lower temperatures than APCVD using \( \text{SiH}_4/\text{NH}_3 \) growth rates are significantly higher. Unlike the azide precursors, \( \text{Si(NMe}_2\text{)}_n\text{H}_{4-n} \) are easier to handle than either \( \text{SiH}_4 \) or \( \text{SiCl}_2\text{H}_2 \).

4 Bibliography