# SYNTHESIS OF SILICON NITRIDE NANOPOWDERS IN AN RF THERMAL PLASMA TORCH: COMPARATIVE STUDY ON DIFFERENT PRECURSORS

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**Abstract**

Synthesis of silicon nitride nanopowders from $SiCl_4$, $SiH_2Cl_2$ and $SiH_4$ precursors and $NH_3$ has been investigated in an inductively coupled RF thermal plasma torch. Effects of the chemical nature and the feed rates of precursors on the yield and characteristics of silicon nitride powders were studied in details. Both the yield and the powder characteristics were greatly depending on the nature of precursors, and in a less extent on the feed rates of reactants. The experimental results indicated that the use of $SiCl_4$ and $SiH_2Cl_2$ is more advantageous for the synthesis of $Si_3N_4$ nanopowders in an RF thermal plasma torch as compared to the use of $SiH_4$.

## Introduction

Ammonolysis of reactive silicon compounds is a feasible way for the technical synthesis of silicon nitride powders of high purity and extreme fineness. Precursors used most frequently include $SiH_4$ [1,2] or its chlorinated derivatives, such as $SiH_2Cl_2$ and $SiCl_4$ [3-6].

The synthesis can preferably be realized under plasma conditions, especially in radiofrequency (RF) induction plasma torches. The RF thermal plasma offers sufficient residence time of reactants in the hot zone due to the large plasma volume and it makes possible to use corrosive precursors.

Plasmachemical $Si_3N_4$ synthesis from $SiCl_4$ [3,5,6] yields in the formation of highly uniform powders with particle sizes of 20-50 nm and BET surfaces greater than 40 $m^2 \cdot g^{-1}$. The morphological characteristics of powders can be traced back to the very high heating and cooling rates occurring in the thermal plasma torches. Composition and crystallinity of powders are influenced by the RF plate power, the flow rates of plasma and sheath gases and the mass flow and ratio of reactants.

Our detailed investigations on the $SiCl_4+NH_3$ reaction in an RF thermal plasma torch [7] showed that the chemical composition (nitrogen content) of amor-

phous $Si_3N_4$ powders was mainly affected by the plate power. Feed rate of $SiCl_4$ and the plate powder proved to be variables of decisive importance in terms of product yield.

Present work was aimed at learning the effect of different silicon containing precursors ($SiCl_4$, $SiH_2Cl_2$ and $SiH_4$) on the properties and yields of $Si_3N_4$ powders in an RF thermal plasma.

## Experimental

The RF induction plasma torch used was of a standard design with a quartz glass plasma confident tube (27 mm I.D.). It was connected to air-cooled quenching and powder collection sections. The plasma powder was provided by a 3-turn induction coil from an RF generator operating at an oscillator frequency of 27.17 MHz.

High-purity argon was used as plasma and sheath gases and also as carrier gas of $SiCl_4$. Both the silicon containing reagents ($SiCl_4$, $SiH_2Cl_2$ and $SiH_4$) and the $NH_3$ were of high-purity. The precursors were injected through transverse slots into the tail flame region, downstream of the coil region.

Silicon nitride powders were subjected to total nitrogen ($N_t$) and oxygen analysis in a LECO N-O analyzer. Their surface chemistry was characterized by XPS investigations. Crystal structure (FTIR and XRD) and specific surface area (BET) were also determined.

The powder yield was defined as a ratio of the actual formation rate of powder against the theoretical one. The theoretical formation rate was calculated by considering the feed rate of silicon containing precursor and the composition of powder formed.

## Results and Discussion

The plate power and flow rate of plasma gas were adjusted to levels which were determined by us as optimum values previously [7]. Thus the plate power was 3 kW and the flow rate of plasma gas was 8 $l \cdot min^{-1}$ (STP) in all runs. System variables investigated in the present work included the chemical composition and feed rates of silicon containing precursors and the feed rate of ammonia. The experimental conditions and some results are presented in Table 1.

The feed rates of silicon containing precursors were set to two levels in terms of silicon feed rate. For all precursors the lower feed rates corresponded to a silicon feed rate of 0.063 $g \cdot min^{-1}$, while the greater ones to a value of 0.149 $g \cdot min^{-1}$.

Two sets of powders were collected in each run: one sample in the torch (T) and an other in the powder collection section (C). Powder from the torch in each run was a bit darker as compared to the other sample. However, there were remarkable differences in the colours of products got from different precursors: the higher was the hydrogen content of the precursor, the darker powder was produced.

Table 1 Experimental conditions and some powder characteristics

| No | ΣV* ($l \cdot min^{-1}$) | R1 ($g \cdot min^{-1}$) | R2 | R2/R1 ratio | Powd. from | Colour | ⌂m (%) | m* ($g \cdot min^{-1}$) | Y (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 26.14 | 0.38[1] | 2.1 | 54,7 | T | white | 2.6 | 0.0446 | 59.1 |
| | | | | | C | white | 4.1 | 0.0180 | |
| 2 | 26.20 | 0.90[1] | 0.8 | 8.8 | T | grey | 2.9 | 0.0567 | 45.4 |
| | | | | | C | grey | 4.0 | 0.0561 | |
| 3 | 26.10 | 0.23[2] | 2.1 | 54.2 | T | yellow | 2.8 | 0.0277 | 75.3 |
| | | | | | C | yellow | 4.7 | 0.0486 | |
| 4 | 26.23 | 0.53[2] | 0.8 | 9.0 | T | light brown | 1.5 | 0.0448 | 67.6 |
| | | | | | C | light brown | 3.2 | 0.1147 | |
| 5 | 19.20 | 0.07[3] | 2.1 | 56.4 | T | dark brown | 0.9 | 0.0109 | 45.0 |
| | | | | | C | dark brown | 2.0 | 0.0299 | |
| 6 | 19.20 | 0.16[3] | 0.8 | 9.4 | T | dark brown | 0 | 0.0385 | 58.3 |
| | | | | | C | dark brown | 2.5 | 0.0702 | |

ΣV* total gas flow (STP), R1 feed rate of silicon containing precursors ([1]$SiCl_4$, [2]$SiH_2Cl_2$, [3] $SiH_4$), R2 feed rate of $NH_3$, R2/R1 molar ratio of reactants, T powder collected in the torch, C powder collected in the powder collection section, ⌂m loss on heating at 400°, 2h, m* formation rate of powder, Y powder yield.

Ammonia was injected in a great excess against the stoichiometry in all tests. Hence, $NH_4Cl$ was formed and condensed along with $Si_3N_4$ in the case of $SiCl_4$ and $SiH_2Cl_2$. In addition to $NH_4Cl$, some $Si(NH)_2$ was also formed in all tests. The powders as formed were subjected to heat treatment in nitrogen at 400°C for 2 hours in order to remove $NH_4Cl$, and $Si(NH)_2$, if any.

The ⌂m values were relatively low as compared to our previous results and to those published elsewhere [6]. The mass loss of powders generated from $SiH_4$ was attributed to the formation and presence of $Si(NH)_2$. On the basis of mass losses hot wall conditions were ensured in this work.

As far as the distribution of powders between the torch and the powder collection section is concerned it was found that both the chemical nature of precursors and

the molar ratio of reactants had an effect on the share of powder collected in the torch.

Even the powder yield depended significantly on the chemical nature of precursors. The highest powder yields were obtained in the $SiH_2Cl_2$ case (Table 1). Increase of the R2/R1 molar ratio increased the yield in the case of $SiCl_4$ and $SiH_2Cl_2$. However, an opposite tendency was detected in the $SiH_4+NH_3$ reaction. More characteristics of powders are presented in Table 2.

Table 2. Bulk chemical composition, specific surface area and crystal structure of powders

| No | Powder from | $N_t$ | $O_t$ (wt%) | $Si_t$ | S ($m^2 \cdot g^{-1}$) | Crystal structure |
|---|---|---|---|---|---|---|
| 1 | T | 38.2 | 2.6 | 59.1 | 65 | amorphous |
| | C | 34.9 | 4.9 | 59.3 | 83 | |
| 2 | T | 37.0 | 2.9 | 59.7 | 70 | amorphous |
| | C | 35.0 | 4.7 | 60.0 | 91 | |
| 3 | T | 32.7 | 2.8 | 64.0 | 52 | amorphous |
| | C | 30.2 | 3.5 | 65.3 | 68 | |
| 4 | T | 33.6 | 3.0 | 62.8 | 55 | amorphous |
| | C | 31.5 | 3.8 | 63.7 | 68 | |
| 5 | T | 26.2 | 2.9 | 70.2 | 40 | amorphous |
| | C | 24.0 | 4.0 | 71.4 | 72 | |
| 6 | T | 16.5 | 3.1 | 79.7 | 42 | amorphous |
| | C | 15.5 | 3.9 | 79.4 | 69 | |

$N_t$, $O_t$ and $Si_t$ total nitrogen, oxygen and silicon contents, S specific surface area

The use of different precursors resulted in quite different $Si_3N_4$ powder compositions. The highest nitrogen content, i.e. the best powder grade was obtained by using $SiCl_4$. However, powders consisting of mainly metallic silicon were produced from $SiH_4$, due to the reducing atmosphere in the given case. In the $SiCl_4+NH_3$ system recombination was dominated by the formation of Si-N bonds, while in the $SiH_4+NH_3$ system formation of Si-Si bonds seemed to be the dominant step. The

$SiH_2Cl_2+NH_3$ system represented an intermediate situation. However, its behaviour was closer to that of the $SiCl_4+NH_3$ system.

Results on the effect of molar ratio on the nitrogen content supported the above findings. Increase of the molar ratio within the given limits led to a small change of the nitrogen content only in the $SiCl_4+NH_3$ and $SiH_2Cl_2+NH_3$ reactions. On the contrary, increase of the molar ratio in the $SiH_4+NH_3$ reaction considerably rose the $N_t$ values.

The chemical nature of precursors hardly influenced the oxygen content of powders. Nevertheless, in all runs the powder in the collection section contained more oxygen than the torch powder, due to the greater specific surface area of the former one. In the plasmathermal silicon nitride powders produced from gaseous or liquid precursors most of oxygen was segregated on the surface of particles, as it was proved by us previously. It means that the oxygen mostly entered into the composition during the handling of the high specific surface area powders in the oxygen and moisture containing ambient atmosphere. The higher was the specific surface area, the more susceptible was the powder to oxidation.

Mean particle size of powders was not measured directly in this study. However, on the basis of S values in Table 2, the mean particle sizes of particular powders fall into the range of 30-80 nm.

According to FTIR and XRD investigations all powders were mainly amorphous, but some (<5%) $\alpha$-$Si_3N_4$ was observed in certain samples.

The above considerations on the oxygen distribution were supported by the results of the XPS measurements (Table 3).

Table 3 Surface chemical compositions of selected powders

| Sample | Precursor | Surface composition (wt%) | | | |
|---|---|---|---|---|---|
| | | $N_s$ | $O_s$ | $Si_s$ | $C_s$ |
| 1T | $SiCl_4$ | 25.7 | 24.2 | 48.0 | 2.1 |
| 3T | $SiH_2Cl_2$ | 26.0 | 22.4 | 48.6 | 3.0 |
| 5T | $SiH_4$ | 29.4 | 17.2 | 49.9 | 3.5 |

$N_s$, $O_s$, $Si_s$ and $C_s$ surface nitrogen, oxygen, silicon and carbon concentrations

The surface carbon content of powders was less as usual. It refers to hot wall synthesis conditions on the one hand, and presence of NH and OH groups on the surface on the other hand. There were remarkable differences in the bulk and surface

compositions of powders (Tables 2 and 3). Surface oxygen contents were much higher, and the surface silicon contents were a bit lower as compared to the corresponding bulk values. The surface nitrogen contents were smaller of the bulk ones in the case of $SiCl_4$ and $SiH_2Cl_2$, and they were greater of the bulk values in the $SiH_4$ powders.

It is worth to mention that while the bulk compositions of the three powders were quite different, their surface compositions were close to each other.

The presented results made possible to draw conclusion on the probable sequence of recombination reactions during the plasmathermal synthesis of silicon nitride powders. In the case of $SiCl_4$ and $SiH_2Cl_2$ precursors the dominant step of recombination was the formation of $Si_3N_4$ and $NH_4Cl$. The powders were oxidized subsequently, when they were contacted with the ambient atmosphere. Using $SiH_4$ as precursor, the first step of recombination was the formation of metallic silicon. It was followed by formation of $Si_3N_4$, either by gas phase reaction or *via* the nitridation of metallic silicon. Then the powders were oxidized in the ambient atmosphere.

The above sequence seems to be the most probable model in the given system. However, we have to mention that it is a simplification of the actual situation, because other species (oxynitrides, diimides etc.) are also forming and they were disregarded now.

According to present level of our knowledge, use of $SiCl_4$ and $SiH_2Cl_2$ is more advantageous in terms of silicon nitride production as compared to the use of $SiH_4$.

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