

LOW PRESSURE CHEMICAL VAPOR DEPOSITION OF SILICON NITRIDE USING MONO- AND DISILYLAMINE

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The Si_3N_4 low pressure Chemical Vapor Deposition process typically involves the reaction of dichlorosilane (SiH_2Cl_2) and ammonia (NH_3) at 780°C because of the excellent properties of the films hence deposited. However, the combination of the precursors results in the generation of NH_4Cl , which deposits in the exhaust line. In an attempt to address this issue, an in-situ QMS study of $\text{SiH}_2\text{Cl}_2\text{-NH}_3$ reaction led the authors to consider the Cl-free monosilylamine SiH_3NH_2 and disilylamine (SiH_3) $_2\text{NH}$ as alternative precursors.

1. In-situ QMS study of DCS-NH₃ reaction

DCS and ammonia were introduced in a chamber consisting of a quartz tube heated by a conventional 3-zone furnace ($T = 780^\circ\text{C}$). The chamber was pumped using a mechanical booster backed by a rotary pump. The pressure was set between ~ 0.5 and 5 Torr by a butterfly valve. A fraction of the gas downstream the furnace was diverted for analysis by QMS.

Several transient molecules have been detected such as $\text{SiH}_2\text{Cl}(\text{NH}_2)$ and diaminosilane (DAS, $\text{SiH}_2(\text{NH}_2)_2$), resulting from successive ammonolyses of DCS. Interestingly, an unexpected molecule, monosilylamine (MSA, SiH_3NH_2), was identified. A reaction mechanism is proposed involving all these species. Finally, we found MSA to convert with time, at least to some extent, to disilylamine (DSA, $(\text{SiH}_3)_2\text{NH}$).

2. Isolation and storage method for silylamines

The setup described above was modified in order to compress and store the synthesized MSA and DSA in a cylinder in order to assess the capability of these molecules to deposit silicon nitride. Additional N_2 could be used as a precursor carrier gas. Different experimental conditions have been performed, with temperature in the $25\text{-}200^\circ\text{C}$ range and pressure typically set at $\sim 30\text{-}40$ Torr.

In agreement with our first observations, a correlation between the conversion of MSA to DSA and ammonia flow rate has been observed, suggesting an equilibrium ruling these 3 species. This assumption was verified and we established the conditions in which MSA or DSA only can be generated. The equilibrium constant for $\text{DSA} + \text{NH}_3 \rightarrow 2 \text{MSA}$ was further determined and found to be $5 \cdot 10^{-3}$. The existence of an equilibrium suggests that MSA-free DSA should be stored in the absence of NH_3 .

3. Deposition experiments with MSA and DSA

First, a series of CVD tests between 760°C and 800°C have been performed using MSA (in NH_3) or DSA (in N_2 , in situ diluted in NH_3) stored in cylinders. These preliminary tests lead to stoichiometric $\text{Si}_{0.75}\text{N}$ films, with very good step coverage when MSA is used, but rather poor one in case of DSA. Conversely, while the deposition rate (DR) with DSA is high, using MSA yields lower DR because of the very large dilution of MSA in ammonia required for its stabilization.

We further built a set-up to in-situ generate either DAS ($\text{SiH}_2(\text{NH}_2)_2$), MSA or DSA, depending on the chosen experimental conditions. This deposition method allows much higher DR thanks to higher precursor concentrations. In agreement with the results obtained with MSA and DSA

stored in cylinders, activation energy of SiN deposition using in-situ generated either MSA or DSA is very close to that of the standard process one.

Summary

The in-situ QMS study of $\text{SiH}_2\text{Cl}_2\text{-NH}_3$ reaction led the authors to consider the Cl-free monosilylamine and disilylamine as alternative precursors for silicon nitride deposition. The resulting films are very good in terms of deposition rates and step coverage, with no undesired byproducts. The conditions to produce, stabilize, and to in situ generate these molecules have been established.

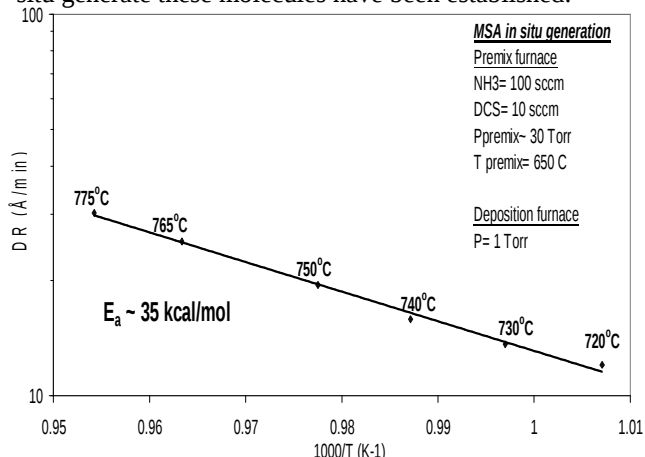


Fig. 1: Deposition rate of SiN films vs. temperature using monosilylamine precursor

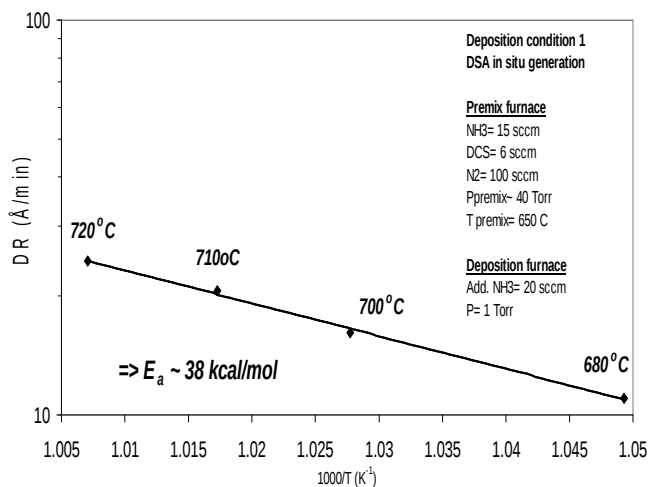


Fig. 2: Deposition rate of SiN films vs. temperature using disilylamine precursor