Preparation of a Soluble Precursor by an Aminolysis Reaction of $Zr(NEt_2)_4$ and Its Pyrolytic Conversion into ZrN

Fei Cheng,[†] Yoshiyuki Sugahara,[*] [†] and Kazuyuki Kuroda[†,††]
[†]Department of Applied Chemistry, School of Science and Engineering, Waseda University, Ohkubo, Shinjuku-ku, Tokyo 169-8555
[††]Kagami Memorial Laboratory for Materials Science and Technology, Waseda University, Nishiwaseda, Shinjuku-ku, Tokyo 169-0051

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A novel soluble precursor with a Zr-N-Zr backbone structure was prepared by an aminolysis reaction of $Zr(NEt_2)_4$ with Pr^iNH_2. Pyrolysis of the precursor under NH_3-N_2 atmospheres led to the formation of ZrN as a main crystalline phase with a ceramic yield of 45.2%. Aggregated particles consisting of very minute particles with diameters of 50-300 nm were obtained.

Zirconium nitride (ZrN) exhibits beneficial properties, such as high melting point, hardness, excellent chemical durability and interesting optical properties.[1] Thin films of ZrN have been used for various applications, including wear-resistant coatings, diffusion barriers in integrated circuits and coating for solar control windows.[2-4] ZrN powders have been prepared commercially by direct nitridation of metallic zirconium and carbothermal reduction of ZrO_2 under nitrogen.[1] Chemical vapor deposition (CVD) process has been investigated for the preparation of ZrN films.[5]

Pyrolytic conversion of inorganic and organometallic compounds into non-oxide ceramics provides an alternative route for the preparation of films and fibers via liquid phase, but it is required that the precursors are soluble or fusible for such applications.[2,6] Extensive work has been reported on the preparation of carbides and nitrides of various main group elements, such as SiC, Si_3N_4, BN, and AlN by this chemical route.[2,6,7] This chemical route has also been developed for the preparation of transition metal nitrides.[2] Insoluble polymeric precursors with highly cross-linked structures were prepared by the ammonolysis of transition metal dialkylamides[8] or *via* an electrochemical route,[9] and were converted into transition metal nitrides *via* pyrolysis. Soluble precursors which were converted into TiN or Ti(N,C) powders, fibers and films *via* pyrolysis were prepared by the aminolysis of $Ti(NMe_2)_4$, since the formation of highly cross-linked structures was suppressed by the introduction of bulky organic groups into the precursors.[10-12] A soluble precursor which was converted into δ-NbN *via* pyrolysis was also prepared by an aminolysis reaction of $Nb(NEt_2)_4$.[13] Bartlett investigated the aminolysis reactions of $Zr(NEt_2)_4$ with excess primary alkylamines ($Zr(NEt_2)_4$:RNH_2=1:15, R=Bu, Pr, Et),[14] but the resultant polymeric products (proposed formula: $[Zr(NR)(NHR)_2]_n$) were insoluble in organic solvents. Only one soluble ZrN precursor $[(CH_3)_3Si]_2NH{\cdot}ZrCl_4$ was reported, but a corrosive HCl by-product evolved during the pyrolysis.[15]

Here we report the preparation of a precursor possessing a Zr-N-Zr backbone structure by an aminolysis reaction of tetrakis(diethylamino)zirconium ($Zr(NEt_2)_4$) with isopropylamine (Pr^iNH_2). Since isopropyl groups are branched, it is expected that the aminolysis reaction will lead to the formation of a soluble product. The precursor was pyrolyzed under NH_3-N_2 atmospheres, and the pyrolyzed product was characterized by compositional analysis, X-ray powder diffraction analysis (XRD), and scanning electron microscopy (SEM).

All the procedures were performed under a protective nitrogen atmosphere using the standard Schlenk technique[16] or a glove box filled with nitrogen. $Zr(NEt_2)_4$ was prepared and distilled (b.p. 120 °C at 0.1 mmHg) based on a previous report.[17] The IR and ^{1}H NMR data were consistent with previous reports for $Zr(NEt_2)_4$;[18] ^{1}H NMR (ppm): 1.11 (triplet, -CH_2CH_3), 3.34 (quadruplet, -CH_2CH_3); IR (cm^{-1}): 1000, 1152 ($\nu(NC_2)$), 550-578 (ν(Zr-N)). Elemental analysis exhibited an empirical formula of $ZrN_{4.3}C_{15.6}H_{40.2}$, which approximately corresponds to $Zr(NEt_2)_4$.

The precursor was prepared by the reaction of $Zr(NEt_2)_4$ with Pr^iNH_2 (Zr : Pr^iNH_2 = 1:5) according to an ideal reaction expressed by Eq. (1).

$$Zr(NEt_2)_4 + xPr^iNH_2 \rightarrow 1/n[Zr(NPr^i)_x(NEt_2)_{4-2x}]_n + 2xHNEt_2 \qquad (1)$$

$Zr(NEt_2)_4$ was dissolved in toluene in a three-neck flask, and Pr^iNH_2 in toluene was slowly dropped into the $Zr(NEt_2)_4$ solution at about 5 °C with stirring. The mixed solution was stirred for 2 h at about 5° C. Then the resultant solution was gradually heated, and finally refluxed for 16 h. An orange solid, which was soluble in benzene and toluene, was obtained after the separation of a small amount of insoluble yellow solid by filtration and removal of toluene under a reduced pressure.

The ^{1}H NMR spectra of the precursor, $Zr(NEt_2)_4$, and Pr^iNH_2 are shown in Figure 1. In the ^{1}H NMR spectrum of the precursor, a quadruplet at 3.34 ppm due to the -CH_2CH_3 of $Zr(NEt_2)_4$ is hardly detected, and many weak signals appear at 3.00-4.80 ppm. In the region for a triplet at 1.11 ppm (for $Zr(NEt_2)_4$) and a doublet at 0.90 ppm (for Pr^iNH_2), some doublets and unresolved peaks are observed at 1.12-1.86 ppm. The

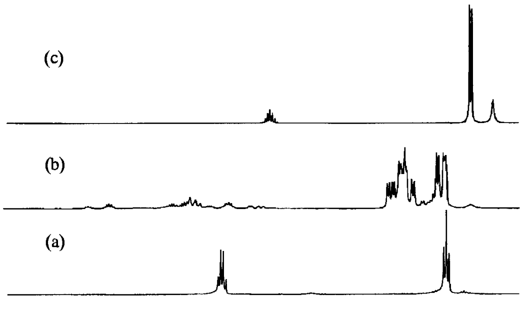

Figure 1. ^{1}H NMR spectra of (a) $Zr(NEt_2)_4$, (b) theprecursor, and (c) Pr^iNH_2 (C_6D_6, 270 MHz).

Table 1. Ceramic yield and characteristics of the product pyrolyzed under NH_3- N_2

Ceramic yield / mass%[a]	45.2
Elemental analysis / mass%	
Zr[b]	81.2
N[c]	11.6
C[c]	0.4
O[c]	3.1
Total	96.3
Empirical formula	$ZrN_{0.93}C_{0.03}O_{0.21}$
Lattice parameter / nm[d]	0.4576

[a] The ceramic yield (Y) was calculated from the masses of the precursor (M_p) and the pyrolyzed residue (M_r), $Y=(M_p/M_r)\times 100$. [b] The amount was determined by inductively coupled plasma emission spectroscopy. [c] The amounts were measured by using LECO TC-436 and CS-444LS instruments. [d] The lattice parameter was calculated by the non-linear least squared method.

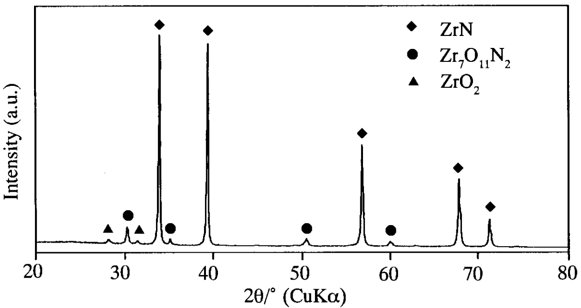

Figure 2. XRD pattern of the product pyrolyzed under NH_3-N_2.

integrated intensity ratio of the signals at 1.12–1.86 ppm to those at 3.00–4.80 ppm is about 6, corresponding to the proton number ratio of CH_3 to CH in the -$CH(CH_3)_2$ group. All of these observations indicate that the aminolysis reaction of $Zr(NEt_2)_4$ with Pr^iNH_2 occurs and isopropyl groups with various environments are present in the precursor. Since no ν(N-H) and δ(N-H) bands were observed in the IR spectrum of the precursor, it is reasonable to consider that the nitrogen atoms in the NPr^i groups of the precursor are mainly present as Zr-N(Pr^i)-Zr imido-bridges, which is different from the assumed environment of nitrogen in the polymeric compound $[Zr(NR)(NHR)_2]_n$ reported by Bartlett.[14] In addition, although the presence of Et groups can not be confirmed in the ^{1}H NMR spectrum of the precursor due to overlapping of signals, a week shoulder band assignable to $\nu_s(CH_2)$ mode of the ethyl groups at around 2829 cm^{-1} [19] was present in the IR spectrum obtained with a hexachloro-1,3-butadiene technique, suggesting that a small amount of NEt_2 groups remains in the precursor (The other three ν(C-H) bands due to ethyl groups show wavenumbers similar to those of isopropyl groups).

Pyrolysis of the precursor under NH_3 flow at 600 °C for 2 h and subsequently under N_2 at 1350 °C for 8 h gave a yellow-gray residue with a ceramic yield of 45.2%. The characteristics of the product are shown in Table 1. The amount of carbon is very small (0.4 mass%), while 3.1% of oxygen, which was probably introduced during the pyrolysis, are present in the product.

The pyrolysis of the precursor under NH_3-N_2 leads to the formation of a well-crystallized NaCl-type compound (Figure 2). However, some weak peaks assignable to $Zr_7O_{11}N_2$ and ZrO_2 are also observed,[20] which is consistent with the presence of oxygen in the product. It has been reported that ZrN, ZrC and ZrO all possess NaCl-type structures with the lattice parameters of 0.4577, 0.4693 and 0.4620 nm, respectively.[20] ZrN can form solid solution with ZrC,[21] and the formation of a Zr(N,C,O) solid solution with an NaCl-type structure was also reported.[22] However, the lattice parameter of the NaCl-type compound in the present study is 0.4576 nm, very close to that of ZrN, indicating that the crystallized NaCl-type compound should be cubic ZrN.

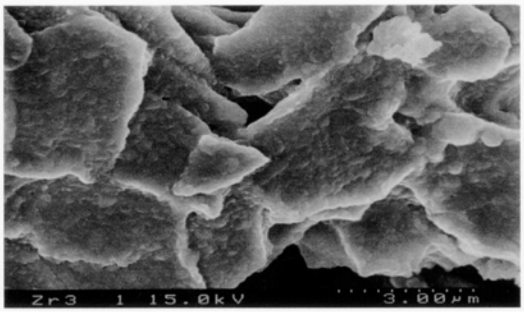

Figure 3. Scanning electron micrograph of the product pyrolyzed under NH_3-N_2.

The morphology of the product was investigated using SEM (Figure 3). Aggregated particles consisting of very minute particles with diameters of 50-300 nm are observed on the surface of the pyrolyzed product. The calculated mean crystallite diameter based on the XRD pattern using the Scherrer equation was 53 nm, consistent with the SEM observation.

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