

A low-temperature and seedless method for producing hydrogen-free Si₃N₄

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A simple, seedless method for the synthesis of Si₃N₄ from a hydrogen-free precursor system (Na₂SiF_{6(s)}-N_{2(g)}) was developed. From thermodynamic calculations and experimental results it is concluded that the gaseous chemical species SiF_x (SiF₄, SiF₃, SiF₂, SiF and Si) formed during the low-temperature dissociation of Na₂SiF₆ in a conventional CVD system react *in-situ* with nitrogen to produce Si₃N₄. Whiskers, fibers, coatings and powders were obtained via the Na₂SiF₆-N₂ system at pressures slightly above atmospheric pressure. Not only does the feasibility of the reactions for Na₂SiF₆ dissociation and Si₃N₄ formation increase with the temperature but also, once the SiF_x chemical species are formed by the former, the latter reaction is even more viable. Amorphous Si₃N₄ is obtained at temperatures of up to 1173 K while crystalline α - and β -Si₃N₄ are formed in the range 1273-1573 K and with processing times as short as 120 minutes. Optimal conditions for maximizing Si₃N₄ formation were determined.

Keywords: Thermodynamics; CVD; Amorphous Si₃N₄; α - and β -Si₃N₄; gas-solid precursors.

Se desarrolló un método simple y sin semillas para la síntesis de Si₃N₄ partiendo de un sistema de precursores libre de hidrógeno (Na₂SiF_{6(s)}-N_{2(g)}). A partir de cálculos termodinámicos y resultados experimentales se concluye que las especies químicas gaseosas SiF_x (SiF₄, SiF₃, SiF₂, SiF and Si) formadas durante la disociación a baja temperatura del Na₂SiF₆ en un sistema convencional de CVD reaccionan *in situ* con el nitrógeno para producir Si₃N₄. Se obtuvieron fibras, fibras cortas discontinuas, recubrimientos y polvos a través del sistema Na₂SiF_{6(s)}-N₂ a presiones ligeramente por encima de la presión atmosférica. Con el incremento en la temperatura no solo aumenta la factibilidad de las reacciones para la disociación del Na₂SiF₆ y formación del Si₃N₄, sino también una vez que se han formado las especies SiF_x por la primera reacción, la segunda reacción es incluso más factible. El Si₃N₄ amorfo se obtiene a temperaturas de hasta 1173 K mientras que el Si₃N₄ cristalino α y β se forman en el rango de temperaturas de 1273-1573 K y con tiempos de procesamiento tan cortos como 120 minutos. Se determinaron las condiciones óptimas para maximizar la formación del Si₃N₄.

Descriptores: Termodinámica; CVD; Si₃N₄ amorfo; Si₃N₄ α y β ; precursores gas-sólido.

PACS: 81.15.Gh; 81.20.Ka; 82.60.-s

1. Introduction

As a consequence of the increasing demand for silicon nitride (Si₃N₄) both for structural and functional applications although it has been under investigation since the 1960's-70's, a considerable number of new or alternative synthesis methods have been proposed over the past 20 years [1-12]. In addition to the former interest in this ceramic material for structural applications, the synthesis of both amorphous and crystalline Si₃N₄ has been intensively investigated for optoelectronic and microelectronic applications [13-21]. Within the semiconductor industry most of the interest in nitrogen-silicon compounds was particularly as thin films for use as passivation layers to protect semiconductor devices, as gate dielectric layers in thin-film transistors (TFT) and as insulator layers to fabricate metal-nitride-oxide-silicon (MNOS) devices [22]. Also, owing to its excellent physicochemical properties and resistance to the diffusion of impurities, Si₃N₄ was considered as a prominent candidate for substituting silicon dioxide in MOS devices [13]. In addition to low-temperature and cost-effective processing characteristics, especially for electronic applications, it is essential that the silicon nitride thin films have a low hydrogen concentration. This is because, according to previous reports, hydrogen from silane and ammonia used during processing causes film degradation [21].

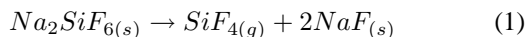
The synthesis route for amorphous, α - and β -Si₃N₄ involving gas phase reactions -commonly referred to as chemical vapor deposition (CVD) - typically starts from silicon gas precursors (silane and halides such as SiCl₄, SiF₄, SiBr₄ and SiI₄) or silicon liquid precursors (metalorganics as tetra-methyl-silane), and mainly from ammonia as a nitrogen gas precursor [23,24]. During processing, the liquid or gas precursors undergo decomposition into more reactive species that further interact to form Si₃N₄. Silane (SiH₄) and silicon tetrachloride (SiCl₄) are the most commonly used silicon precursors while ammonia is the most preferred nitrogen precursor. The reason why NH₃ is preferred over N₂ is because the latter is thermally and chemically more stable than the former, and therefore more difficult to dissociate. Specifically, while the ionization potential for N₂ is 15.576 eV, the corresponding value for NH₃ is 10.2 eV [25]. Consequently, the synthesis of Si₃N₄ using only N₂ (to obtain, accordingly, nitride deposits free of hydrogen), and conventional CVD systems with common silicon precursors has long been a challenging task.

The film contamination issue with hydrogen and the impracticality of using nitrogen in conventional CVD reactors has been addressed from two different perspectives: (1) using hydrogen-free silicon precursors (SiCl₄, SiBr₄, SiI₄ and SiF₄) and (2) coupling additional devices to standard CVD systems. As regards the first approach, although SiCl₄ is

the most frequently used halide, it has been reported that it tends to polymerize and consequently clog the reactor's exit port [26].

With respect to the second approach, the conventional chemical vapor deposition (CVD) system has been modified to plasma assisted CVD, essentially as a means of promoting dissociation of the gas molecules into more reactive radicals, atoms or ions. The most common adaptations include remote enhanced CVD (RECVD), electron cyclotron resonance CVD (ECRCVD) and inductively coupled plasma CVD (ICP-CVD) [13,15,16,19-21,24]. And although plasma-enhanced chemical vapor deposition (PECVD) is the most frequently used technique (in terms of lowering the substrate temperature), it has the disadvantage of potential film degradation by contamination with hydrogen from silane (SiH₄) and ammonia (NH₃) [19].

Recently, a novel synthesis method for Si₃N₄ using a silicon solid precursor was proposed [12]. The method is based on the ability of some solids to form highly reactive chemical species that react with nitrogen-containing precursors (N₂ or N₂-NH₃) in a conventional CVD reactor, taking advantage of the intrinsic thermal gradients within the reactor to produce key reactive chemical species from Na₂SiF₆. Due to its good stability at atmospheric pressure and at room temperature, as well as to its relatively low decomposition temperature (\approx 823 K), Na₂SiF₆ has been considered by several authors for various purposes, other than the synthesis of silicon nitride [27-29]. It should be recognized that in all previous research it was assumed that the only gaseous reaction product formed during the thermal decomposition of Na₂SiF₆ was silicon tetrafluoride (SiF₄) [27-29]:



Since the proposed synthesis method combines the use of gas (N₂, NH₃ and N₂-NH₃ mixes) and solid precursors (Na₂SiF₆), it is referred to as a hybrid precursor-based method. Some of the potential benefits of the proposed method [12], with respect to existing commercial and alternative routes, are as follows:

- 1.- *in situ* processing, because the silicon gas species (SiF₄, SiF₃, SiF₂, SiF and Si) are formed in the same reactor in which Si₃N₄ is produced,
- 2.- versatility, because it makes it possible to synthesize Si₃N₄ with a variety of morphologies (whiskers/fibers, films/coatings and particles),
- 3.- silicon nitride can be produced without the use of seeds of this ceramic material,
- 4.- economical, because by taking advantage of the intrinsic thermal gradients within the tube reactor, the process makes it possible to save energy,
- 5.- low-pressure process, because it is carried out at pressures slightly above atmospheric pressure,

6.- since the silicon solid precursor (Na₂SiF₆) is stable and safe at room temperature, it is used as a safe-deposit compound for the silicon gas species,

7.- the process offers the potential of producing Si₃N₄ in pure nitrogen in a simple thermal gradient reactor.

The reasons behind the possibility to produce this ceramic in nitrogen only are the subject matter of the present work. In this paper the authors explain in detail why it is possible to produce Si₃N₄ in a simple thermal gradient CVD system using only nitrogen, and propose a mechanism for Na₂SiF₆ dissociation and Si₃N₄ formation.

2. Experimental

The experimental work is divided into two parts. The first part corresponds to the optimization of the processing parameters to maximize formation of Si₃N₄ and the second one to the proposition of a mechanism for Na₂SiF₆ dissociation and Si₃N₄ formation in the Na₂SiF₆-N₂ system. Parameter optimization was carried out by means of a Taguchi experimental design and analysis of variance (ANOVA) while the mechanism was proposed on the basis of experimental results and thermodynamic predictions using the FactSage software and databases.

2.1. Apparatus

Figure 1a is a schematic diagram of the experimental set-up used in the study. The reactor consists of a horizontal alumina tube furnace (76.20 cm long \times 3.80 cm in diameter) provided with end-cap fittings to control the process atmosphere. A reactor of this type is characterized by the thermal gradients along the tube's longitudinal direction, as shown through the temperature profile measured in the reactor (see

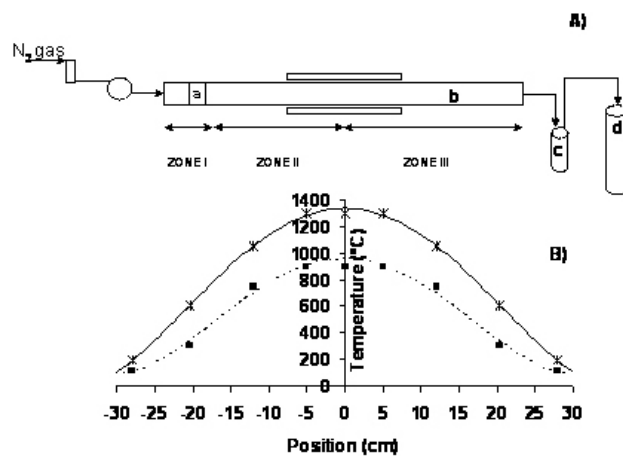


FIGURE 1. Schematic diagram of the experimental set-up indicating position of: (a) solid precursor, (b) substrates, (c) powder collector and (d) neutralizer. (B) Thermal gradients along the reactor longitudinal direction.

Fig. 1b). The thermal gradients are used to strategically induce Na_2SiF_6 (the Si solid precursor) decomposition, stimulate development of the reactions for Si_3N_4 synthesis and heat the substrates for Si_3N_4 deposition. The appropriate temperature range for Na_2SiF_6 decomposition (523-823 K) was determined previously by thermal analysis [30]. The reactor is also provided with gas inlets and outlets to supply the nitrogen precursors as well as to make it possible to remove the gas reaction products (which are made to bubble into distilled water contained in a closed deposit). Two thermocouples placed strategically within the reactor are used to monitor the solid-precursor and substrate temperatures. Gas flow meters and manometers at the reactor entrance and exit ports make it possible to control the processing parameters during the synthesis trials.

2.2. Synthesis and characterization

The synthesis trials were carried out in the conventional CVD reactor described above. In order to investigate the effect of the processing variables on the characteristics of deposited Si_3N_4 and optimize the processing parameters, a Taguchi experimental design supported by analysis of variance (ANOVA) was used [31]. In the first part of the study, the processing parameters time, temperature, pressure and amount of Na_2SiF_6 were examined at two levels (60 and 120 minutes, 1173 and 1573 K, 17 and 19 mbars, and, 0 and 25 g, correspondingly). Additional tests were carried out at temperatures of 1153, 1303, 1453 and 1606 K each for 0, 35, 70 and 140 min. The Na_2SiF_6 compacts were located near the reactor entrance, where the temperature can be varied between 386-578 and 465-873 K and the substrates were placed within the reactor in specific positions where the temperature can be controlled between 1173 and 1573 K, depending on the processing temperature. In this regard, the processing temperature and substrate temperature are two different parameters considered in the experiment. A substrate specimen, however, can be treated at a given processing temperature but at the same time at different substrate temperatures, depending on its position within the reactor. As both Na_2SiF_6 dissociation and Si_3N_4 formation occur in the same reactor, the synthesis route is referred to as an *in situ* process. The substrates consist of SiC_p/Si cylindrical performs (37 mm in diameter \times 25.4 mm long) with 50% porosity prepared by the uniaxial compaction of the corresponding powders, both with an average particle size of 25 μm . As illustrated in Fig. 1, to facilitate the description of the events occurring during synthesis, the reactor was divided into three different zones, namely, Na_2SiF_6 dissociation (Zone I), Si_3N_4 formation (Zone II) and Si_3N_4 deposition (Zone III). Once the silicon precursor (Na_2SiF_6) and the substrates were placed in their corresponding positions, the reactor was closed and the system was heated at a rate of 15 $^\circ\text{C}/\text{min}$ in ultra high purity (UHP) nitrogen to the test temperature, maintained isothermally for the corresponding test time (according to the experimental design) and cooled

to room temperature at 15 $^\circ\text{C}/\text{min}$. After cooling to room temperature, the substrates were removed from the reactor to determine the amount of Si_3N_4 deposited, as well as for microstructure characterization using Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX).

Reaction mechanisms for Na_2SiF_6 dissociation and Si_3N_4 formation are proposed on the basis of thermodynamic predictions and experimental results. Accordingly, CVD phase diagrams for the $\text{Na}_2\text{SiF}_6\text{-N}_2$, $\text{SiF}_4\text{-N}_2$, $\text{SiF}_3\text{-N}_2$, $\text{SiF}_2\text{-N}_2$, and SiF-N_2 systems as well as Ellingham diagrams for the dissociation reaction of Na_2SiF_6 and for the reaction through which Si_3N_4 is formed were constructed using the FactSage software and databases. FactSage is the fusion of two well-known software packages in the field of computational chemistry: FACT-Win (formerly F*A*C*T) and ChemSage (formerly SOLGASMIX). Phase stability diagrams were constructed graphing absolute temperature (K) vs. molar ratio of the silicon precursor divided by the sum of the silicon precursor and nitrogen precursor (for instance, $\text{SiF}/(\text{SiF}+\text{N})$). Ellingham diagrams were constructed graphing the Gibbs free energy of the reactions (calculated using FactSage) as a function of temperature. All calculations were carried out at a constant pressure of 1032 mbars (1 atm).

3. Results and discussion

3.1. Optimization of the processing parameters

Analysis of variance provides insight into the optimum process parameters and makes it possible to estimate the percent contribution of each of the parameters tested to the variability in the measured quantities (in this particular case, the amount of Si_3N_4 deposited) [31]. Results from the experimental design considering the variables time, temperature, pressure and amount of Na_2SiF_6 showed that this last one is the processing parameter that most significantly influences (with a relative contribution of 99%) the formation of Si_3N_4 and that the effect of the other parameters can be neglected. The amount of Na_2SiF_6 was expected to produce a strong effect on Si_3N_4 formation because it supplies the silicon precursor, which is an essential ingredient. This result ultimately substantiates the view that Si_3N_4 is formed via the thermal decomposition of Na_2SiF_6 and not through a conventional nitridation process. In view of this result, as a second approach of the process optimization, only the parameters pressure, temperature and time were considered in the experimental design (setting the amount of Na_2SiF_6 at 25 g). Results from the analysis of variance (ANOVA) are shown in Table I. According to ANOVA, pressure is the parameter with the most significant effect on the amount of Si_3N_4 formed (with a relative contribution of 34%) followed by temperature (31%) and time (31%). The remaining 4% is due to experimental error. Figure 2 is a chart of the main effect of each of the processing parameters tested (at two levels) on the amount of deposited

Si₃N₄ (the response variable). This graph indicates that, although the amount of silicon nitride is enhanced by the second level of temperature, time and amount of Na₂SiF₆, the second level of the latter significantly impacts the magnitude of the response variable. And, although the improvement seems to be irrelevant, it is also clear that it is better to use the lowest level of pressure. Accordingly, the optimum conditions to maximize Si₃N₄ formation from the Na₂SiF₆-N₂ system are: 1573 K, 120 minutes, 17 mbars, and a Na₂SiF₆ compact of 25 g.

TABLE I. ANOVA table for Si₃N₄ formation in the Na₂SiF_{6(s)}-N_{2(g)} system.

Parameters	DF	SS	V	F	P(%)
Time	1	0.0105	0.010	0.298	31
Temperature	1	0.0105	0.010	0.298	31
Pressure	1	0.0113	0.011	0.328	34
Error	1	0.0090	0.001	0.001	4
Total	3	0.032	0.032	0.964	100

DF: Degrees of freedom, SS: sum of squares, V: variance, F: Variance ratio, P: Percentage contribution.

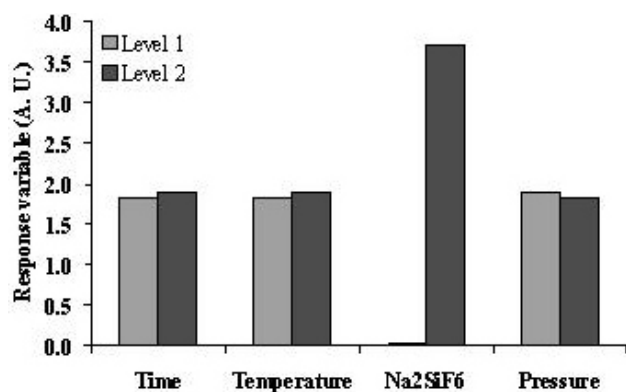


FIGURE 2. Principal effects of independent variables used in the optimization of the processing parameters to maximize the amount of deposited Si₃N₄(the response variable).

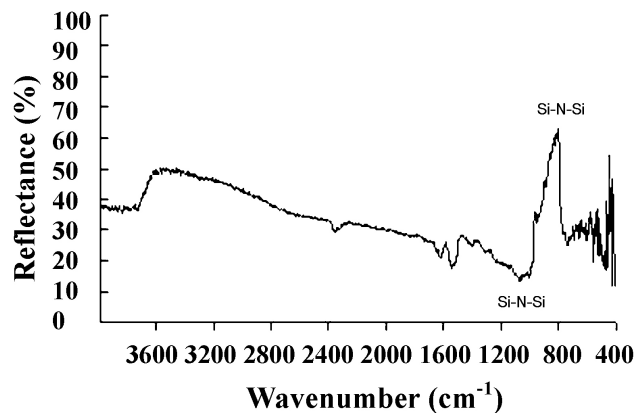


FIGURE 3. FT-IR spectrum corresponding to a specimen treated at a processing temperature and substrate temperature of 1173 K.

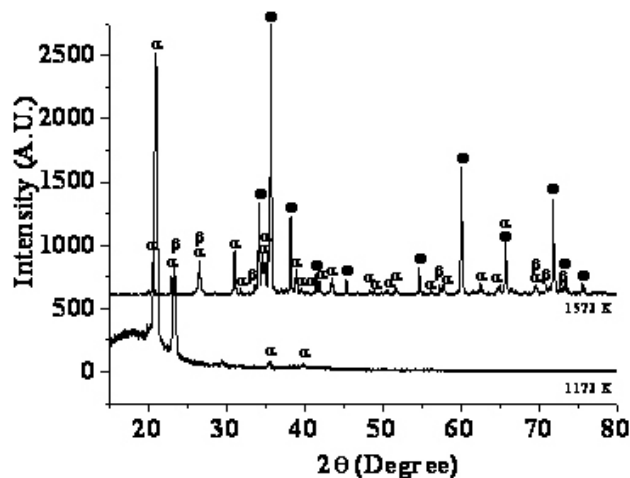


FIGURE 4. XRD patterns of specimens treated both at a processing temperature of 1573 K but while the first was studied at a substrate temperature of 1173 K, the second one at 1573 K. ●corresponds to SiC, α and β represent α- and β-Si₃N₄, respectively.

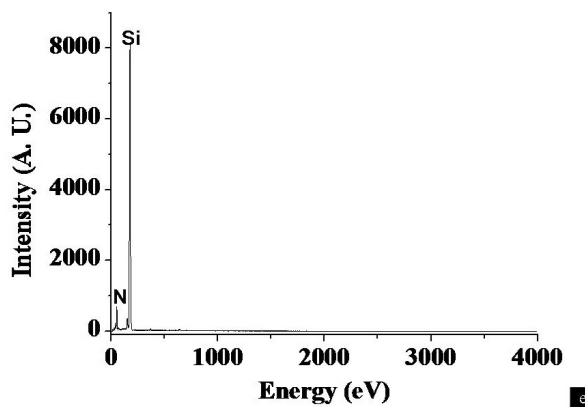
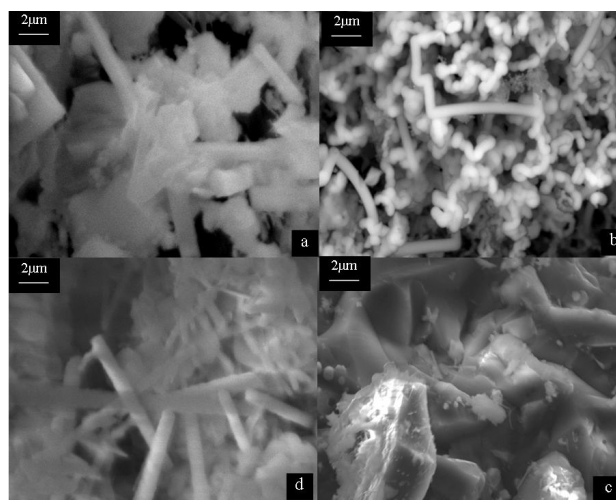


FIGURE 5. SEM photomicrographs showing Si₃N₄ deposited as: a) and b) whiskers, c), fibers d) coatings. e) Typical EDX spectrum obtained during analysis by SEM.

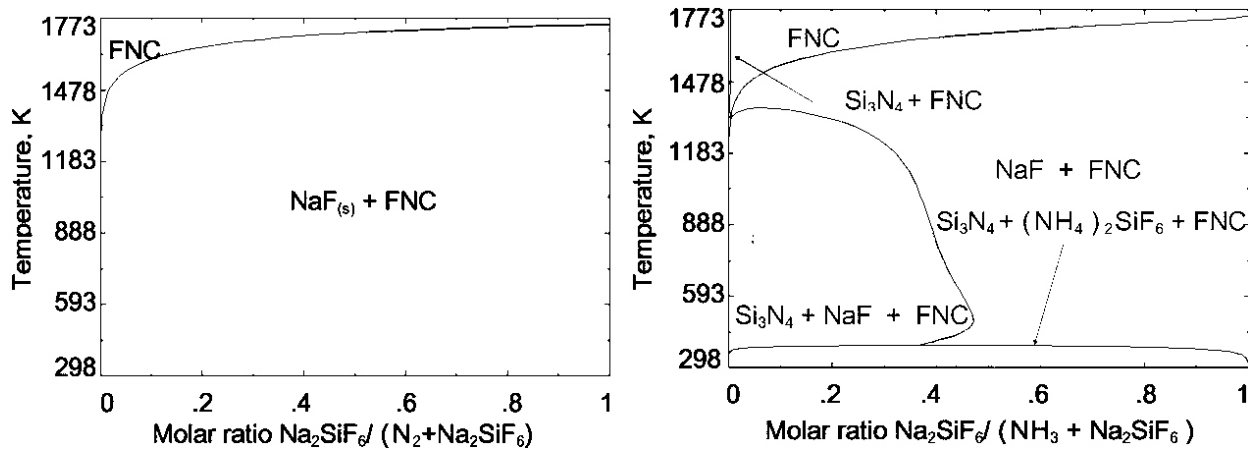


FIGURE 6. CVD phase diagram for (a) $\text{Na}_2\text{SiF}_6\text{-N}_2$ and (b) $\text{SiF}_4\text{-N}_2$ systems.

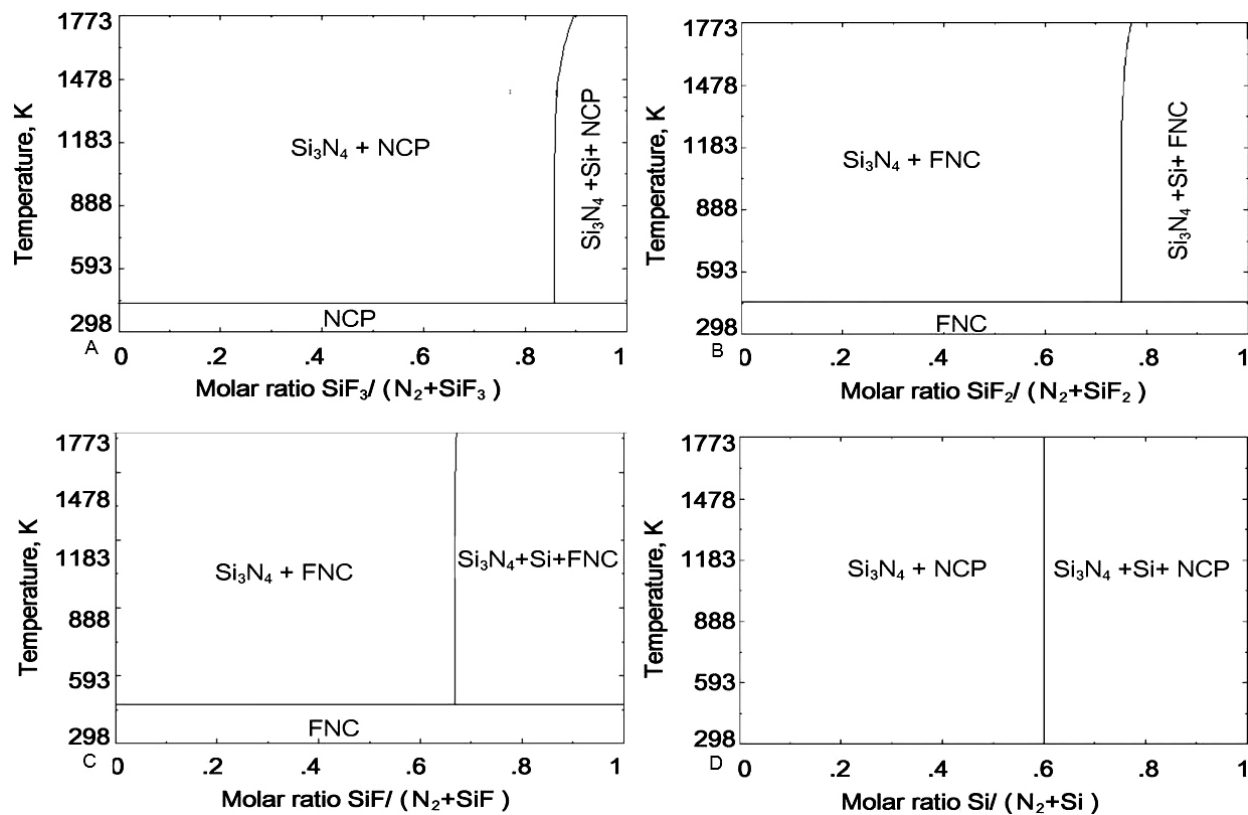


FIGURE 7. CVD phase diagrams for: (a) $\text{SiF}_3\text{-N}_2$, (b) $\text{SiF}_2\text{-N}_2$, (c) SiF-N_2 and, (d) Si-N_2 systems.

3.2. Microstructure characterization

In the case of specimens processed at low temperatures (below 1173 K), evidence of the Si-N-Si stretching mode at the characteristic wavenumber of $800\text{-}1200\text{ cm}^{-1}$ in FT-IR spectra suggests the presence of amorphous Si_3N_4 in the as-deposited condition. The same wavelength range has been reported by several authors in the identification of Si-N-Si bonds, characteristic of silicon nitride [32-36]. Figure 3 shows the FT-IR spectrum of a specimen obtained at a substrate temperature of 1173 K (which also corresponds to the

processing temperature). Conversely, above 1273 K analyses by X-ray diffraction indicate the formation of crystalline Si_3N_4 . Figure 4 shows two diffractograms corresponding to specimens both of which were tested at a processing temperature of 1573 K. However, in the first specimen the substrate temperature was 1173 K while in the second the substrate temperature was 1573 K. The former shows the presence of a hump-like region characteristic of amorphous phases, and also some reflections of low intensity corresponding to $\alpha\text{-Si}_3\text{N}_4$. The slight displacement in the $\alpha\text{-Si}_3\text{N}_4$ peaks is associated with the transition from amorphous to crystalline sil-

icon nitride. The XRD pattern for 1573 K shows the presence of both α - and β -Si₃N₄. Moreover, results indicate that α -Si₃N₄ is formed predominantly at temperatures between 1273 and 1573 K while β -Si₃N₄ is produced only at the processing temperature of 1573 K. Analysis by SEM shows that Si₃N₄ can be deposited in a wide variety of morphologies including whiskers, fibers, coatings and powders (see Figs. 5a, 5b, 5c, and 5d). As shown in Fig. 5e, the presence of only silicon and nitrogen peaks in the EDX spectra confirms formation of crystalline Si₃N₄ by the synthesis route presented in this work.

3.3. Thermodynamic study and mechanism

Thermodynamic equilibrium predictions (see Figs. 6a and 6b) show that in the temperature range 294-1773 K it is not possible to deposit Si₃N₄ either from the SiF₄-N₂ system or through the Na₂SiF₆-N₂ system. In the former there is no condensed phase is obtained at all while in the latter the only solid reaction product is NaF. In the aforementioned phase diagrams the regions where only gas chemical species coexist are denoted as non-condensed phase (NCP) fields. Interestingly, in previous [12] and in current work (as was shown in the preceding section), fibers/whiskers, powders and coatings of α - and β -Si₃N₄ were obtained above 1273 K. This is in contrast with earlier studies on the synthesis of Si₃N₄ via CVD by feeding SiF_{4(g)} and the nitrogen precursors (N₂ and NH₃) separately to the reactor, in which it was concluded that ammonia is preferred over pure nitrogen [26]. Thermodynamics also predicts that in the absence of the solids Na₂SiF₆ and NaF the direct gas phase reactions of SiF₄, SiF₃, SiF₂, SiF and Si with nitrogen lead to the formation of Si₃N₄ as a condensed phase (see Figs. 7a, 7b, 7c, and 7d). It should be noted that in all previous research into the thermal decomposition of Na₂SiF₆ it has simply been assumed that SiF₄ is the only gas reaction product (according to reaction (1)) [27-29]. Moreover, in no single report such an assumption ever been proven.

Equilibrium thermodynamic predictions show that, during the thermal decomposition of Na₂SiF₆ in nitrogen, the gas species SiF₃, SiF₂, SiF and Si are feasible in addition to SiF₄ and that at a given temperature the partial pressures of these chemical species increase with an increase in the F: Si ratio. Figure 8 shows plots of $\log_{10} \text{Pressure}$ vs. *temperature* for SiF₃, SiF₂, SiF and Si. From this figure it is evident that the SiF₃ chemical species appears at lower temperatures than the rest of the species and that at a fixed temperature it is the species with the highest partial pressure. These predictions together with the synthesis experimental results suggest that during the thermal decomposition of Na₂SiF₆ not only the SiF₄ species is produced but also - depending on the temperature- other reactive chemical species (SiF₃, SiF₂, SiF and Si) that facilitate the formation of Si₃N₄. It is also likely that the high F:Si ratio gas-species (mainly SiF₄) tend to further dissociate into lower F:Si ratio species. Hence, by the proposed route and in accordance with the arrangement

of the Si precursor and the substrate within the reactor (see Fig. 1), Na₂SiF₆ works only as a silicon store in Zone I of the reactor in such a manner that as it decomposes, the produced gas species react with the flowing nitrogen in a high temperature region (Zone II) where only gas phase reactions take place, *i.e.*, where the Na₂SiF₆ and NaF solid phases do not intervene.

The argument on the thermodynamic unfeasibility for Si₃N₄ formation directly from SiF_{4(g)} and pure nitrogen, and the possibility of synthesizing Si₃N₄ during the thermal decomposition of Na₂SiF₆ in nitrogen (as in the current work) due to the evolution of other gas species with a lower F:Si ratio, can be reinforced by means of an analysis of energetic and thermochemical-stability aspects for SiF₄, SiF₃, SiF₂, SiF, Si and N₂. The main issue relates to the high energy required to dissociate the N₂ and SiF₄ precursors into more reactive species. According to previous calculations by others, the dissociation energy values for SiF₄ and nitrogen are 170 ± 10 [32] and 225.94 ± 0.14 kcal/mol [25], respectively, while those for SiF₃, SiF₂ and SiF are 118 ± 10 , 153 ± 5 and 130 ± 3 kcal/mol, correspondingly. On the other hand, the heats of formation (ΔH_f°) for SiF₄, SiF₃, SiF₂ and SiF, decrease in the following order: -386 ± 0.2 , -235 ± 20 , -136 ± 0.2 and -2 ± 3 kcal/mol, respectively [37]. Clearly since the SiF₃, SiF₂ and SiF species require less energy to dissociate than SiF₄ and N₂, their propensity to intervene in chemical reactions is higher. Moreover, they will dissociate up continuously and faster than SiF₄ and N₂. These energetic and thermochemical parameters together suggest that, although more heat is evolved during SiF₄ formation, the lower dissociation energies for SiF₃, SiF₂ and SiF, represent a significant advantage in forming Si₃N₄. Also, because of its lower dissociation energy and by the partial pressure values shown in Fig. 8, it appears that SiF₃ is the gas species that most actively participates in the reaction for Si₃N₄ formation.

According to the above discussion, it is proposed that Na₂SiF₆ dissociates through a set of parallel and consecutive reactions that give place to other gaseous species in addition

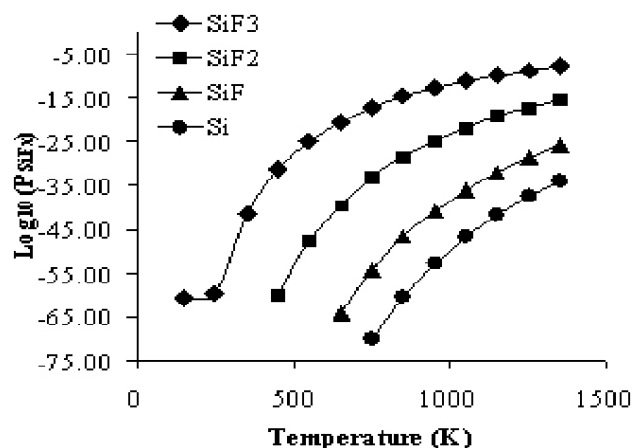


FIGURE 8. Equilibrium partial pressure (atm) of the silicon gas species (SiF_x) formed from Na₂SiF₆ decomposition in nitrogen.

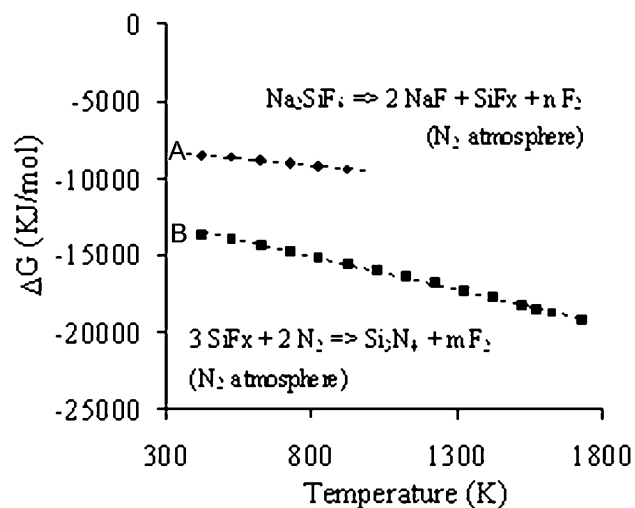
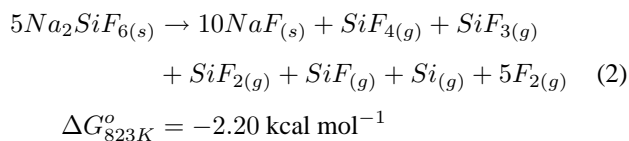
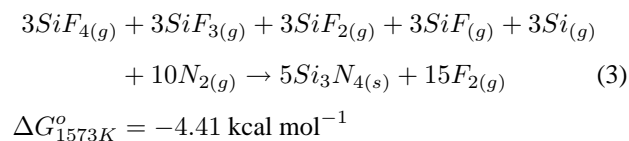


FIGURE 9. Ellingham diagrams for: a) decomposition of Na_2SiF_6 in nitrogen and, b) formation of silicon nitride from the reaction of SiF_x species with nitrogen.

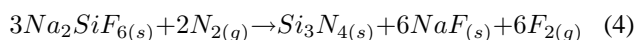
to SiF_4 and that these species react with nitrogen to silicon produce nitride. Depending on the temperature, the parallel reactions produce directly the SiF_4 , SiF_3 , SiF_2 , SiF and Si species while the consecutive ones consist of the subsequent dissociation of the species formed in the parallel events, *i.e.*, $\text{SiF}_4 \rightarrow \text{SiF}_3 \rightarrow \text{SiF}_2 \rightarrow \text{SiF} \rightarrow \text{Si}$. According to previous work, the decomposition of Na_2SiF_6 corresponds to a zero-order reaction with activation energy of 37.3 kcal/mol [30]. Details on the decomposition kinetics are reported elsewhere [30]. The overall decomposition reaction can be represented by:



Likewise, a mechanism for silicon nitride formation through the $\text{Na}_2\text{SiF}_6\text{-N}_2$ system is suggested. The highly reactive species (SiF_4 , SiF_3 , SiF_2 , SiF and Si) generated from Na_2SiF_6 dissociation react with nitrogen to form Si_3N_4 as a stable solid phase by means of a set of parallel reactions. The total reactions can be summarized as follows:



Finally, the abridged reaction for synthesis of silicon nitride in nitrogen from the thermal decomposition of sodium hexafluorosilicate is:

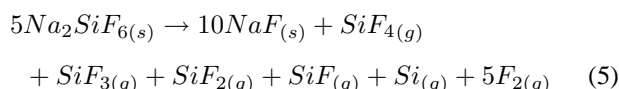


It should be noted that both solid reaction products (Si_3N_4 and NaF) involved in reaction (4) were formed in the

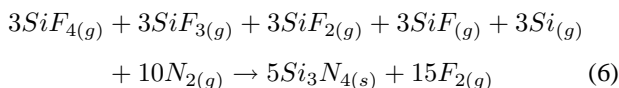
current work. However, due to the experimental arrangement they are located in different places within the reactor, *i.e.*, they are not mixed up. From the Ellingham diagrams corresponding to Na_2SiF_6 dissociation (in the temperature range 423–823 K) and Si_3N_4 formation (in the temperature range 423–1723 K), shown in Fig. 9, it can be confirmed that not only the feasibility for both reactions increases with temperature but also once the SiF_x species are formed, the reaction for Si_3N_4 formation is even more viable than that for Na_2SiF_6 dissociation.

4. Summary and conclusions

Si_3N_4 was successfully synthesized in a conventional CVD reactor from a hybrid precursor system ($\text{Na}_2\text{SiF}_{6(s)}\text{-N}_{2(g)}$). The process is based on the formation of Si-F gas chemical species (SiF_x) produced from the thermal dissociation of Na_2SiF_6 in flowing nitrogen. While amorphous silicon nitride is formed between 1173 and 1273 K, $\alpha\text{-Si}_3\text{N}_4$ and $\beta\text{-Si}_3\text{N}_4$ are produced in the temperature ranges 1273–1573 K and above 1573 K, respectively. Anova results show that pressure is the processing parameter that most significantly influences the formation of Si_3N_4 , with a relative contribution of 35%, followed by processing temperature (32%) and time (32%). The optimum processing parameters to maximize the amount of silicon nitride in $\text{Na}_2\text{SiF}_6\text{-N}_2$ system are: 1573 K, 120 minutes and 17 mbars. The Na_2SiF_6 dissociation mechanism in the temperature range from 423 to 823 K is represented by the following reaction:



And the Si_3N_4 formation mechanism in the temperature range from 473 to 1873 K is summarized through the following reaction:



Although thermodynamics predicts the unfeasibility of synthesizing Si_3N_4 in the $\text{Na}_2\text{SiF}_6\text{-N}_2$ system, the proper arrangement of the silicon precursor and the substrates within the reactor, successfully enabled the production of Si-F gas species (apart from SiF_4) ready to react with nitrogen.

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