

Note

Structural Characterization of a Polyaluminosilazane Precursor Prepared by Polymerizing Hexamethylcyclotrisilazane with Aluminum Acetylacetonate[†]

CHU, Zeng-Yong* (楚增勇) FENG, Chun-Xiang (冯春祥) SONG, Yong-Cai (宋永才)
LI, Xiao-Dong (李效东) XIAO, Jia-Yu (肖加余)

Key Laboratory of New Ceramic Fibers & Composites, National University of Defense Technology, Changsha, Hunan 410073, China

A new polyaluminosilazane precursor was prepared by polymerizing hexamethylcyclotrisilazane (HMCTS) with aluminum acetylacetonate and the structure of the precursor was characterized by FT-IR and XPS analysis. Result shows that aluminum was incorporated mainly in form of Al—N bond. Oxygen was also detected and found that it was mainly bonded to silicon.

Keywords polyaluminosilazane, hexamethylcyclotrisilazane, aluminum acetylacetonate, XPS, FT-IR

Introduction

Si₃N₄/SiC composites, which have enhanced fracture strength in comparison with monolithic Si₃N₄ materials, are candidate materials for high-temperature application as engine and turbine parts or as cutting tools, as well as having importance for microelectronic devices.^{1,2} However, the conventional fabrication of dense composites is difficult, owing to the different sintering behavior of the Si₃N₄ and SiC powder particles used as the starting materials.³ One promising alternative route is to start from silicon carbonitrides, Si_{3+x}N₄C_{x+y}, which are single phase materials with a homogeneous distribution of silicon, carbon and nitrogen at an atomic level.⁴ Usually, polysilazane precursors containing Si—N—Si units have been used because a single phase of Si/C/N could be obtained by pyrolysis.^{1,5}

However, the polysilazane derived ceramics are easy to crystallize at temperature higher than 1440 °C due to evolution of nitrogen.⁵ To solve the problem, the polysilazanes can be chemically modified to produce quaternary systems like Si/B/C/N,⁶ which have shown a much improved thermal stability as well as a more controlled crystallization behavior. Besides boron, another promising candidate is aluminium since AlN, Al₂O₃, SiAlON and other Al-containing materials show interesting properties such as high strength, high hardness or resistance to ther-

mal shock and oxidation. Up to now, polyaluminosilazanes (PASNs) have been synthesized either by polymerizing hexamethylcyclotrisilazane (HMCTS) with triethylaluminum (TEA)⁷ or by the condensation reaction between AlH₃-N(CH₃)₃ and Si(NHCH₃)₄ at -78 °C.⁸ However, the above aluminum-containing reagents are either very air-sensitive or too costly to be commercially used. Instead, we synthesized a new PASN using aluminum acetylacetonate [Al(AcAc)₃] and the structure of the precursor was studied by FT-IR and XPS analysis.

Experimental

All liquid organosilicon compounds were purchased from Xinghuo Organosilicon Factory and purified by distillation. Xylene was commercially available and was dried by refluxing over sodium and distilled under a nitrogen atmosphere. Al(AcAc)₃ was purchased from Aldrich chemical company and used as received. Reactions were carried out in oven dried glass equipment with flowing high purity nitrogen as the protecting gas.

The PASN was synthesized as follows: In a 250-mL three-necked, round-bottomed flask equipped with a reflux condenser, a dropping funnel and a gas inlet tube, 5.0 g of aluminum acetylacetonate was added firstly, then 100 mL of freshly distilled xylene and 10 mL of HMCTS were charged by syringe after the air in the flask was replaced by dry nitrogen. The reaction mixture was heated up to the boiling point of xylene and maintained at the temperature for 30 h, then the solvent was removed by distillation under nitrogen. The brown solid was dried under vacuum to give 11.2 g of brittle material. PASN is somewhat sensitive to air and moisture, so it should be kept under an inert atmosphere.

Fourier-transform infrared (FT-IR) spectra were ob-

* E-mail: Z.Y.Chu@163.net; Tel.: 0731-4576247; Fax: 0731-4573166

Received February 28, 2003; revised May 5, 2003; accepted May 13, 2003.

Project supported by the National Advanced Materials Committee of China (No. 715-011-016).

[†]Dedicated to Professor ZHOU Wei-Shan on the occasion of his 80th birthday.

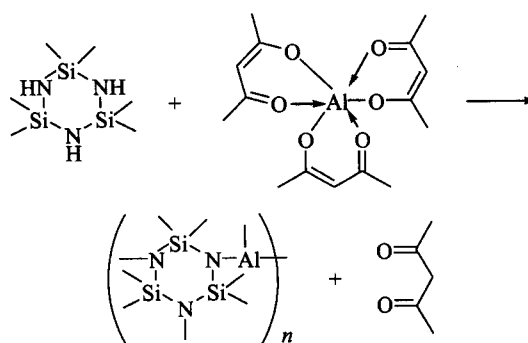
tained with a Perkin-Elmer 2000 IR spectrometer in the wavenumber range 4000–400 cm^{-1} using standard procedures. Aluminum and oxygen content were analyzed instrumentally at the National Key Laboratory of Powder Metallurgy of China. Molecular weight distributions were determined by gel permeation chromatography (GPC) by using a Waters-244 analyzer and s-Styragel columns calibrated with polystyrene standards and by using tetrahydrofuran (THF) as diluents at a flow rate of 0.5 mL/min. The X-ray photoelectron spectroscopy (XPS) was recorded (FRR XPS spectrometer) with Al $K\alpha$ as the excitation source on the fresh fracture surface of PASN. The pressure in the spectrometer was at the 10^{-9} Pa level. The binding energies were obtained with respect to the C_{1s} peak of graphitic carbon at 284.1 eV.

Result and discussion

The FT-IR spectra of HMCTS and PASN are shown in Fig. 1 (a) and (b) respectively. The peak at 925 cm^{-1} was typical of asymmetric stretching of Si–N–Si, while the peak at 700 cm^{-1} was Si–C symmetric stretching. The peaks at 3392 and 1170 cm^{-1} were assigned to the N–H bond and the peaks at 2950, 2900 and 1410 cm^{-1} were assigned to the C–H bond. A sharp absorption at 1250 cm^{-1} was due to the deformation of Si–CH₃. In addition, a sharp peak at 1080 cm^{-1} may be assigned to the cyclic structure of HMCTS or Si–O bond.^{1,9}

As to the difference, the strong N–H peaks in HMCTS became too weak to be detected in PASN. At the same time, Al–N peak located near the C–H bond at 1400 cm^{-1} came to appear. Based on this point, It is known that the polymerization process was done by the formation of Al–N bond with the consumption of N–H bond. As shown in Scheme 1, acetylacetonate was generated as a byproduct in the process.

Scheme 1



Also, a weak peak at 1710 cm^{-1} could be detected in PASN, which is probably due to H–O–H (H_2O) vibration introduced during measurement.

Fig. 2 is the XPS wide scan of the fresh fracture surface of PASN. The peaks assigned to Al_{2p} (74.2 eV), Si_{2p} (101.9 eV), Si_{2s} (160.5 eV), N_{1s} (398.2 eV), O_{1s} (531.9 eV) and oxygen auger are visible.¹⁰ According to the area ratio of the main peaks, an empirical formula like $\text{Si}_{2.0}\text{N}_{0.7}\text{Al}_{0.1}\text{O}_{0.3}\text{H}_x$ could be proposed. This is in good agreement with the elemental analysis, which showed Al and O content were 3.01%, 4.86%, respectively. The precursor has a number-average-molecular-weight of 1324 and could be solved in benzene, toluene, xylene, THF and so on. Accordingly, the precursor has similar properties to those reported in the literature,^{7,8} but superior in that the raw material is relatively stable and cheap.

To obtain more information about the structure, the core level deconvolution spectra of the main peaks are shown in Fig. 3. The Si_{2p} peak was deconvoluted into 100.5, 102.1 and 104.2 eV and assigned to Si–N, Si–C and Si–O,¹¹ respectively. It is obvious that Si is bonded mainly to C, N and weakly to O.

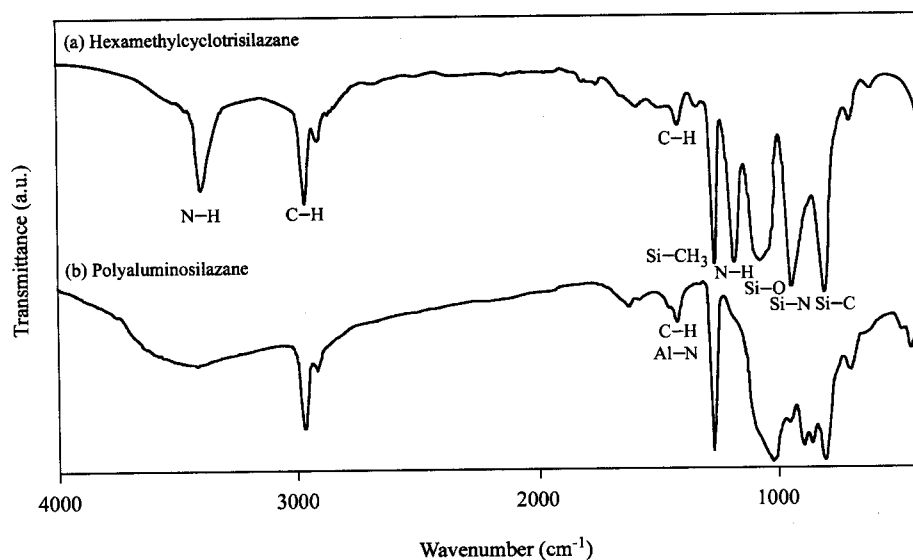


Fig. 1 FT-IR spectra of the (a) hexamethylcyclotrisilazane and (b) polyaluminosilazane.

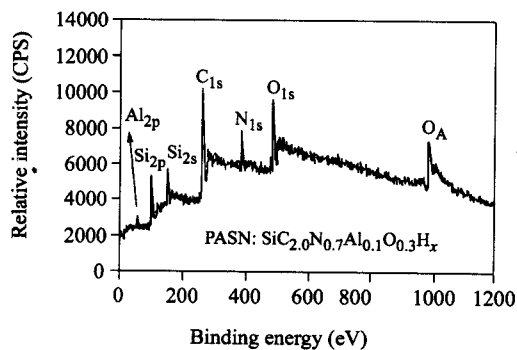


Fig. 2 XPS wide scan of the fresh fracture surface of polyaluminosilazane.

The deconvoluted peaks of C_{1s} centered at 284.5, 283.0 and 286.4 eV were assigned to C—Si, C—H and C—O or C = O.^{12,13} The binding energies of C—O and C = O were near.¹⁴ Also, the deconvoluted N_{1s} incorporated N—Si (398.0 eV) and N—Al (400.5 eV), and the deconvoluted O_{1s} incorporated O—Si (532.4 eV) and O = C or O—C (530.9 eV). Due to weakness, the Al_{2p} peak could not be deconvoluted but showed a main peak assigned to Al—N bond at 74.4 eV.¹⁵ As an unwanted element, oxygen was found mainly bonded to silicon. It may come from HMCTS as Si—O bond or from the environment when exposed to air.

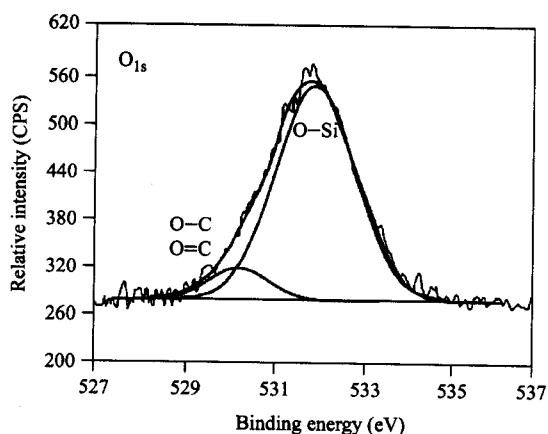
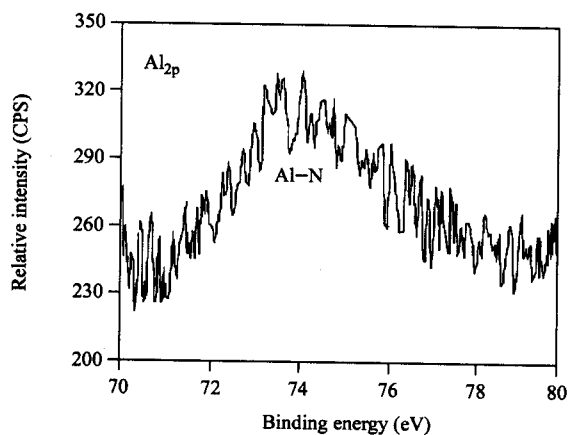
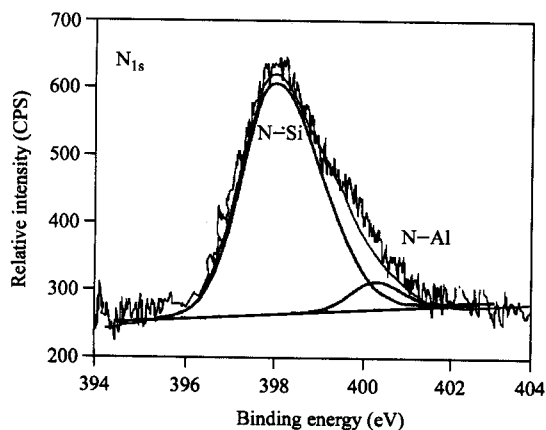
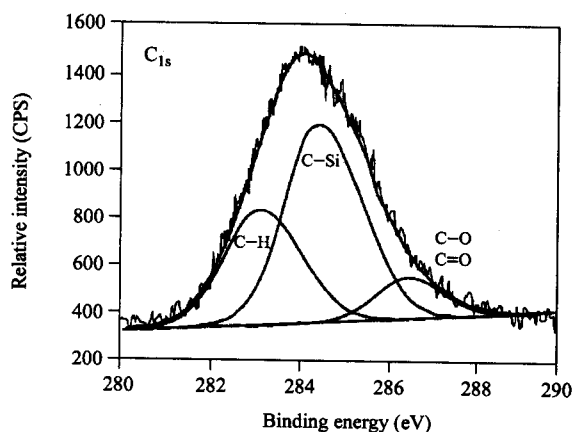
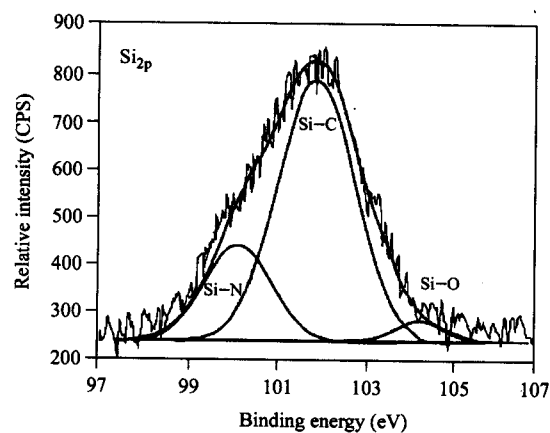


Fig. 3 Core level deconvolution spectra of Si_{2p} , C_{1s} , N_{1s} , Al_{2p} and O_{1s} .

Conclusion

A new PASN was prepared by polymerizing HMCTS with a relatively stable and cheap reagent, $\text{Al}(\text{AcAc})_3$. During the synthetic process, Al—N crosslinking bond was generated as a result of the reaction between N—H bond and Al—O bond. Oxygen was also detected in the precursor due to some experimental factors and further work is undergoing to prepare oxygen-free PASNs so as to produce Si/Al/C/N quaternary ceramics.

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(E0302284 SONG, J. P.; FAN, Y. Y.)