Trialkoxysiloxy Complexes as Precursors to $MO_2 \cdot 4SiO_2$ (M = Ti, Zr, Hf) Materials

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Interest in low-temperature chemical routes to ceramic materials is based largely on the potential for generating metastable structures with unusual properties or on development of improved processing methods. The sol–gel method in particular has attracted attention as a low-temperature route to oxide materials.[1] This method can be extended to the synthesis of mixed-metal oxides; however, the formation of homogeneous materials can be complicated by differences in hydrolysis rates for the starting metal compounds.[2] Nonetheless, sol–gel processes have been utilized to produce (for example) TiO_2- or ZrO_2-containing silicates in the form of thin films, fibers, or monoliths.[3] Materials of this type find applications that take advantage of their optical properties, chemical inertness, high melting points, insulating properties, and fracture toughness.

We are investigating use of alkoxysiloxy transition-metal complexes as single source precursors to homogeneous metal silicate networks and here report preliminary results regarding low-temperature conversion of the compounds $M[OSi(O^tBu)_3]_4$ [M = Ti (1), Zr (2), Hf (3)] to $MO_2 \cdot 4SiO_2$ materials. As precursors to silicates, these compounds have the advantage that the transition metal and silicon atoms are initially bonded only to oxygen. Also, the *tert*-butoxy groups undergo thermal eliminations of isobutylene, which cleanly remove all the carbon as volatile material. Given the chemistry involved in the resulting condensation steps, silicate networks containing a homogeneous distribution of transition-metal ions are expected to form. Here we show that these reactions can be employed to cast thin films and to generate rather unusual microstructures. Hrncir has previously shown that zirconium and hafnium siloxides of the type $M(OSiR_3)_4$ (R_3 = Et_3, $Me_2{}^tBu$, Me_2Ph, $MePh_2$, Ph_3) decompose over a wide temperature range (350–600 °C) to give $Mo_2 \cdot 4SiO_2$ materials.[4]

Compound 1 was prepared by refluxing a toluene solution of $HOSi(O^tBu)_3$ (4 equiv) and $Ti(NEt_2)_4$ (1 equiv) for 4 h. Pure, crystalline 1 was obtained by cooling a pentane solution of the crude product to −78 °C. Compounds 2 and 3 were synthesized by addition of a pentane solution of $HOSi(O^tBu)_3$ (4 equiv) to a pentane solution of the appropriate amide complex $M(NEt_2)_4$ (1 equiv) at 0 °C. The resulting reaction mixture was allowed to warm to room temperature and stir for 6 h. Removal of all volatiles gave a white solid, which was crystallized from pentane at −40 °C. In benzene solution, 1 and 3 are monomeric whereas 2 exists as a dimer. Abe has previously reported a synthesis for 2 and has described titanium derivatives related to 1.[5,6] Compounds 1–3 undergo hydrolysis to liberate $HOSi(O^tBu)_3$ and produce metal oxide gels.

Thermal gravimetric analysis (TGA) curves for 1–3 (Figure 1) show precipitous weight losses corresponding to elimination of isobutylene and water.[7] Minimal de-

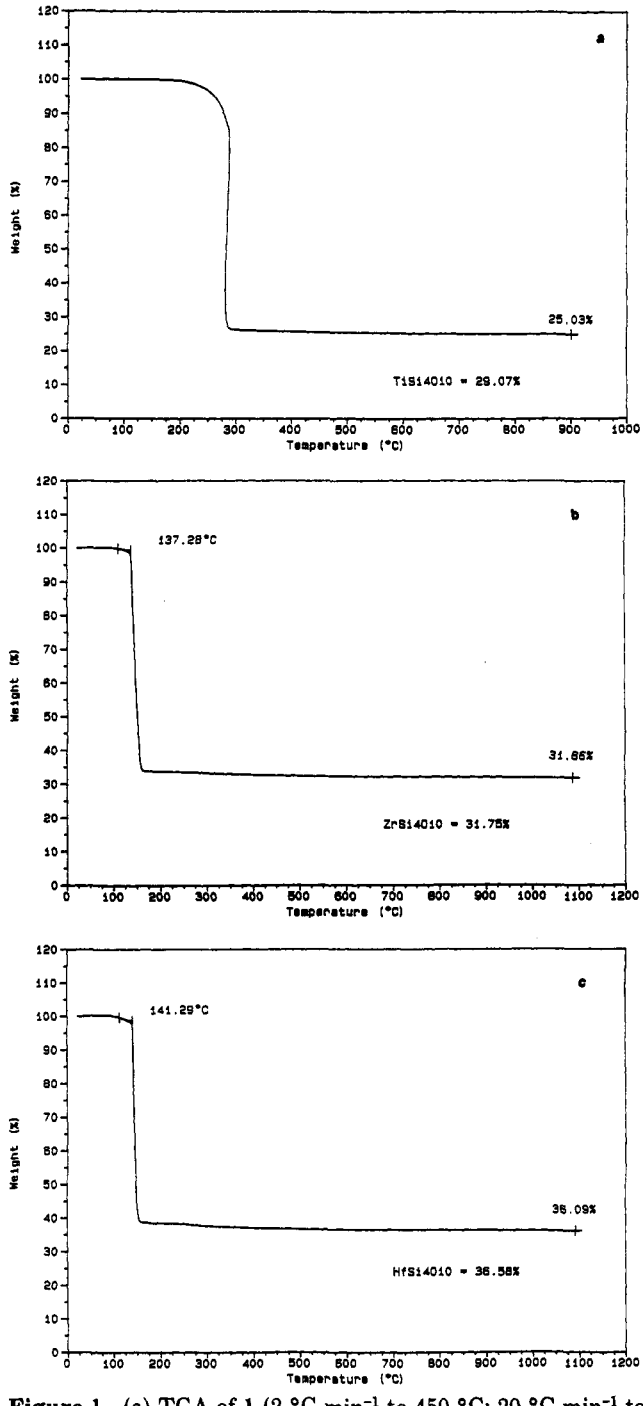

Figure 1. (a) TGA of 1 (2 °C min^{-1} to 450 °C; 20 °C min^{-1} to 900 °C). (b) TGA of 2 (2 °C min^{-1} to 200 °C; 20 °C min^{-1} to 1100 °C). (c) TGA of 3 (2 °C min^{-1} to 200 °C; 20 °C min^{-1} to 1100 °C).

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(6) Abe, Y.; Kijima, I. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 466.

(7) Thermal analyses were obtained with a Du Pont Model 2000 system.

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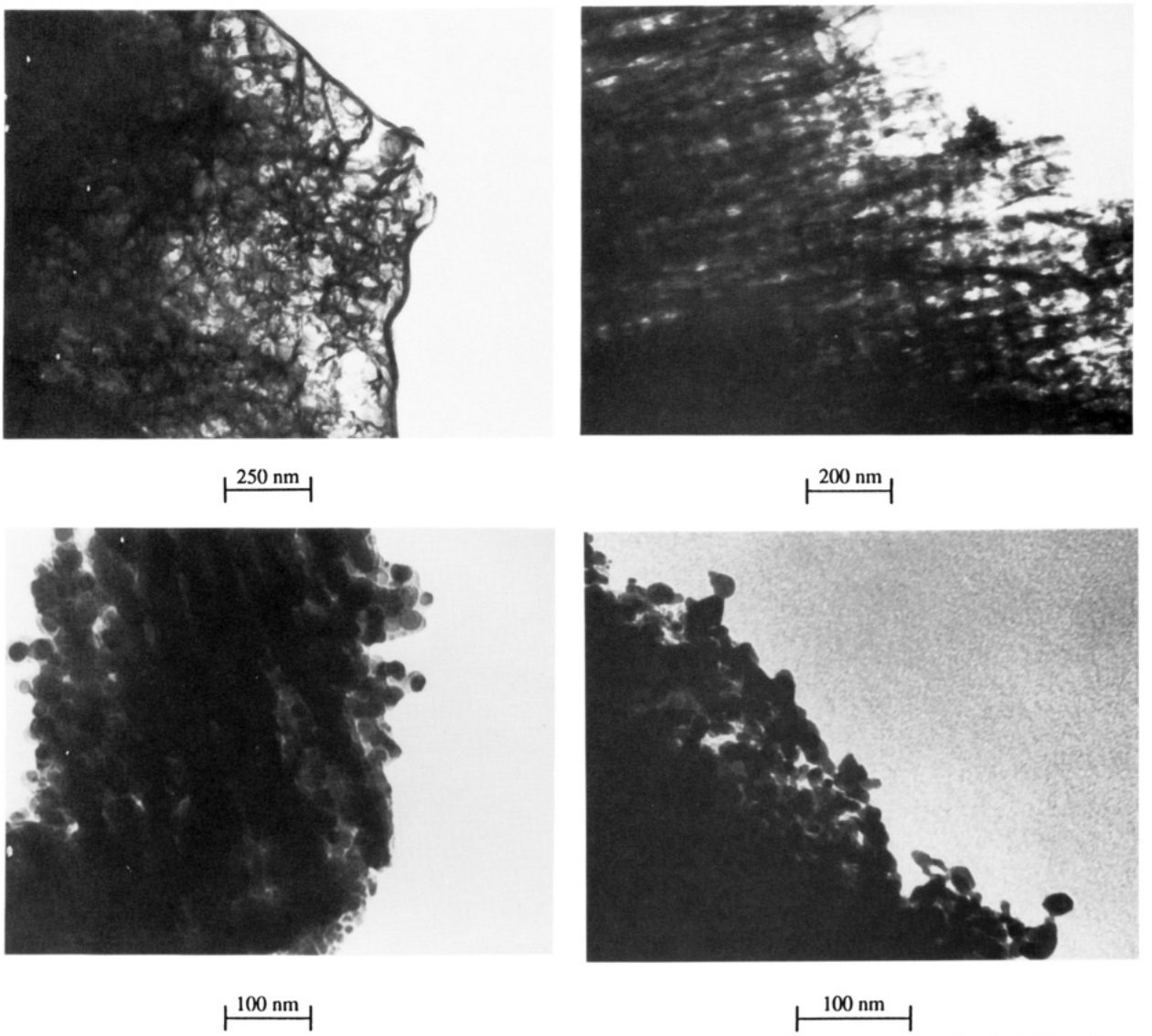

Figure 2. TEM micrographs of material from decomposed **2** and **3**. (a) $ZrO_2 \cdot 4SiO_2$ heated to 400 °C (2 h, O_2). (b) $ZrO_2 \cdot 4SiO_2$ heated to 800 °C (4 h, O_2). (c) $ZrO_2 \cdot 4SiO_2$ heated to 1200 °C (4 h, O_2). (d) $HfO_2 \cdot 4SiO_2$ heated to 400 °C (2 h, O_2).

hydration continues slowly thereafter, until a constant weight corresponding to quantitative formation of $MO_2 \cdot 4SiO_2$ is established. These thermolyses occur at remarkably low temperatures, particularly for **2** and **3**, which exhibit onset temperatures of 137 and 141 °C, respectively. The higher temperature required for decomposition of **1** may result from greater steric crowding about the smaller titanium center, which could restrict the molecular motion required for decomposition. The volatile products of thermolysis of **2** at 190–200 °C (5 min) were collected by vacuum transfer and identified as isobutylene (11.7 equiv/Zr), water (5.4 equiv/Zr), and *tert*-butyl alcohol (trace). This stoichiometry is approximately represented by eq 1.

$$\tfrac{1}{2}\{Zr[OSi(O^tBu)_3]_4\}_2 \xrightarrow[190\text{–}200\ °C]{10^{-3}\ mmHg} ZrO_2 \cdot 4SiO_2 + 12CH_2{=}CMe_2 + 6H_2O + {}^tBuOH\ (trace) \quad (1)$$

Crystallizations and phase transformations were followed by X-ray powder diffraction (XRD), differential thermal analysis (DTA), and electron microscopy. The $ZrO_2 \cdot 4SiO_2$ system has been examined in greatest detail. Surprisingly, crystals of **2** retain their shape and morphology (in going from transparent to opaque) after decomposition at 1200 °C, with very little shrinkage (≤10%). Samples of $ZrO_2 \cdot 4SiO_2$ are amorphous to 1100 °C (by XRD), and an exothermic process at 1150–1400 °C (observed by DTA) corresponds to crystallization of finely dispersed tetragonal zirconia (t-ZrO_2). Heating $ZrO_2 \cdot 4SiO_2$ to 1500 °C for 6 h under argon produces a mixture of monoclinic zirconia (m-ZrO_2), t-ZrO_2 (1:5 ratio), and cristobalite.[8] Rapid quenching of $ZrO_2 \cdot 4SiO_2$ from 1500 to 0 °C gave a material for which the ratio of m-ZrO_2 to t-ZrO_2 was maintained.

Transmission electron micrographs (TEMs) of samples of **2** decomposed at 400 °C (2 h in an O_2 flow) reveal a fibrous structure (Figure 2a), which is characterized by a surface area of 118 $m^2\ g^{-1}$ (BET method). Further heating to 800 °C (4 h, O_2) produces an ordered, interpenetrating network of thin fibers (Figure 2b) and a surface area of 82 $m^2\ g^{-1}$. The crystallization of zirconia at 1200 °C (4 h, O_2) is apparent in TEM photographs (Figure 2c), which show small crystallites (6–21 nm) embedded in an amorphous silica matrix. The sintering that results from the latter thermal treatment reduces the surface area to 36 $m^2\ g^{-1}$.

Whereas the thermolysis chemistry of **2** and **3** appears to be quite similar, there are significant differences in the materials that are generated. The $HfO_2 \cdot 4SiO_2$ material

(8) $MO_2 \cdot 4SiO_2$ samples were quenched in air to room temperature unless otherwise noted.

Figure 3. SEM micrograph of $ZrO_2 \cdot 4SiO_2$ thin film spun onto quartz from a 1% solution of **2** in benzene.

produced at 400 °C (2 h, O_2) is composed of 8–32-nm particles (Figure 2d). In samples heated to 1000 °C, t-HfO_2 (or cubic hafnia, c-HfO_2) is present, and samples taken to 1460 °C contain t-HfO_2 (or c-HfO_2), m-HfO_2 (in roughly equal amounts), and cristobalite.

Heating **1** to 400 °C results in amorphous $TiO_2 \cdot 4SiO_2$, from which finely dispersed anatase crystallizes at 1000 °C (by XRD). Samples taken to 1400 °C contain anatase, rutile, and cristobalite.

The low temperatures at which **2** and **3** thermally decompose allow for the convenient formation of silicate networks in solution. Refluxing **2** in xylenes for 10 h produces viscous, nearly transparent fluids and small amounts of particulate matter. Removal of the volatiles in vacuo leaves a white, amorphous $ZrSi_4O_x(OH)_y$ powder that has a BET surface area of 520 $m^2\ g^{-1}$, and looses 27% of its weight when heated to 1150 °C (by TGA). This powder is composed of ca. 0.1–3-μm agglomerates (by scanning electron microscopy) made from smaller, nonspherical 30–70 nm particles (by TEM). The dehydration of $ZrSi_4O_x(OH)_y$ was monitored by ^{29}Si NMR spectroscopy of the isolated powder (dried in vacuo), which revealed a very broak peak which moved from −99 to −110 ppm as the sample was heated from 25 to 1200 °C. Annealing this material at 1200 °C (4 h, O_2) results in a significant reduction of the surface area to ca. 3 $m^2\ g^{-1}$. At higher temperatures, the same crystallization behavior described above for $ZrO_2 \cdot 4SiO_2$ is observed.

Hydrocarbon solutions of **2** and **3** have been used to cast thin films of $ZrO_2 \cdot 4SiO_2$ and $HfO_2 \cdot 4SiO_2$ onto quartz. For example, a 1% solution of **2** in benzene was spun onto a quartz disk, and the disk was then heated to 400 °C under O_2 for 30 min. Examination of the resulting film by SEM (Figure 3) revealed a smooth, crack-free surface. Similar $HfO_2 \cdot 4SiO_2$ films prepared from a 1% solution of **3** in cyclopentanone have thicknesses ranging from 70–90 nm (Dektak 3030 profilometer).

In conclusion, the chemical thermolyses described here represent an alternative approach to the synthesis of nanocomposite silicate materials. The solid-state conversions can produce porous ceramic materials with ordered microstructures. Further investigations are in progress to probe the possibility that formation of ordered microstructures may be controlled via directionality imposed on the condensation process by the crystalline lattice of the precursor compound. The chemistry involved in this process can be applied to sol–gel-like processes in nonpolar media and should allow the homogeneous incorporation of a wide variety of dopants (e.g., polymers or additional metal ions). We are currently investigating the use of the gellike $[MSi_4O_x(OH)_y]_z$ solutions for fashioning films, fibers, and monoliths.

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Photoimaging of Electronically Conducting Polymeric Networks[1]

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Introduction

It is widely recognized that advances in polymer chemistry have played a pivotal role in the development of integrated circuitry. Of particular note are the advances in photolithography which have been achieved by designing high-resolution polymer photoresists for patterning semiconductors, metals, and insulators.[2,3] Polymer photoresists are chosen to exhibit the following properties: good adhesion, high thermal stability, desirable dissolution characteristics, and sensitivity to high-energy irradiation. In the majority of cases, there is little consideration of intrinsic electronic properties exhibited by the resist because it usually plays no role in device operation. In cases where the resist is an integral component of the chip, such as in multichip modules, it is chosen to have electronically insulating properties.[4]

π-Conjugated polymers are under intense investigation because of their semiconductor properties and nonlinear optical activity in the neutral state and their high electronic conductivity in the partially oxidized state. These polymers suffer from long-term stability in the oxidized state which might limit their usefulness. However, one can envisage their application in microelectronic devices where protection from the environment by encapsulation is a mature science and is critical to the stability of a device. A possible application of these materials is the formation of interconnects or channels of defined resistivity for microchips and printed circuitry. This requires their deposition in the form of thin highly defined channels. Several reports which address this challenge have appeared

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