

# Synthesis and Thermal Behavior of Polymeric Precursor for Carbon-Free Silicon Oxynitride Ceramic

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Received 9 December 2010; accepted 25 March 2011

DOI 10.1002/app.34577

Published online 9 August 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** A new polymeric precursor, perhydropolysiloxazane (PSNO), for silicon oxynitride (SiON) ceramic was synthesized by a simple one-pot procedure involving partial hydrolysis of  $\text{H}_2\text{SiCl}_2$  and the following ammonolysis reaction of the hydrolyzed intermediates with  $\text{NH}_3$ . The structure of new polymer was characterized with perhydropolysiloxane (PHSO) and perhydropolysilazane (PHSN) as reference substances. The conversion of PSNO to ceramic

was investigated by TGA, FT-IR, and solid  $^{29}\text{Si}$ -NMR analyses. A Si-rich  $\text{Si}_2\text{N}_2\text{O}$  ceramic was produced upon pyrolysis of PSNO at  $1400^\circ\text{C}$  under  $\text{N}_2$  atmosphere. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1094–1099, 2012

**Key words:** silicon oxynitride; inorganic polymer; precursor; synthesis; pyrolysis

## INTRODUCTION

Silicon oxynitride ceramic has attracted intensive attention since its discovery as Sinote in 1964, due to its specific properties such as heat resistance, antioxidation, anticorrosion, optic and electrical properties.<sup>1</sup> The ceramic has found versatile applications in the fields of high-temperature resistant ceramic composite, high-performance fiber, and dielectric film.<sup>2–5</sup> Various approaches to silicon oxynitride ceramic, for example, nitridation of silicon or silicon dioxide at elevated temperature,<sup>6,7</sup> solid-phase reaction between silicon nitride and silicon dioxide aided by metal oxides,<sup>8–10</sup> Chemical vapor deposition (CVD) process,<sup>5</sup> and polymeric precursor route<sup>11–16</sup> have been reported. Among them, the polymeric precursor route, namely fabrication of ceramics by pyrolysis of polymeric precursor, has drawn great interest in recent years. Attributed to its advantages in manufacture of advanced ceramics, such as possibility to acquire ceramics with tailored compositions from designable molecular precursors, feasibility to obtain

various types of ceramic materials by conventional polymer-forming techniques, the method has been extensively studied in preparation of various Si-based ceramics.<sup>17,18</sup> However, compared with the work on preparation of SiC, SiCN, and SiBCN ceramics via polymeric precursor route, the research on fabrication of SiON ceramic by the method is very limited. The reported polymeric precursors for the ceramic generally contain organic groups. For example, by pyrolysis of the copolymer synthesized from polymethylsiloxane and polymethylsilazane at  $1660^\circ\text{C}$  under  $\text{N}_2$  atmosphere, Yu et al. obtained  $\alpha$ - $\text{Si}_3\text{N}_4/\text{Si}_2\text{N}_2\text{O}$  composite.<sup>11–14</sup> While Gunji et al. prepared  $\text{Si}_2\text{N}_2\text{O}$  ceramic upon treatment of an isocyanato group-containing polymeric precursor above  $900^\circ\text{C}$  under  $\text{NH}_3$  or  $\text{N}_2$  atmosphere.<sup>15</sup> Scheffler et al. achieved SiC- $\text{Si}_2\text{N}_2\text{O}$  composite by pyrolyzing poly(methylsisesquioxane)/Si mixture at  $1500^\circ\text{C}$  under nitrogen atmosphere.<sup>16</sup> Due to the use of organic group-containing precursors, it is difficult to completely exclude carbon from the pyrolytic residues by adjustment of pyrolytic conditions in the above routes. On the other hand, to obtain a carbon-free SiON ceramic, the use of organic group-free precursor should provide more convenient and direct approach. Funayama et al.<sup>19</sup> studied conversion mechanism of perhydropolysilazane into silicon nitride-based ceramics, and found oxygen exist in the resulting ceramic as impurity due to accidental accumulation during the polymer synthesis and ceramic conversion. Their results imply SiON ceramics should be prepared by pyrolysis of

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Contract grant sponsor: National Key Laboratory of Advanced Functional Composite Materials, Aerospace Research Institute of Materials & Processing Technology; contract grant number: 9140C5602050904.

perhydropolysilazane under proper condition. However, little attention has been paid on fabrication of SiON ceramic from perhydropolysilazane and other organic group-free polymeric precursor.<sup>20</sup> In addition, except perhydropolysilazane, there is no report on other precursor that show good processability and free from organic groups.

In this work, we will present a new processable liquid organic group-free polymeric precursor for silicon oxynitride ceramic which was synthesized by a convenient one-pot procedure. The detailed synthesis, characterization, thermal analysis of the new precursor, as well as high temperature behavior of the new polymer-derived ceramic will be described.

## EXPERIMENTAL

### General

All manipulations were performed under dry nitrogen atmosphere using Schlenk techniques.  $\text{H}_2\text{SiCl}_2$  and  $\text{NH}_3$  stored in compression cylinder were purchased from Qinyang Guoshun Optic-electric Gas Corp. and Yongchang Chemical Co., respectively, and used as received. Diethyl ether ( $\text{Et}_2\text{O}$ ) and tetrahydrofuran (THF) were freshly distilled from sodium benzophenone ketyl before use. Deionized water was from Institute of semiconductor, Chinese Academy of Sciences.

FTIR spectra were obtained from a Bruker Tensor 27 FTIR spectrometer. Molecular weights of polymeric precursor were estimated by a gel permeation chromatography (GPC) with polystyrene standard calibration using a Waters 1515 high-performance liquid chromatography (HPLC) pump equipped with four Styragel columns (HR 0.5, HR 0.5, HR 1, HR 2) and a Waters 2414 refractive-index detector at 25°C in THF (1.0 mL/min). The viscosity was measured on a Brookfield HADV-II viscometer at 25°C.  $^1\text{H}$  spectra were recorded in  $\text{CDCl}_3$  solution with Bruker AVANCE 400 spectrometer at 400 MHz.  $^{29}\text{Si}$  spectra were recorded in  $\text{CDCl}_3$  solution with Bruker DMX 300 spectrometer at 300 MHz. Solid cross polarization/magic angle spinning (CP/MAS)  $^{29}\text{Si}$ -NMR experiments were carried out on a Bruker AVANCE 400 spectrometer at 400 MHz. Thermal gravimetric analyses were carried out on a SII EXSTAR TG/DTA6300 instrument under  $\text{N}_2$  or air atmosphere at a heating rate 10°C/min. XRD measurements were carried out on a Rigaku D/M4  $\times$  2500 diffractometer with  $\text{Cu-K}\alpha$  radiation. SEM investigation and its associated energy-dispersive X-ray microanalysis (EDX) were run on a HITACHI JEOL S-4300 instrument.

### Synthesis

To a solution of  $\text{H}_2\text{SiCl}_2$  (101 g, 1 mol) in  $\text{Et}_2\text{O}$  (300 mL), a mixture of deionized water (4.5 g, 0.25 mol)

and THF (60 mL) was added dropwise under vigorous stirring at  $-30^\circ\text{C}$ . After completion of dropping, the reaction mixture was stirred for another 2 h at the temperature. Then  $\text{NH}_3$  was introduced into the mixture under vigorous stirring until no further  $\text{NH}_3$  was absorbed, which was monitored by flowing rate of  $\text{NH}_3$ . Then the mixture was allowed to warm to room temperature. After removal of precipitate by filtration, the filtrate was condensed under reduced pressure to give 40 g of polymeric precursor (PSNO) in 60% yield based on  $\text{H}_2\text{SiCl}_2$ , as a colorless viscous liquid. To confirm the structure of PSNO, perhydropolysiloxane (PHSO) and perhydropolysilazane (PHSN) were synthesized by the reaction of  $\text{H}_2\text{SiCl}_2$  and  $\text{H}_2\text{O}$  in a molar ratio of 1 : 0.9 according to reported method<sup>20</sup> and full ammonolysis of  $\text{H}_2\text{SiCl}_2$  with  $\text{NH}_3$  at  $-30^\circ\text{C}$ , respectively.

### Curing and pyrolysis

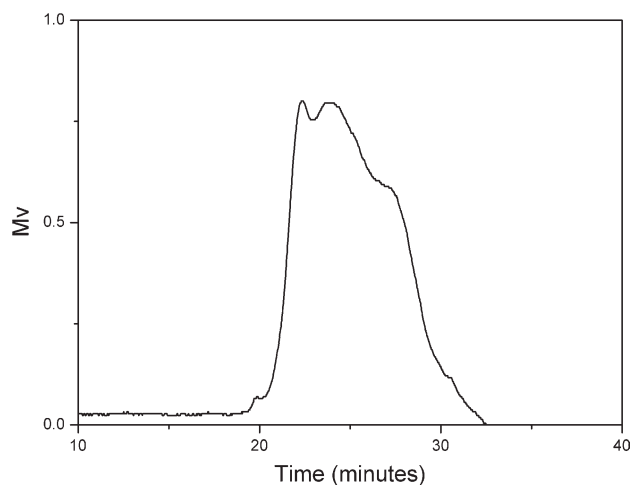
Thermal curing of the PSNO was carried out at 200°C for 6 h under  $\text{N}_2$  atmosphere. The cured sample is transparent and hard solid. The cured bulk precursors were pyrolyzed in a tube furnace (Sentro Tech. Corp.) from room temperature to the given temperature in a flowing  $\text{N}_2$  atmosphere at a heating rate of 5°C/min, and dwelled at final temperature for 2 h before cooled down to room temperature at a rate of 5°C/min. The resulting ceramic is yellow rigid material.

## RESULTS AND DISCUSSION

### Synthesis and characterization

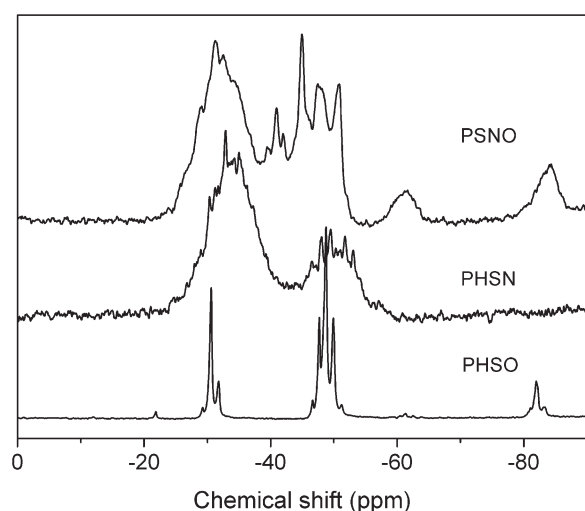
The synthesis of PSNO is a two-step procedure. In the first step, partial hydrolyzation of  $\text{H}_2\text{SiCl}_2$  produced a mixture, which is mainly composed of linear polysiloxane containing terminated Si-Cl groups, cyclosiloxane, and unreacted  $\text{H}_2\text{SiCl}_2$ . Then the mixture reacted with excess amount of  $\text{NH}_3$  to form PSNO. The as-synthesized PSNO shows good fluidity with the dynamic viscosity of 60 mPa s at 25°C. The number average molecular weight ( $M_n$ ) of PSNO is 804, with its polydispersity distribution index 3.2 (Fig. 1).

To confirm the structure of PSNO, partially hydrolyzed product of  $\text{H}_2\text{SiCl}_2$  (PHSO) and ammonolysis product of  $\text{H}_2\text{SiCl}_2$  (PHSN) were synthesized, respectively. The  $^{29}\text{Si}$ -NMR spectrum of PSNO was compared with those of PHSO and PHSN for signal assignment. As shown in Figure 2, in the  $^{29}\text{Si}$ -NMR spectrum of PHSO, the signals between  $-32$  and  $29$  ppm are attributed to terminated  $\text{ClSiH}_2\text{O}$ -, and the complex peaks between  $-51$  and  $46$  ppm are due to the coexisting linear polysiloxane and  $[\text{H}_2\text{SiO}]_n$  cyclics ( $n = 4-6$ ).<sup>21</sup> The peaks around  $-83$  ppm are

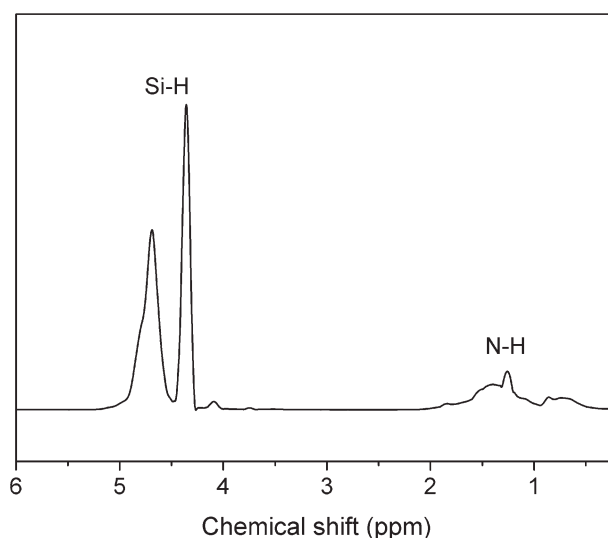


**Figure 1** GPC trace of PSNO in tetrahydrofuran:  $M_n = 804$ ,  $M_w = 2318$ .

attributed to  $\text{HSi(O-)}_3$ , which is derived from hydrolysis of Si-H bonds in aqueous solvent. In the spectrum of PHSN, the signals between  $-35$  and  $32$  ppm are assigned to  $\text{H}_2\text{Si(NH-)}_2$ , while peaks around  $-54$  to  $45$  ppm are attributed to  $\text{HSi(NH-)}_3$ .<sup>22</sup> According to the  $^{29}\text{Si-NMR}$  data of PHSO and PHSN, the group of peaks between  $-37$  and  $28$  ppm in the  $^{29}\text{Si-NMR}$  spectrum of PSNO is assigned to  $\text{H}_2\text{Si(NH-)}_2$  and the signals between  $-51$  and  $43$  ppm are attributed to the mixture of  $\text{HSi(NH-)}_3$  and  $[\text{H}_2\text{SiO-}]_n$ . The new emerging peaks around  $-40$  ppm are due to  $-\text{NHSiH}_2\text{O-}$  from ammonolysis of  $\text{ClSiH}_2\text{O-}$ . Si-H bonds are easily cleaved in basic aqueous solution, and thus in the  $^{29}\text{Si-NMR}$  spectrum of PSNO, medium-intensity signals corresponding to  $\text{HSi(O-)}_3$  and  $-\text{NHSiH(O-)}_2$  are also observed around  $-83$  ppm and  $-60$  ppm, respectively. The broadened peaks in the  $^1\text{H-NMR}$  spectrum of PSNO (Fig. 3) suggest a complex structure of the polymer. The broad peak at  $4.6$  ppm is due to cyclic or linear



**Figure 2**  $^{29}\text{Si-NMR}$  spectra of PSNO, PHSN, and PHSO.



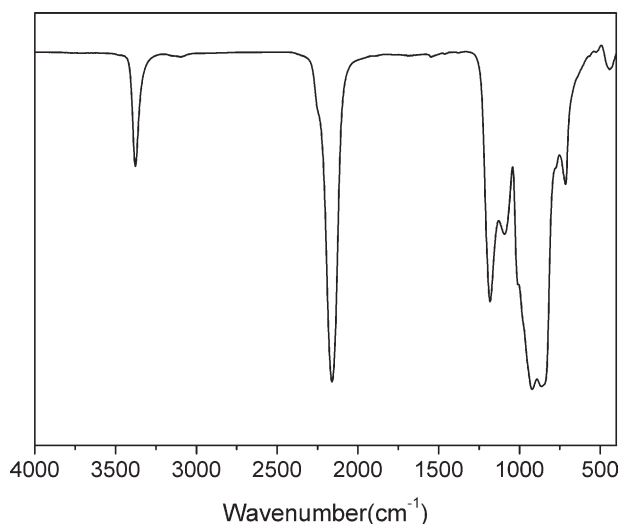
**Figure 3**  $^1\text{H-NMR}$  spectrum of PSNO.

$\equiv\text{SiH}$  while the sharp peak at  $4.3$  ppm is attributed to  $=\text{SiH}_2$ . The broad peaks between  $0.7$  and  $1.7$  ppm are assigned to  $\equiv\text{SiNH}$ .<sup>12,13</sup>

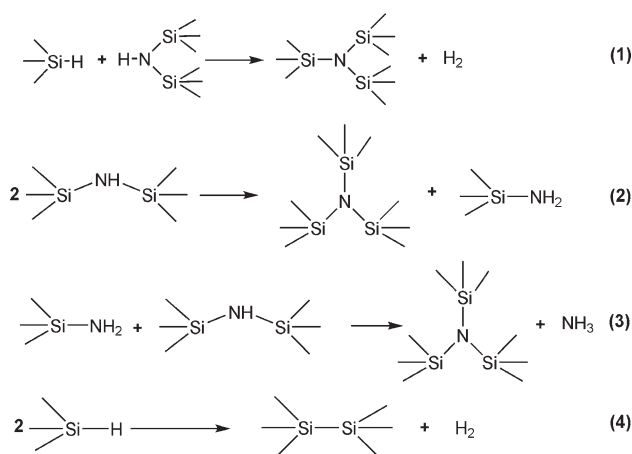
The structure of PSNO is further confirmed by FTIR spectrum. As shown in Figure 4, the peaks ascribed to Si-NH-Si groups include N-H stretching at  $3382\text{ cm}^{-1}$  and Si-N vibrations at  $1180\text{ cm}^{-1}$ . The strong absorption at  $2187\text{ cm}^{-1}$  is attributed to stretching mode of Si-H bond. The peaks at  $1075$  and  $462\text{ cm}^{-1}$  are assigned to stretching and rocking vibrations of Si-O-Si, respectively. Asymmetric stretching of Si-N-Si results in absorption signals at  $927$ ,  $832$ , and  $706\text{ cm}^{-1}$ .

#### Curing and ceramic conversion of PSNO

The obtained polymer PSNO contains a large amount of volatile linear and cyclic oligomers, which results in a moderated ceramic yield (70%) upon

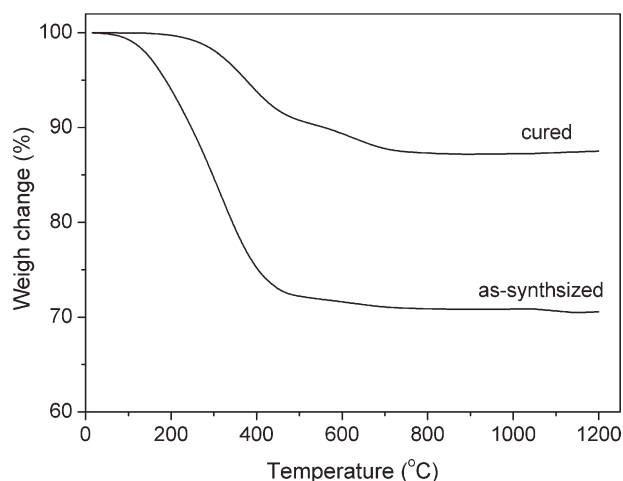


**Figure 4** FTIR spectrum of PSNO.



**Scheme 1** Postulated curing and pyrolysis mechanism for PSNO.

pyrolysis up to 1000°C under nitrogen atmosphere. Formation of crosslinking framework before decomposition or volatilization of the precursors is an effective way to increase the ceramic yield. PSNO undergoes dehydrogenation and transamination reactions (Scheme 1) to form a highly crosslinked structure after treated at 200°C for 6 h, which dramatically reduces the weight loss before 300°C derived from escape of volatile cyclic or linear components in the precursor. As a result, the ceramic yield of cured PSNO at 1200°C achieves 87%, which is higher by 17% than that of uncured sample (Fig. 5). The cured PSNO shows two stages of weight loss in the range of 200 to 450°C and 450 to 800°C, respectively. The 8% weight loss (200–450°C) in the first stage is ascribed to the release of NH<sub>3</sub> and H<sub>2</sub> gases by transamination and dehydrogenation reactions (reactions, (1), (2), and (3) in Scheme 1). The weight loss in second stage (450–800°C) is about 5%, mainly resulting from dehydrogenation reactions

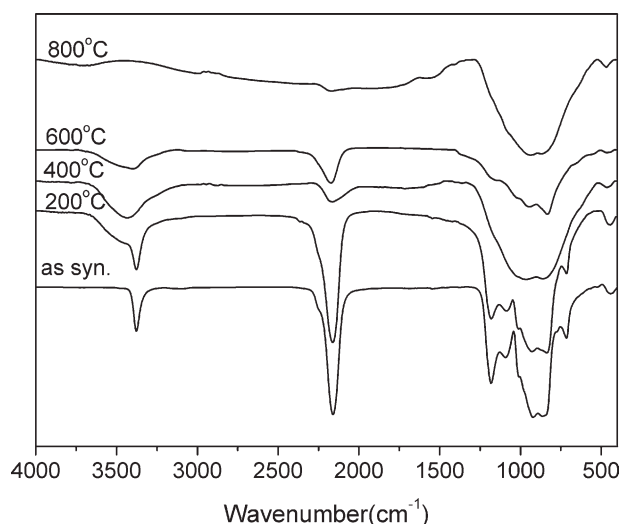


**Figure 5** TGA curves of the as-synthesized and cured PSNO at a heating rate of 10°C/min under N<sub>2</sub>.

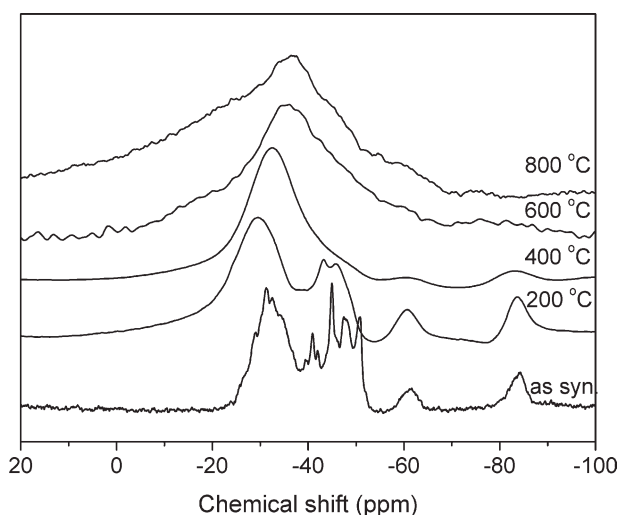
(reaction (1) and (4) in Scheme 1).<sup>23</sup> Above 800°C, no noticeable weight loss is observed, indicating the conversion of polymer to ceramic is nearly completed. Whereas, for as-synthesized PSNO, due to the release of un-crosslinked low molecular weight oligomers, a large weight loss in the first stage is observed. The process further reduces dehydrogenation reactions above 450°C. Thus, the as-synthesized PSNO shows less weight change in the second stage.

To investigate the conversion of the polymer to ceramic, FTIR and solid <sup>29</sup>Si-NMR analyses were performed on samples obtained by treatment of PSNO at 200, 400, 600, 800°C, respectively. In the FTIR spectra (Fig. 6), the intensities of Si-H (2178 cm<sup>-1</sup>) and N-H (3382 cm<sup>-1</sup>) gradually decrease with the treated temperature. For the sample obtained at 600°C, the peak of N-H at 3382 cm<sup>-1</sup> and Si-NH-Si at 1180 cm<sup>-1</sup> are very weak, indicating the transamination reaction is almost completed. The absence of Si-H absorption in the sample obtained at 800°C suggests a completed dehydrogenation reaction in the range of 600 to 800°C. Additionally, the peaks around 1000 cm<sup>-1</sup> get broadened with the rise of temperature. For the sample obtained at 800°C, only one broad peak around 900 cm<sup>-1</sup> is observed, which suggests an amorphous SiON structure.

In the <sup>29</sup>Si CP/MAS NMR spectra of PSNO (Fig. 7), all the peaks get broadened with rise of the treated temperature. After curing at 200°C, the peak assigned to -NHSiH<sub>2</sub>O- disappears. Upon treated at 400°C, the signals ascribed to H<sub>2</sub>Si(NH)<sub>2</sub>, HSi(NH)<sub>3</sub> and [H<sub>2</sub>SiO]<sub>n</sub>, -NHSiH<sub>2</sub>O- merge into one broad peak located at -34 ppm. These results indicate the formation of three-dimensional structure due to transamination and dehydrogenation reaction. The broad peak at -34 ppm further shifts to -40 ppm



**Figure 6** FTIR spectra of PSNO treated at different temperature (a) as-synthesized, (b) 200°C, (c) 400°C, (d) 600°C, and (e) 800°C.

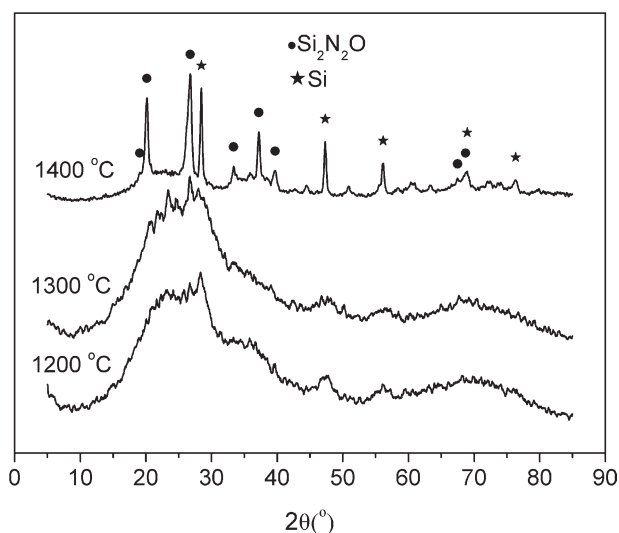


**Figure 7**  $^{29}\text{Si}$ -NMR spectra of PSNO treated at different temperature (a) as-synthesized, (b) 200°C, (c) 400°C, (d) 600°C, and (e) 800°C.

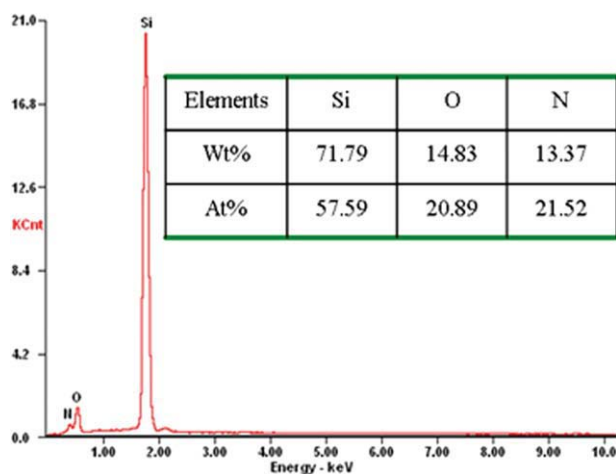
with the rise of temperature from 400 to 800°C, accompanied by the decrease of the signal at  $-83$  ppm. For the sample pyrolyzed at 800°C, only a broad peak in the range of  $-80$  to  $0$  ppm is observed, which further demonstrates the amorphous properties of silicon oxynitride ceramic.

#### XRD and high-temperature thermal gravity analysis

The crystallization behavior of PSNO-derived silicon oxynitride ceramic was investigated by XRD. As shown in Figure 8, the ceramic keeps amorphous up to 1300°C, with only one broad peak exists in the XRD pattern. For the sample annealed at 1400°C, the characteristic peaks corresponding to  $\text{Si}_2\text{N}_2\text{O}$  appear



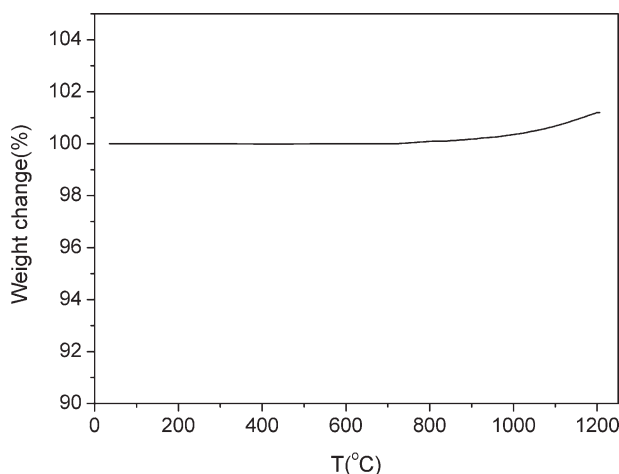
**Figure 8** X-ray diffraction patterns of PSNO pyrolyzed at different temperature under  $\text{N}_2$  atmosphere.



**Figure 9** EDX analysis of silicon oxynitride ceramic obtained by pyrolyzing PSNO at 1400°C (inset Table is the element composition). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

at  $2\theta = 20^\circ, 27^\circ, 37^\circ$  as marked in the spectrum, together with other weaker reflections. Besides, the peaks at  $2\theta = 28^\circ, 48^\circ, 56^\circ$  suggest existence of crystallized Si. The EDX (Fig. 9) analysis on different regions of the ceramics indicates the final ceramic has a relative composition of  $\text{Si}_{2.76}\text{N}_{1.03}\text{O}$ .

Oxidation stability of the ceramic obtained at 1400°C was evaluated by TGA under air, as shown in Figure 10. TGA trace shows a negligible weight change before 1000°C, and an as low as 1.2% weight gain at 1200°C. These facts suggest that the PSNO-derived silicon oxynitride ceramic may be slightly oxidized under the experimental condition. However, for the ceramic samples before and after treated at 1200°C in air, no obvious difference was observed between their SEM analysis of the morphology and EDX analysis of surface composition. Further study on oxidation-resistant property of the PSNO-derived ceramic is in progress in our group.



**Figure 10** Weight gain of silicon oxynitride ceramic under air atmosphere.

## CONCLUSIONS

A new liquid, organic group-free polymeric precursor, PSNO, for silicon oxynitride ceramic was synthesized by combination of partial hydrolysis and ammonolysis reaction of  $\text{H}_2\text{SiCl}_2$  in one pot. The structure of PSNO was characterized by means of FTIR and NMR analysis with partially hydrolyzed product of  $\text{H}_2\text{SiCl}_2$  (PHSO) and ammonolysis product of  $\text{H}_2\text{SiCl}_2$  (PHSN) as reference substances. The new precursor shows good processability and high ceramic yield. The silicon oxynitride ceramic produced from PSNO at  $1400^\circ\text{C}$  is silicon-rich and shows excellent resistance to oxidation. The organic group-free polymeric precursor may have potentials as dielectric materials in electronic devices, coating materials, and high-temperature ceramic materials.

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