Borazine-type single source precursor with vinyl to SiBCN ceramic

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A single source precursor of borazine derivative (B[NH(Si(CH₃)₂CH=CH₂)]NH₃ (TSAB)) was designed for electronic applications. The result of thermo gravimetric analysis combined with mass spectrometry shows a ceramic yield of 60.7%. The X-ray photo-electron spectroscopy confirms that the siliconboron carbonitride (SiBCN) ceramic is obtained. The powder X-ray diffraction pattern and Raman spectra show that the graphite and a little hexagonal BN are formed after pyrolysis at 1500°C. The room temperature conductivity increases with the pyrolysis temperature, the highest is approximately 10⁻⁻⁸ (Ω cm⁻¹) for SiBCN ceramic from cured TSAB pyrolyzed at 1500°C. Photoluminescence is observed in the visible range. The peaks appear at 417, 466, 498, and 593 nm (2.97, 2.66, 2.49, and 2.09 eV, respectively).

Key-words : Borosilazane, Single source precursor, SiBCN ceramic, Electronic property, Photoluminescent emission

1. Introduction
Polymer derived ceramics (PDCs) are a novel and attractive material. PDCs have excellent thermal stability, high-temperature mechanical properties, and oxidation/corrosion resistance. They also exhibit tunable semi-conducting behavior and significant piezoresistivity, allowing the fabrication of microsensors and microelectronic devices.¹⁻⁵ Silicon carbon-nitride (SiCN) ceramics have been widely used in preparing devices in microelectromechanical systems (MEMS), where SiCN can be imparted with electrical properties by altering its microstructure through varying the material synthesis conditions.⁶⁻⁸ Hermann et al. introduced boron into the SiCN systems. They found that boron doping leads to enhanced p-type conductivity, and the conductivity (room temperature) of the ceramics increases with the annealing temperature from 10⁻⁸ to 10⁻⁴ (Ω cm⁻¹).⁹ Qian et al. used a swarm structure search method combined with density functional theory to explore the electronic properties of SiBCN ceramics. They found that SiBCN exhibits a wide direct band gap and high carrier mobility.¹⁰

A single source precursor for SiBCN ceramic is here presented. It is specially designed to provide the final ceramic great electronic properties for MEMS or other electronic devices. The single source precursor is selected to ensure that the distribution of constitution elements is highly homogeneous in the pre-ceramic polymer and the final ceramic.¹¹⁻¹⁵ The borazine derivative is appropriate for single source precursor because the borazine ring is a rigid unit which can suppress the conformational changes inside the random network. The ceramics derived from borazine precursors also exhibit enhanced hardness, stiffness and high temperature durability.¹⁶ An active group is required to ensure the crosslinkage of the precursor. In our previous study, we introduced acrylate groups into borazine ring to prepare UV-curable single source precursors for SiBCN ceramics.¹⁷⁻¹⁹ We found that these precursors had excellent performance of photo-polymerization reaction, but the ceramic yield was low for the incorporation of many acrylate groups. To solve this problem, we selected vinyl groups, which replaced the acrylate groups to eliminate the negative effect on ceramic yield. The vinyl groups can promote polymerization by heating without the use of curing agent or under UV-irradiation with a curing agent that contains S–H¹⁰ bond or Si–H¹¹ bond. Moreover, vinyl groups can improve the amount of carbon content which is the main conductive phase in high C-containing PDCs.²²,²³

In the present study, we present a single source precursor B,B′,B‴-Tris([dimethyl(vinyl)silyl]amino)borazine (TSAB). The specially designed precursor TSAB contains borazine ring as the backbone, and vinyl groups as the functionalized periphery. The electronic property and photoluminescence (PL) performance of the final ceramics are tested.

2. Experimental procedure
2.1 General
All reactions were carried out under argon (99.999%) atmosphere in absolutely dry reaction condition. Tetrahydrofuran, hexane and dichloromethane were distilled
2.2 Synthesis of TSAB (Fig. 1)

2.2.1 Synthesis of Me$_2$CH–CH$_2$Si–NH–SiMe$_3$ (pentamethylvinyldisilazane, PVDS)

An amount of 0.1 mol vinyldimethylchlorosilane and 0.1 mol hexamethyldisilazane were mixed in a Schlenk flask and vigorously stirred at 60°C for two days. The byproduct trimethylchlorosilane was removed by slow evaporation under reduced pressure. The final product is unstable and stored in the flask for further use.

2.2.2 Synthesis of Me$_2$CH–CH$_2$Si–NH–BCl$_2$ (vinyldimethylsilyldichloroborylamine, VSDA)

The 0.1 mol PVDS was added dropwise into 0.2 mol boron trichloride under stirring at −70°C. The reaction was continued for another 4 h at room temperature. The byproduct trimethylchlorosilane and excess boron trichloride was removed by evaporation under reduced pressure and the product was purified by vacuum distillation.

2.2.3 Synthesis of (B{NH[Si(CH$_3$)$_2$CH=CH$_2$]$_2$}-NH)$_3$ (B,B′,B″-Tris[dimethyl(vinyl)silyl] amino)borazine, TSAB)

Under stirring, hexamethyldisilazane was added dropwise to the solution of 0.1 mol VSDA in 10 ml hexane at −70°C. When the solution reached the room temperature, the mixture was stirred for another 48 h. The hexane was removed by vacuo. The product was dissolved in tetrahydrofuran and then purified by silica gel column chromatography separation. The final product was concentrated by vacuo.

2.3 Preparation of the pre-ceramic and the final SiBCN ceramic

The 0.04 g initiator dicumyl peroxide was added into the solution of 2 g TSAB in 5 ml dichloromethane (See Supporting Information). When the initiator was dissolved, the solvent dichloromethane was stripped by vacuo. Then the mixture was filled in an inert corundum crucible which was placed in a tube furnace (GSL-1700X, Kejing New Mater. Ltd., Hefei, China). Under slightly flowing argon, the sample was heated at a rate of 5 K min$^{-1}$ up to 130°C and maintained for 1 h and then up to 160°C for 2 h and up to 190°C for 1 h to complete the polymerization of the precursor (See Supporting Information), and then raised to different temperature (1200, 1400, 1500°C) and maintained for another 4 h.

2.4 Characterizations

$^1$H-, $^{13}$C- and $^{11}$B- nuclear magnetic resonance (NMR) spectra were obtained using a Bruker Avance 400 MHz apparatus in C$_2$D$_2$. Fourier transform infrared (FTIR) spectra of the samples were obtained with a Bruker Tensor 27 spectrometer in KBr pellets.

Simultaneous thermo gravimetric analysis coupled with mass spectrometry (TG-MS) was performed using a simultaneous thermoanalyzer STA 449 F3 coupled with a quadrupole mass spectrometer QMS 403 C Äolos (Netzsch GmbH & Co., Selb, Germany) in a temperature range between 40 and 900°C and with a heating rate of 10 K/min under an argon atmosphere (a gas flow of 50 mL/min).

X-ray photo-electron spectroscopy (XPS) measurement of the ceramic was conducted on a K-Alpha spectrometer (Thermo Fisher Scientific, Waltham, USA), and the core level spectra were measured using a monochromatic
of the corresponding groups are listed in Table 2. Apart from the strong stretching mode of the NH group at 3435 cm\(^{-1}\), \(^{25}\) the typical bands for alkyl groups are in the range of 2800–3100 cm\(^{-1}\), \(^{25}\) and the stretching vibration of the vinyl group is at 1600 cm\(^{-1}\). \(^{26}\) TSAB shows an extremely intense absorption at 1470 cm\(^{-1}\), which is formed from the antisymmetric stretching vibration of the borazine ring. \(^{25}\) The Si–N bond is at 947 cm\(^{-1}\), and the Si–C bond is at 764 cm\(^{-1}\). \(^{25}\)

### 3.2 Pre-ceramic polymer and its transformation to ceramic

TSAB can be polymerized via addition polymerization of the vinyl groups under heating. The change in the chemical structure is shown in Fig. 2, confirming that the polymerization is preceded by the addition polymerization of vinyl groups. Evidently, the stretching vibration of the vinyl group at 1600 cm\(^{-1}\) disappeared after polymerization. The peak between 1250 and 1500 cm\(^{-1}\) is broadened after polymerization, because of the –CH\(_2–\) groups formed during the addition polymerization of the vinyl groups, the bending vibration of –CH\(_2–\) appears between 1380 and 1450 cm\(^{-1}\). \(^{27}\) Figure 2(b) also shows the stretching mode of B–NH–B appeared at 3441 cm\(^{-1}\), and the new peak that emerged at 3230 cm\(^{-1}\) is the NH group linked to vinylsilyl, which was vinylsilyl prior to polymerization. \(^{28}\) The antisymmetric stretching vibration of the borazine ring

![Fig. 2. FTIR spectra of (a) TSAB molecular, (b) polymer, (c) ceramic.](image)

### Table 1. NMR spectroscopic data of the TSAB molecule

| Nucleus | Observed multiplicity | \(\delta\)/ppm | Assignment |
|---------|-----------------------|---------------|------------|
| \(^1\)H | singlet               | 0.15          | Si–CH\(_3\) |
| \(^1\)H | singlet               | 2.45          | Si–NH–B    |
| \(^1\)H | singlet               | 4.32          | B–N\(_2\)–B |
| \(^1\)H | doublet               | 5.811/6.0     | –CH=CH\(_2\) |
| \(^1\)H | triplet               | 6.3           | –CH=CH\(_2\) |
| \(^10\)B | singlet              | 3.24          | Si–T(B)    |
| \(^10\)B | singlet              | 130.9         | –CH=CH\(_2\) |
| \(^10\)B | singlet              | 141.26        | –CH=CH\(_2\) |
| \(^11\)B | singlet             | 28.46         | BN\(_3\)    |

![Table 2. FTIR of the TSAB molecule, polymer and ceramic](image)
The stretching vibration of Si–N appeared at 1467 cm\(^{-1}\), and that of Si–C at 751 cm\(^{-1}\).\(^{25,28}\)

The pyrolytic conversion of the cured TSAB into an amorphous silicon boron carbonitride was monitored by thermo gravimetric analysis combined with mass spectrometry (TG/MS). The TG/MS curves are shown in Fig. 3. In the molecular structure of TSAB, the borazine ring acts as the rigid unit, and the vinyl groups ensure the formation of the three-dimensional network. These factors ensure the high ceramic yield of the cured TSAB. The thermolysis of the cured TSAB is mainly accompanied by the evolution of gaseous hydrocarbons CH\(_x\) (x = 1–3, m/z = 13–15), CH\(_4\) (m/z = 16), NH\(_3\) (m/z = 17), H\(_2\)O (m/z = 18), CH\(_3\)CH\(_2\) (m/z = 25, 26, 29, and 30), and oligomer fragments (m/z = 44 and 45). The TG/MS result shows that the thermal degradation of the cured TSAB proceeds in two stages, with a ceramic yield of 61%. From 100 to 200°C, the mass loss of 19.5% is mainly caused by the emission of water and NH\(_3\), where the sample was moistened by air before measurement. In the first step of conversion from 200 to 400°C, the mass loss of 14.1% is caused by the polycondensation and crosslinking of the polyborocarbosilazane through transamination reaction, where the emission of NH\(_3\) and CH\(_4\) is found. The temperature range between 400 and 700°C marks the second step of the pyrolysis. The conversion process from polymer to ceramic continues, the emission of alkyl segments and CO\(_2\) can be observed. A mass loss of 5.7% is observed during this phase.

### 3.3 Final ceramic

The strong IR absorption of the ceramic material at 1396 cm\(^{-1}\) [Fig. 2(c)] can undoubtedly be assigned to the antisymmetric stretching mode of borazine ring. It occurs between 1367 and 1400 cm\(^{-1}\) in the solid state.\(^{24,25}\) Thus, the borazine ring introduced via the single source precursor TSAB has become part of the final random network. Other typical structural increments such as Si–N and Si–C (700–900 cm\(^{-1}\)) can be identified from their corresponding broad bands.\(^{24,25}\)

Figure 4 shows that XPS was used to study the surface element composition of the SiBCN ceramic from pyrolysis of cured-TSAB at 1200°C. The Si 2p XPS spectrum shows that the binding energy of silicon was centered at 102.9 eV, suggesting the Si–N bond.\(^{29}\) The B 1s XPS spectrum shows two possible boron chemical states with binding energies centered at 192.1 and 190.9 eV, which were attributed to B–O bonding and B–N bonding respectively.\(^{30}\) The N–B peak appears at 398.2 eV,\(^{30}\) and the other peak appears at 400.11 eV, which can be attributed to N–C bond.\(^{29}\) Compared to N–B bonds, the content of N–Si bonds is relatively small. The expected N–Si bonds at 398 eV overlap with the N–B peak.\(^{31}\) The C 1s spectrum confirms that the carbon atoms were mainly bonded carbon atoms (286 eV).\(^{29}\)

The patterns obtained by powder XRD analysis are presented in Fig. 5. The phase structure of SiBCN ceramic at different pyrolysis temperatures (argon atmosphere) is recorded. The crystals were identified from the XRD patterns (graphite carbons, hexagonal, PDF-89-8487; h-BN, hexagonal, PDF-34-0421). The carbons begin to change from disordered to crystalized at 1400°C because of the accumulation of carbon atoms, and the graphite-carbons appeared at 1500°C. At the same time, the graphite-like h-BN crystals were formed. The crystals of Si\(_3\)N\(_4\) and SiC were constrained owing to the presence of boron atoms. The Raman spectra were used to further examine the fine structure of the as-prepared ceramic at 1200 and 1400°C (Fig. 6). Two Raman bands were observed, as follows: the intensive peak appeared at 1350 cm\(^{-1}\), which is attributed to the disorder-induced D band, and the other intensive peak at 1600 cm\(^{-1}\) is attributed to the G band caused by
Fig. 4. (A) Survey scan XPS spectra for the final ceramic derived from TSAB, (B) deconvoluted Si 2p core-level spectrum, (C) deconvoluted B 1s core-level spectrum, (D) deconvoluted C 1s core-level spectrum, (E) deconvoluted N 1s core-level spectrum.

Fig. 5. XRD powder pattern of the SiBCN ceramic after pyrolysis at different temperature.

Fig. 6. Raman spectra of the SiBCN ceramic after pyrolysis at different temperature.
much higher than that of the SiCN materials [10]. The high frequency intralayer $E_{2g}$ vibration mode of h-BN always appears near 1367 cm$^{-1}$ [33,34]. From 1200 to 1400°C, the peak at 1350 cm$^{-1}$ does not shift and there appear no peaks around at 1367 cm$^{-1}$ so that the h-BN does not form at 1400°C. The results of the XRD patterns and Raman spectra show that the ceramic remains amorphous until 1500°C, and that the peaks of graphite and h-BN appeared at 1500°C.

The electronic conductivity of the ceramic was tested by the linear four-probe test. The room temperature conductivity of the SiBCN ceramic derived from TSAB is much higher than that of the SiCN materials [10–9,10–7 (Ω cm)$^{-1}$]. The conductivity is $8 \times 10^{-6}$ (Ω cm)$^{-1}$ for ceramic obtained at 1200°C, $4.23 \times 10^{-5}$ (Ω cm)$^{-1}$ for 1400°C and $3.94 \times 10^{-4}$ (Ω cm)$^{-1}$ for 1500°C. The conductivity increases with the pyrolysis temperature, especially after the formation of graphite, where the conductivity increased by an order of magnitude from 1400 to 1500°C. The SiBCN ceramic is a wide direct band gap semiconductor. The valence band is mainly composed of C and N $2p_z$ state, and the conduction band is mainly composed of B $2p_y$ and Si $3p_z$ states. The charge is mainly located at the C atoms in the valence band, and mainly situated at the Si and B atoms in the conduction band. The vinyl group promotes the free-carbon in the final ceramic and forms the formation of graphite, which is beneficial for the conductivity. However, the amount of carbon is not sufficient to form a percolation network. Thus, the origin of the electric conductivity of the SiBCN ceramic derived from TSAB is still semiconductor.

The carbon exists in the form of C–C. The accumulation of the carbon stimulates the formation of free-carbon and its crystalline state, which is beneficial to the electronic property but unsafe to the optical properties. The free-carbon tends to quench luminescence, [35] and the graphite has gapless band structure. [36] The PL behavioral study was carried out to analyze the photoluminescent property of the SiBCN ceramic from pyrolysis of cured TSAB at 1400°C. The SiBCN ceramic powder is excited at 380 nm wavelength and the normalized PL spectrum is depicted in Fig. 7. The emission spectrum was composed of a group of peaks centered at 417, 466, 498, and 593 nm (2.97, 2.66, 2.49, and 2.09 eV, respectively), and the strongest PL peak appeared at 417 nm, indicating the promising luminescent property of the final SiBCN ceramic. Except free-carbon, the final ceramic also contained amorphous BN and amorphous SiN. The amorphous BN revealed a wide range of luminescence based on structural defects, composition, and crystallinity from high energy ultraviolet emissions centered at 3.8 eV to deep-blue PL at approximately 2.88 eV at room temperature. [37–39] The SiN had broad emission band at the maximum of $\sim$2.3 eV, which was ascribed to the defects from Si–Si and N–N bonds, and Si and N dangling bonds. [40] The emissions of the final SiBCN ceramic derived from TSAB were in the visible range and at energies of 3.0–2.0 eV, which fall between the range of BN and SiN. Therefore, these luminescence peaks could be an effect of alloying of BN and SiN. [39] The luminescence originates in band to band transitions (more precisely, transitions between tails in energy bands) and band (band tail) to discrete level transitions; the discrete levels originate in structure defects. [41] Most likely, the luminescent centers can be attributed to the band tail recombination. [42] The PL peaks of BN and SiN shift and the intensity is also changed in the SiBCN ceramic. The peak at 2.97 eV is ascribed to BN, [39] and the other peaks from 1.9 to 2.9 eV are ascribed to SiN. [40]

4. Conclusions

A borazine derivative TSAB is synthesized successfully as a single source precursor for the preparation of SiBCN ceramic. The siliconboron carbonitride ceramic (SiBCN) is obtained by pyrolysis of the cured TSAB with a ceramic yield at 60.7%. In the final ceramic, boron atoms were mainly bonded to nitrogen atoms. Majority of the silicon atoms bonded to nitrogen atoms. The carbon atoms mostly existed as C–C. XRD powder pattern and Raman spectra showed that the ceramic remained amorphous until 1500°C at the argon atmosphere. The graphite and h-BN appeared at 1500°C. The conductivity increased with the pyrolysis temperature, especially after the formation of graphite. The room temperature conductivity of the ceramics obtained at 1200, 1400, and 1500°C is $8 \times 10^{-6}$ (Ω cm)$^{-1}$, $4.23 \times 10^{-5}$ (Ω cm)$^{-1}$, and $3.94 \times 10^{-4}$ (Ω cm)$^{-1}$, respectively. The room temperature PL spectra showed four PL peaks in the visible range and at energies of 3.0–2.0 eV. These luminescence peaks could be an effect of alloying of BN and SiN. These results suggest that the ceramic derived from TSAB might be a potential candidate for optoelectronic and electronic applications.

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