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# Novel zirconium nitride precursor: synthesis, decomposition pathway, and pyrolysis of $[(CH_3)_3Si]_2NH{\cdot}ZrCl_4$

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The reaction of hexamethyldisilazane with zirconium tetrachloride furnishes an adduct, $[(CH_3)_3Si]_2NH{\cdot}ZrCl_4$, which is soluble in dichloromethane. The decomposition of $[(CH_3)_3Si]_2NH{\cdot}ZrCl_4$ proceeds with the elimination of trimethylchlorosilane and hydrogen chloride and is complete at 600 °C. The resulting powder is amorphous zirconium nitride which is highly susceptible to hydrolysis and oxidation. The pyrolysis of the precursor in a dynamic vacuum or ammonia atmosphere at 600 °C and subsequent sintering of the powder at 900 °C furnishes crystalline zirconium nitride. Transmission electron microscopy of the powder shows that the particles are coated with a thin zirconium oxide layer. Crystalline zirconium nitride powder, free from zirconium oxide impurities, is obtained if the sintering is carried out at 1075 °C.

## Introduction

In recent years there have been extensive efforts to prepare a variety of metal nitrides by ceramic precursor routes.[1] These routes are considered to be advantageous as compared to classical methods due to the ease of preparation of the materials at low temperatures as powders, fibers, or films. The ceramic precursors can also be employed as binders and as *in situ* sources of ceramic phases in the fabrication of metal–matrix[2] or ceramic–matrix composites.[3] Since they undergo extensive shrinkage during processing, ceramic precursors are not suitable in the fabrication of net shapes.[4] However, they can be employed in the fabrication of net shapes if they are mixed with active fillers.[4]

Ceramic precursor routes for group IV metal nitrides are limited to titanium nitride.[1] There is only one report describing the preparation of zirconium nitride from $Zr_5[N(C_2H_5)_2](NH_2)_3(NH)_5(N)_2$ obtained by the ammonolysis of $Zr[N(C_2H_5)_2]_4$.[5] This precursor is insoluble in common organic solvents and can be pyrolyzed at 800 °C for conversion to zirconium nitride containing *ca.* 3% residual carbon. The applications of this precursor are limited due to its insolubility. Thus there is a need to find precursors which are soluble in common organic solvents in order to develop new applications. It is important to point out that several known applications of zirconium nitride such as coatings on cutting tools,[6] binders for the preparation of high tensile strength alloys,[7] and anti-reflective films on glass[8] are of value to the automotive industry provided that low cost methods can be developed.

We have recently shown that a titanium nitride precursor, $Me_3SiNHTiCl_3$, can be employed for the low temperature preparation of titanium nitride,[9] $Si_3N_4$–TiN nitride composites,[10] and in the fabrication of titanium nitride films on alumina substrates by a single dipcoat-firing sequence.[11] We are currently investigating the deposition of early transition metal nitrides and carbides on substrates which are used in the fabrication of cutting tools. Here, we describe the preparation of a new single source zirconium nitride precursor, $[(CH_3)_3Si]_2NH{\cdot}ZrCl_4$ **I**. This precursor readily dissolves in dichloromethane opening up the opportunities to develop new applications.

## Experimental

All experiments were carried out in an inert atmosphere in a dry box or using standard vacuum line techniques. Dichloromethane was freshly distilled over phosphorus pentaoxide. Commercial zirconium tetrachloride and hexamethyldisilazane were used as received. Elemental analysis was carried out at Galbraith Laboratories.

The NMR spectra were recorded on a Bruker AC-200 instrument. Thermogravimetric analysis was carried out on a Perkin Elmer TA7 instrument. IR spectra of the samples were obtained on a Perkin Elmer FT2000 IR instrument. Simultaneous TGA–IR studies were carried out on a Perkin Elmer TA7 TGA coupled with a Perkin Elmer FT2000 IR instrument. Images and energy dispersive X-ray analyses were obtained using a Hitachi HF-2000 field emission transmission electron microscope equipped with a Noran ultra-thin-window detector system.

### Preparation of $[(CH_3)_3Si]_2NH{\cdot}ZrCl_4$, I

Hexamethyldisilazane (4.15 g, 25.7 mmol) was added to a suspension of zirconium tetrachloride (6.0 g 25.7 mmol) in *ca.* 50 ml dichloromethane. The reaction mixture was allowed to stir for 72 h to obtain an almost clear solution. The trace amount of insoluble material was filtered out and the filtrate was concentrated until a small amount of solid started to precipitate. The solution was stored at −20 °C and the crystals were isolated by removing the supernatant liquid with a syringe. The crystals were washed with *ca.* 10 ml cold dichloromethane and dried in vacuum. Elemental Anal. Calc. for $C_6Cl_4H_{19}NSi_2Zr$: C, 18.27; H, 4.86; N, 3.55. Found C, 17.05; H, 4.27; N, 3.93%. IR (KBr pellet, $cm^{-1}$): 3132m(br), $\nu$(NH); 2962ms, $\nu_{as}$(CH) of Me—Si—N; 2905w, $\nu_s$(CH) of Me—Si; 1523m, 1408m, $\delta_{as}$ (Me—Si); 1266s, $\delta_s$(C—Si) of Me—Si—N; 1153s, 1073s, 849s, $\rho$(C—Si) of MeSi; 760m and 742m, $\rho$(MeSi); 661, $\nu_{as}(SiC)_3$. $^1$H NMR ($CD_2Cl_2$): $\delta$ 0.45 (m).

### Pyrolysis of $[(CH_3)_3Si]_2NH{\cdot}ZrCl_4$, I

A 2.65 g sample of **I** was placed in a quartz tube and heated to 600 °C at a rate of 10 °C $min^{-1}$ under dynamic vacuum. After maintaining the sample at 600 °C for 2 h, a gray white residue (0.67 g) was collected. The sample was amorphous and sensitive to oxidation under ambient condition.

The pyrolysis of **I** (2.0 g) at 900 °C (10 °C $min^{-1}$, hold 2 h)

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under dynamic vacuum furnished a golden black residue (0.3 g). This residue contained <0.5% C, 2.0% Cl and 2.4% Si.

The pyrolysis of **I** (4.1 g) was also carried out in an ammonia atmosphere at 900 °C (10 °C min$^{-1}$, hold 2 h). The resulting golden brown solid (0.82 g) showed <0.5% C, 1.6% Cl and 2.6% Si.

The pyrolysis of **I** (2.0 g) at 1075 °C (10 °C min$^{-1}$, hold 2 h) furnished a golden powder (0.28 g) which did not exhibit silicon or chlorine in its energy dispersive spectra (EDS).

## Results and Discussion

Precursor, $[(CH_3)_3Si]_2NH{\cdot}ZrCl_4$ **I**, can be easily prepared by stirring a mixture of hexamethyldisilazane with zirconium tetrachloride in dichloromethane for 72 h [eqn. (1)]. After removing a small amount of insoluble materials, the compound can be recrystallized by storing the filtrate at −20 °C.

$$[(CH_3)_3Si]_2NH + ZrCl_4 \rightarrow \underset{\textbf{I}}{[(CH_3)_3Si]_2NH{\cdot}ZrCl_4} \qquad (1)$$

The crystals can be isolated by removing the liquor with a syringe and can be readily dissolved in dichloromethane. Upon drying in vacuum, the crystals turn into a powder suggesting that the solvent is part of the crystals. The dry powder has very poor solubility in deuterated dichloromethane and is thermally unstable at ambient temperatures which makes its structural characterization difficult. Polar solvents (*e.g.* THF) can not be used since they replace hexamethyldisilazane in **I**. The IR spectrum of this powder shows the expected absorptions for $(CH_3)_3Si$[12] and ZrCl[13] groups. The $^1H$ NMR spectrum shows a multiplet centered at $\delta$ 0.45 suggesting a complex structure. Efforts to grow single crystals of **I** were unsuccessful.

### Proposed decomposition pathway for $[(CH_3)_3Si]_2NH{\cdot}ZrCl_4$

The simultaneous TGA–IR analysis of **I** (Fig. 1) shows the weight loss during pyrolysis and the IR spectra of the evolved species. The sample for TGA–IR studies was heated at a rate of 40 °C min$^{-1}$ from 30 to 600 °C following an initialization delay (during which no data were recorded) of 1 min. It showed weight losses [Fig. 1(a)] of 30.0, 13.9 and 23.3% in the 30–190, 190–270 and 270–440 °C ranges, respectively. A gradual weight loss of 4% took place in the 440–600 °C range. Simultaneous IR spectral studies of the evolved species are shown in Fig. 1(b). The IR data show that the sample starts to eliminate trimethylchlorosilane immediately on heating and hydrogen chloride at 320 °C. The elimination of both species stops at 420 °C. These two species can account for the loss of 61.8 wt.%. Further weight reduction occurs with the loss of chlorine, which can not be identified by IR spectroscopy. Based on the TGA–IR data, the following decomposition pathway can be proposed [eqn. (2)–(4)]:

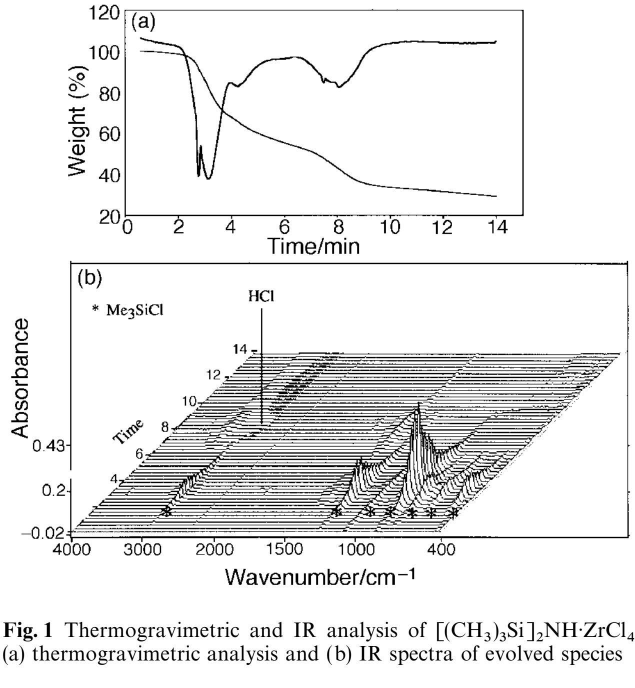

**Fig. 1** Thermogravimetric and IR analysis of $[(CH_3)_3Si]_2NH{\cdot}ZrCl_4$; (a) thermogravimetric analysis and (b) IR spectra of evolved species

$$[(CH_3)_3Si]_2NH{\cdot}ZrCL_4 \xrightarrow{-(CH_3)_3SiCl} (CH_3)_3SiNHZrCl_3 \qquad (2)$$

$$(CH_3)_3SiNHZrCl_3 \xrightarrow[-HCl]{-(CH_3)_3SiCl} NZrCl \qquad (3)$$

$$NZrCl \xrightarrow{-Cl} ZrN \qquad (4)$$

The elimination of trimethylchlorosilane in the first step of the decomposition of **I** requires a 27.4% weight loss [eqn. (2)] and the elimination of trimethylchlorosilane and hydrogen chloride in the second step requires a 36.4% weight loss [eqn. (3)]. A weight loss of 30% essentially consisting of trimethylchlorosilane is observed in the range 30–190 °C, suggesting that the elimination of the second equivalent of trimethylchlorosilane begins before the complete elimination of the first equivalent of trimethylchlorosilane. In the second step, a weight loss of 37.2% takes place in the temperature range 190–270 °C due to the loss of trimethylchlorosilane and hydrogen chloride and probably some chlorine. A total weight loss of 73.3% should occur for the complete conversion of **I** to zirconium nitride. Since a weight loss of 71% is observed, the sample contains some residual chlorine after heating at 600 °C [eqn. (4)].

### Thermal treatment of $[(CH_3)_3Si]_2NH{\cdot}ZrCl_4$

The pyrolysis of **I** was carried out in vacuum and in a dynamic ammonia atmosphere at 600, 900, and 1075 °C to find the optimum conditions to obtain zirconium nitride. Pyrolysis at 900 °C under a dynamic ammonia atmosphere does not seem to offer advantages over pyrolysis in a dynamic vacuum. Zirconium nitride samples obtained by pyrolysis under either of the two conditions contained silicon and chlorine and were susceptible to oxidation under ambient conditions. The zirconium nitride formed at 1075 °C in a dynamic vacuum does not show O, Si or Cl in its energy dispersive spectrum and does not oxidize under ambient conditions. The characterization of the zirconium nitride samples, prepared under different conditions, is presented below.

The gray–black powder, formed on the pyrolysis of **I** in a dynamic vacuum at 600 °C, does not show any diffraction peaks in its X-ray powder diffraction pattern (XRD) and is highly sensitive to atmospheric humidity.

The golden black powder, obtained at 900 °C in a dynamic vacuum from **I**, exhibits diffraction peaks corresponding to crystalline zirconium nitride (JCPDS no. 35–753). If the pyrolysis of **I** is carried out in a dynamic ammonia atmosphere at 900 °C, a light golden brown crystalline zirconium nitride (JCPDS no. 35–753) is obtained. This sample is comparable to the sample prepared in vacuum at 900 °C. Transmission electron microscopy of **I**, performed in a dynamic vacuum, shows that the material is comprised of particles of size 70–150 nm [Fig. 2(A)]. Each particle has a uniform coating which varies in thickness from 5 to 10 nm. The energy dispersive spectra (EDS) of particle coatings show only Zr and O, suggesting a pure oxide structure, whereas the core spectrum shows primarily Zr and N. The high resolution micrograph of a particle [Fig. 2(B)] shows lattice fringes, calculated by fast Fourier transform (FFT), within the coating corresponding to tetragonal $ZrO_2$ (111) (JCPDS no. 17–0923). The lattice is highly oriented, suggesting that the coating is essentially a single crystal over the core ZrN particle. The fringes seen at the outer edges of the coating were also observed to continue

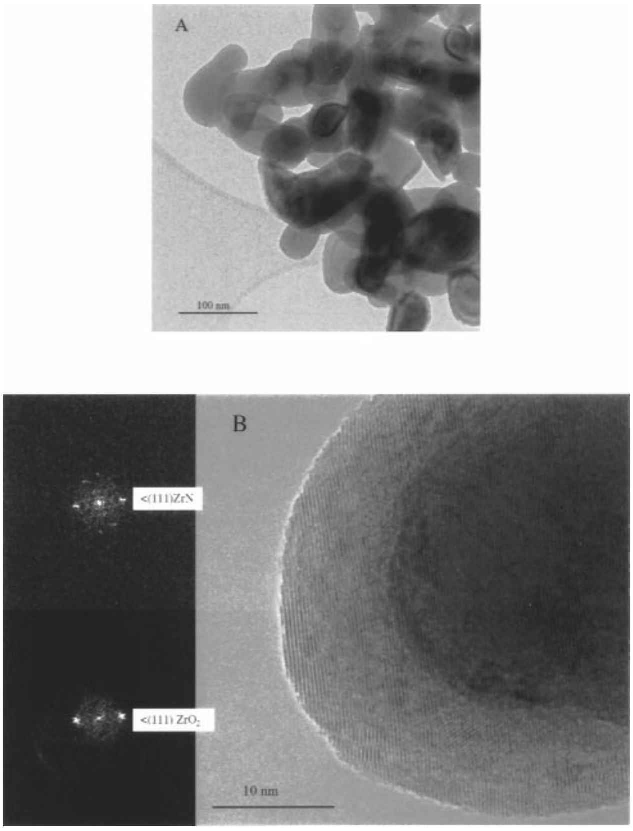

**Fig. 2** Transmission electrom micrographs of zirconium nitride prepared at 900 °C (A); the particle size is in the range 70–150 nm, (B) the lattice fringes correspond to (111) of $ZrO_2$

through the core particles structure, as shown in the FFT from the core (inset). This is further evidence that the coating is a single crystal on a given particle. Such a coating structure suggests a heterogeneous nucleation mechanism in which the oxide film either nucleated at a single point on the particle surface and grew epitactically from that point to form the complete film, or, alternatively, a uniform, amorphous coating subsequently crystallized heterogeneously to form the final single crystal structure observed. The FFT from the core also shows ZrN (111) periodicities. These data suggest that the samples prepared at 900 °C are susceptible to oxidation due probably to incomplete crystallization of zirconium nitride.

The gold colored powder, obtained from **I** at 1075 °C in a dynamic vacuum, shows sharp peaks at $2\theta = 33.94, 39.46, 56.98, 67.90, 71.35, 84.73°$ in its XRD pattern (Fig. 3) due to crystalline zirconium nitride. The lattice parameter, *a*, calculated from (111) and (200) is $4.567 \pm 0.0008$ Å which is close to that for stoichiometric zirconium nitride[14] (4.577 Å). In the film analysis, the formation of nitrogen-rich zirconium nitride has been identified by the increase in the lattice parameter calculated from the (111), (200) and (331) diffraction peaks.[15] The largest increase is seen in the lattice parameter ($a = 4.65$ Å) calculated from the (111) diffraction peak, which is generally the plane of orientation of the films. However, in bulk powders the stress of the film is not present and a somewhat smaller increase is expected. In our samples, the increase in the lattice parameter calculated from either (111) or (200) diffraction peaks is negligible, suggesting that our samples are stoichiometric zirconium nitride. The 1075 °C material is comprised of particles of size 30–150 nm [Fig. 4(A)] and the energy dispersive spectra from the particles show the presence of only zirconium and nitrogen. The high resolution micrograph of Fig. 4(B) shows lattice fringes corresponding to ZrN (111) as measured from FFT. These results suggest that sintering ZrN at 1075 °C stabilizes the material towards oxidation.

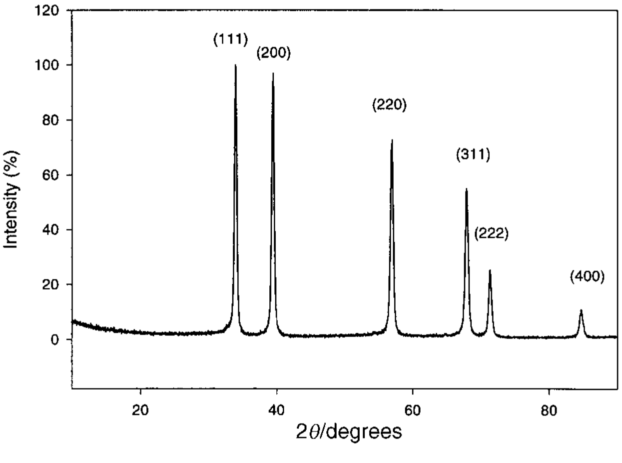

**Fig. 3** X-Ray powder diffraction (Cu-K$\alpha$ radiation) of the product of pyrolysis (*in vacuo*, 1075 °C) of $[(CH_3)_3Si]_2NH\cdot ZrCl_4$

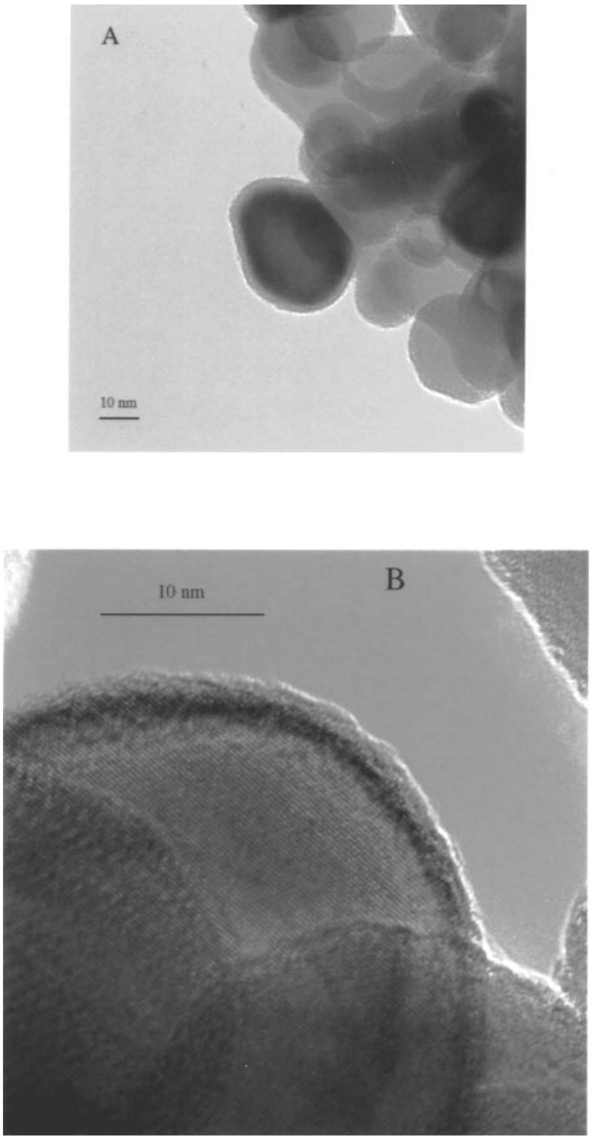

**Fig. 4** Transmission electron micrographs of zirconium nitride sintered at 1075 °C; (A) the particle size is in the range 30–150 nm, (B) the lattice fringes correspond to (111) of ZrN

## Conclusions

In conclusion, we have shown that $[(CH_3)_3Si]_2NH\cdot ZrCl_4$ **I** can be easily prepared from low cost starting materials. The

TGA–IR analysis of **I** shows that $Me_3SiCl$ and HCl are eliminated during pyrolysis. The zirconium nitride materials require sintering at 1075 °C since samples prepared below this temperature are susceptible to oxidation under ambient conditions. The solubility of **I** in dichloromethane opens up the possibility of new applications. The fabrication of thin films, metal–matrix composites, and ceramic–matrix composites employing this precursor is in progress and will be presented in a future paper.

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