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The thermal analysis system and tube furnace purchased on this grant have been used to conduct initial studies on the conversion of alkoxysiloxy derivatives to metal silicate solid state materials. These results, pertaining to titanium, zirconium, and hafnium, are described.

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DURIP Synthesis and Study of Preceramic Polymers/Ceramic Precursors, Metal Silicides, and Polymers with Unique Optical and Electronic Properties

Final Technical Report

The thermal analysis system and tube furnace purchased on this grant have been used to conduct initial studies on the conversion of alkoxysiloxy derivatives to metal silicate solid state materials. These results, pertaining to titanium, zirconium, and hafnium, are described below.

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.<sup>1</sup> 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.<sup>2</sup> Nonetheless, sol-gel processes have been utilized to produce (for example) TiO<sub>2</sub>- or ZrO<sub>2</sub>-containing silicates in the form of thin films, fibers, or monoliths.<sup>3</sup> 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 (alkoxy)siloxy 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<sup>t</sup>Bu)<sub>3</sub>]<sub>4</sub> [M = Ti (1), Zr (2), Hf (3)] to MO<sub>2</sub>·4SiO<sub>2</sub> materials. As siloxide 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 elimination of isobutylene, which cleanly remove all the carbon as volatile material. Given the chemistry involved in the resulting condensation steps, silicate

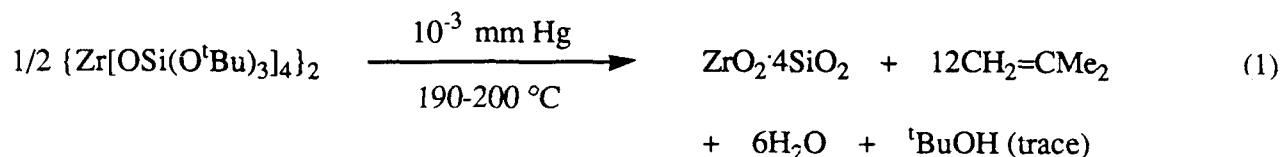
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networks containing a homogeneous distribution of transition metal ions are expected to form. Here we show that these reactions can be employed to cast thin films, and to generate rather unusual microstructures. Hrnair has previously shown that zirconium 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.<sup>4</sup>

Crystalline, pentane-soluble 1-3 were prepared by reactions of the appropriate amido derivatives,  $M(NEt_2)_4$ , with 4 equivalents of  $HOSi(O^tBu)_3$  in pentane. 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. 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.<sup>7</sup> Minimal dehydration 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 equivalents/Zr), water (5.4 equivalents/Zr), and *tert*-butanol (trace). This stoichiometry is approximately represented by equation 1.

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Crystallizations and phase transformations were followed by X-ray powder diffraction (XRD), differential thermal analysis (DTA), and electron microscopy. The  $\text{ZrO}_2 \cdot 4\text{SiO}_2$  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  $1200\text{ }^\circ\text{C}$ , with very little shrinkage ( $\leq 10\%$ ). Samples of  $\text{ZrO}_2 \cdot 4\text{SiO}_2$  are amorphous to  $1100\text{ }^\circ\text{C}$  (by XRD), and an exothermic process at  $1150\text{--}1400\text{ }^\circ\text{C}$  (observed by DTA) corresponds to crystallization of finely dispersed t- $\text{ZrO}_2$ . Heating  $\text{ZrO}_2 \cdot 4\text{SiO}_2$  to  $1500\text{ }^\circ\text{C}$  for 6 h under argon produces a mixture of m- $\text{ZrO}_2$ , t- $\text{ZrO}_2$  (1:5 ratio), and cristobalite.<sup>8</sup> Rapid quenching of  $\text{ZrO}_2 \cdot 4\text{SiO}_2$  from  $1500\text{ }^\circ\text{C}$  to  $0\text{ }^\circ\text{C}$  gave a material for which the ratio of m- $\text{ZrO}_2$  to t- $\text{ZrO}_2$  was maintained.

Transmission electron micrographs (TEM's) of samples of **2** decomposed at  $400\text{ }^\circ\text{C}$  (2 h in an  $\text{O}_2$  flow) reveal a fibrous structure (Figure 2a), which is characterized by a surface area of  $118\text{ m}^2\text{ g}^{-1}$  (BET method). Further heating to  $800\text{ }^\circ\text{C}$  (4 h,  $\text{O}_2$ ) produces an ordered, interpenetrating network of thin fibers (Figure 2b), and a surface area of  $82\text{ m}^2\text{ g}^{-1}$ . The crystallization of zirconia at  $1200\text{ }^\circ\text{C}$  (4 h,  $\text{O}_2$ ) 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  $36\text{ m}^2\text{ g}^{-1}$ .

Whereas the thermolysis chemistry of **3** and **4** appears to be quite similar, there are significant differences in the materials that are generated. The  $\text{HfO}_2 \cdot 4\text{SiO}_2$  material produced at  $400\text{ }^\circ\text{C}$  (2 h,  $\text{O}_2$ ) is composed of 8-32 nm particles (Figure 2d). In samples heated to  $1000\text{ }^\circ\text{C}$ , t- $\text{HfO}_2$  (or c- $\text{HfO}_2$ ) is present, and samples taken to  $1460\text{ }^\circ\text{C}$  contain t- $\text{HfO}_2$  (or c- $\text{HfO}_2$ ), m- $\text{HfO}_2$  (in roughly equal amounts), and cristobalite.

Heating **1** to 400 °C results in amorphous  $\text{TiO}_2 \cdot 4\text{SiO}_2$ , 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 formation of the silicate networks to be conveniently be carried out 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  $\text{ZrSi}_4\text{O}_x(\text{OH})_y$  powder that has a BET surface area of  $520 \text{ m}^2 \text{ g}^{-1}$ , and loses 27% of its weight when heated to 1150 °C (by TGA). This powder is composed of ca. 0.1-3  $\mu\text{m}$  agglomerates (by scanning electron microscopy) made from smaller, non-spherical 30-70 nm particles (by TEM). The dehydration of  $\text{ZrSi}_4\text{O}_x(\text{OH})_y$  was monitored by  $^{29}\text{Si}$  NMR spectroscopy of the isolated powder (dried in vacuo), which revealed a very broad 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,  $\text{O}_2$ ) results in a significant reduction of the surface area to ca.  $3 \text{ m}^2 \text{ g}^{-1}$ . At higher temperatures, the same crystallization behavior described above for  $\text{ZrO}_2 \cdot 4\text{SiO}_2$  is observed.

Hydrocarbon solutions of **2** and **3** have been used to cast thin films of  $\text{ZrO}_2 \cdot 4\text{SiO}_2$  and  $\text{HfO}_2 \cdot 4\text{SiO}_2$  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  $\text{O}_2$  for 30 min. Examination of the resulting film by SEM (Figure 3) revealed a smooth, crack-free surface. Similar  $\text{HfO}_2 \cdot 4\text{SiO}_2$  films prepared from a 1% solution of **3** in cyclopentanone have thicknesses ranging from 70 to 90 nm (Dektak 3030 profilometer).

In conclusion, the chemical thermolyses described here represent an alternative approach to the synthesis of silicate materials. The solid state conversions produce porous ceramic materials that can have ordered microstructures. Continuing investigations are attempting to probe the

possibility that formation of such 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 non-polar 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 gel-like  $[\text{MSi}_4\text{O}_x(\text{OH})_y]_z$  solutions for fashioning films, fibers and monoliths.

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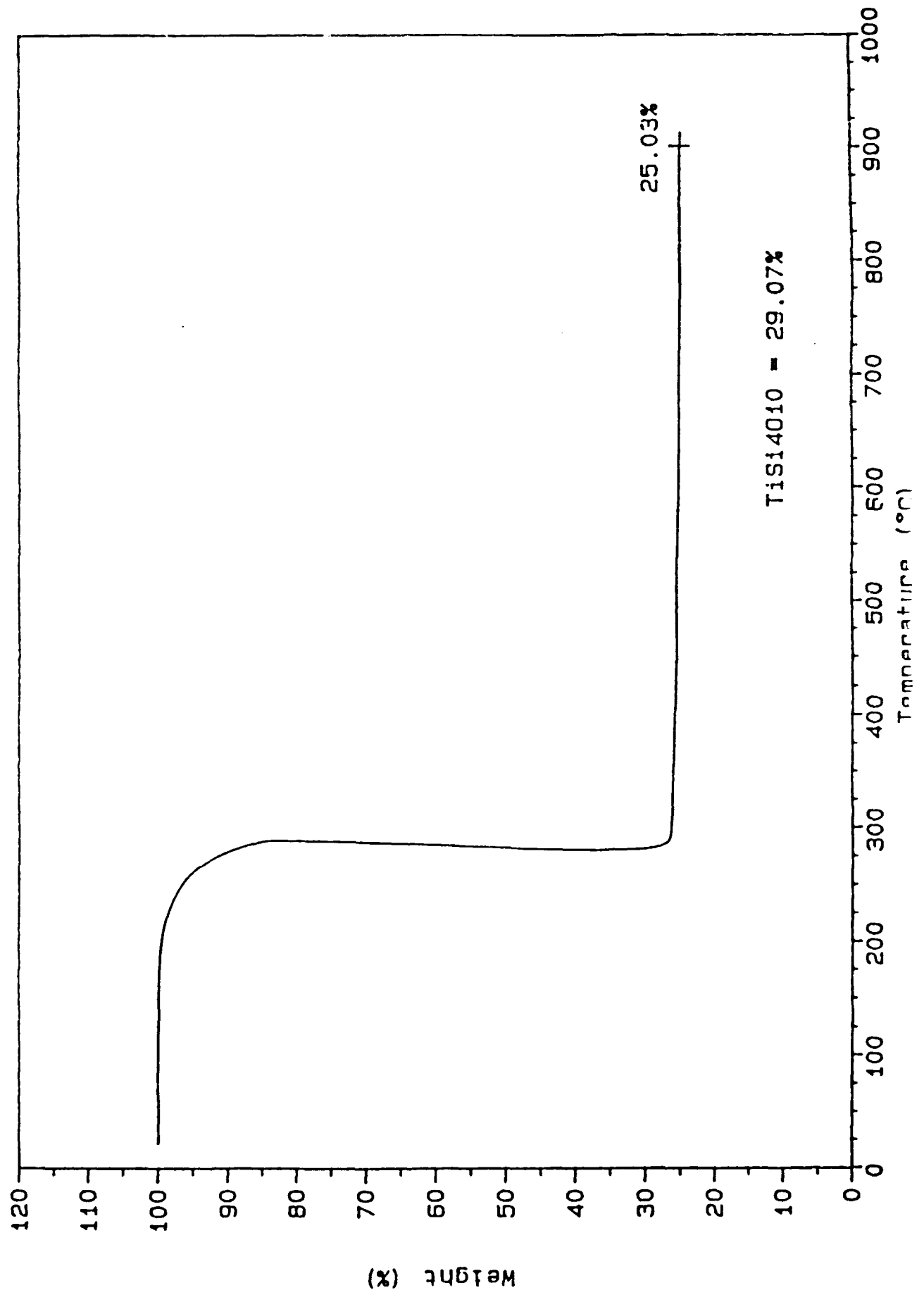
- 1 See for example: *Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronics, and Specialty Shapes*, edited by L. C. Klein (Noyes Publications, Park Ridge, New Jersey, 1988); D. R. Ulrich, in *Transformation of Organometallics into Common and Exotic Materials: Design and Activation*, NATO ASI Series E: Appl. Sci. No 141, edited by R. M. Laine (Martinus Nijhoff Publishers, Amsterdam, 1988), p. 103; H. Schmidt, *J. Non-Cryst. Solids* **100**, 51 (1988).
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- 6 Y. Abe and I. Kijima, *Bull. Chem. Soc. Japan* **43**, 466 (1970).
- 7 Thermal analyses were obtained with a Du Pont Model 2000 system.
- 8  $\text{MO}_2\cdot 4\text{SiO}_2$  samples were quenched in air to room temperature unless otherwise noted.

### Figure Captions

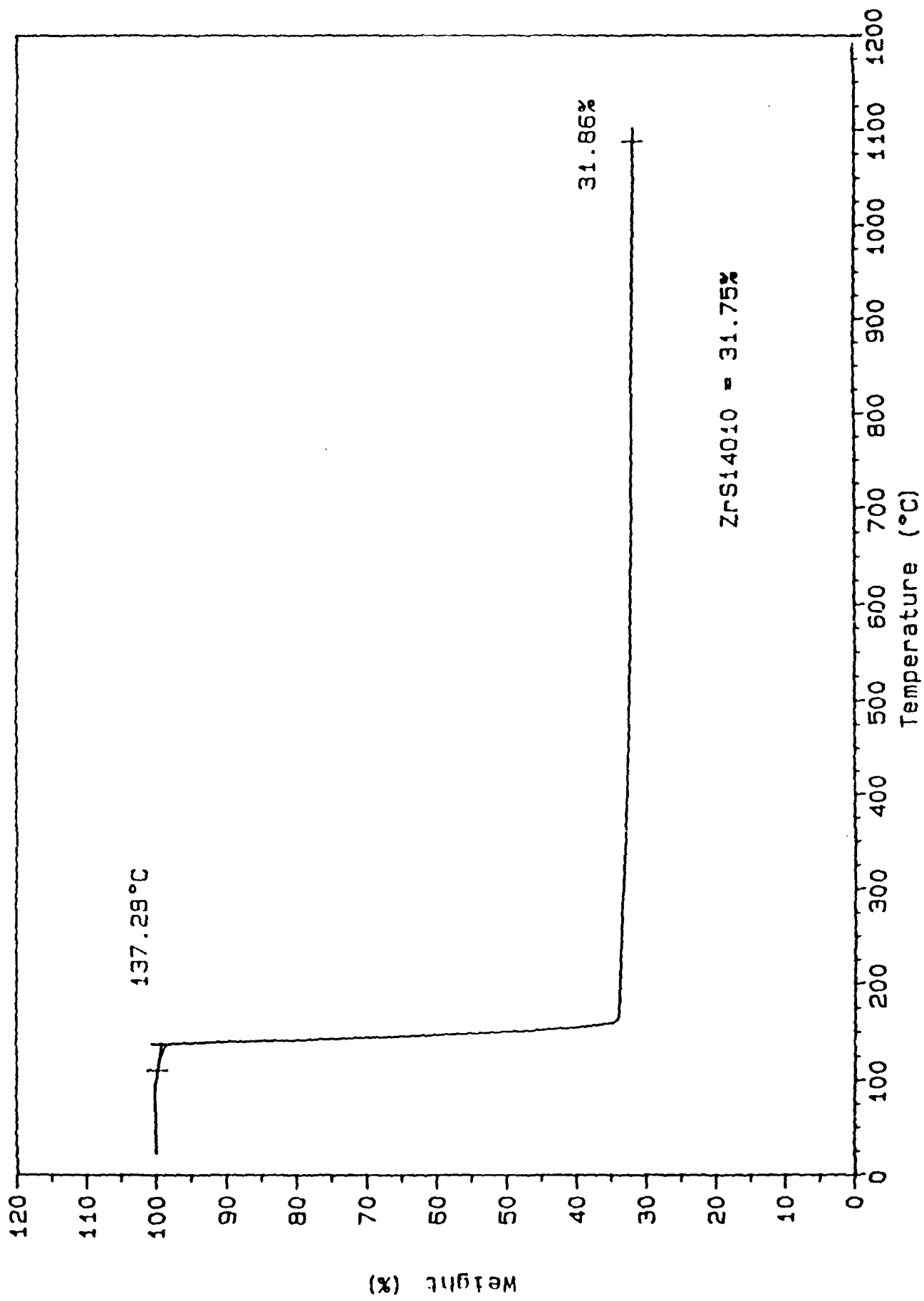
**Figure 1.** (a) TGA of **1** ( $2\text{ }^{\circ}\text{C min}^{-1}$  to  $450\text{ }^{\circ}\text{C}$ ;  $20\text{ }^{\circ}\text{C min}^{-1}$  to  $900\text{ }^{\circ}\text{C}$ ). (b) TGA of **2** ( $2\text{ }^{\circ}\text{C min}^{-1}$  to  $200\text{ }^{\circ}\text{C}$ ;  $20\text{ }^{\circ}\text{C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

**Figure 2.** TEM micrographs of material from decomposed **2** and **3**. (a)  $\text{ZrO}_2\cdot 4\text{SiO}_2$  heated to  $400\text{ }^{\circ}\text{C}$  (2 h,  $\text{O}_2$ ). (b)  $\text{ZrO}_2\cdot 4\text{SiO}_2$  heated to  $800\text{ }^{\circ}\text{C}$  (4 h,  $\text{O}_2$ ). (c)  $\text{ZrO}_2\cdot 4\text{SiO}_2$  heated to  $1200\text{ }^{\circ}\text{C}$  (4 h,  $\text{O}_2$ ). (d)  $\text{HfO}_2\cdot 4\text{SiO}_2$  heated to  $400\text{ }^{\circ}\text{C}$  (2 h,  $\text{O}_2$ ).

**Figure 3.** SEM micrograph of  $\text{ZrO}_2\cdot 4\text{SiO}_2$  thin film spun onto quartz from a 1% solution of **2** in benzene.







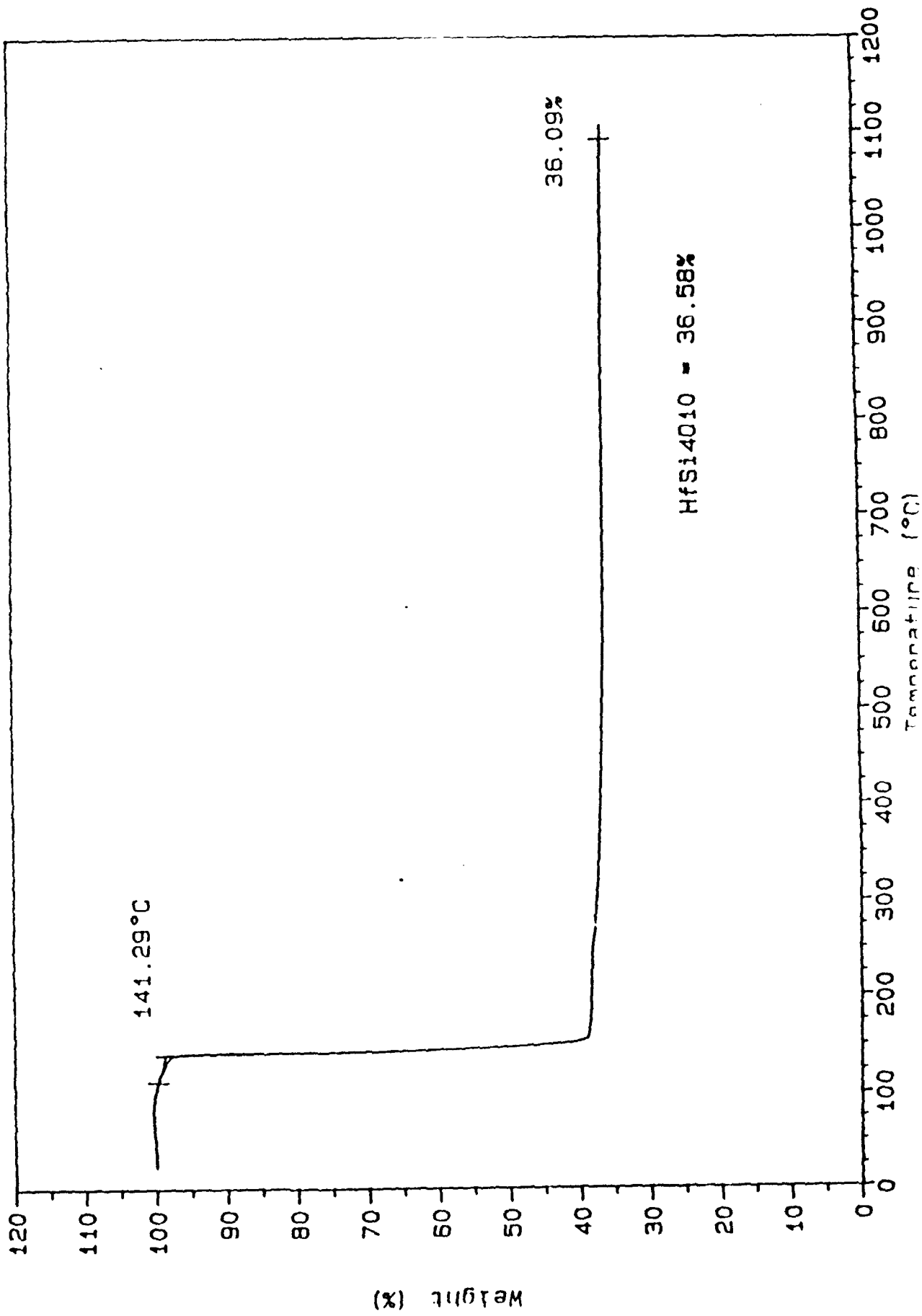
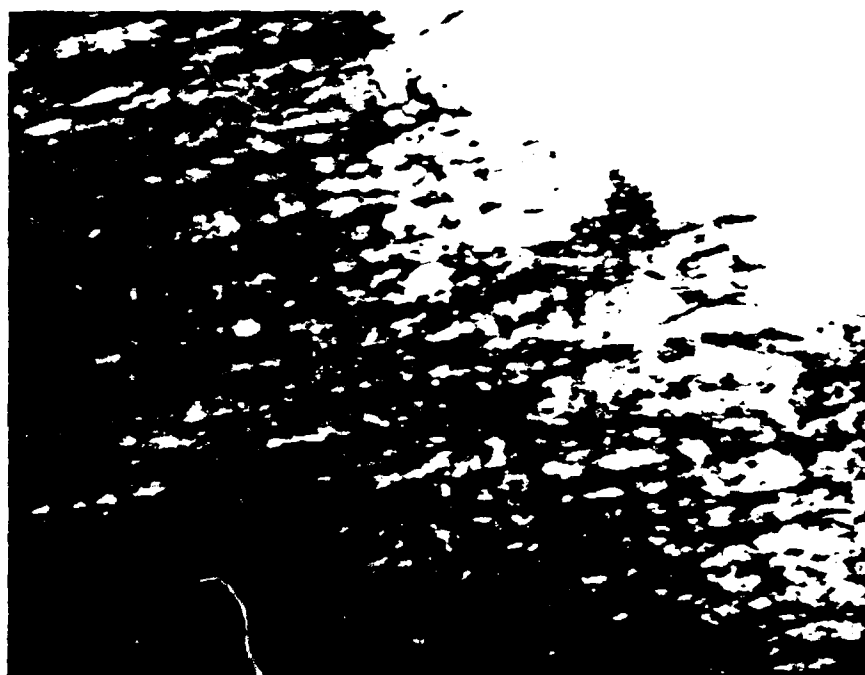


Figure 2a



250 nm

Figure 2b



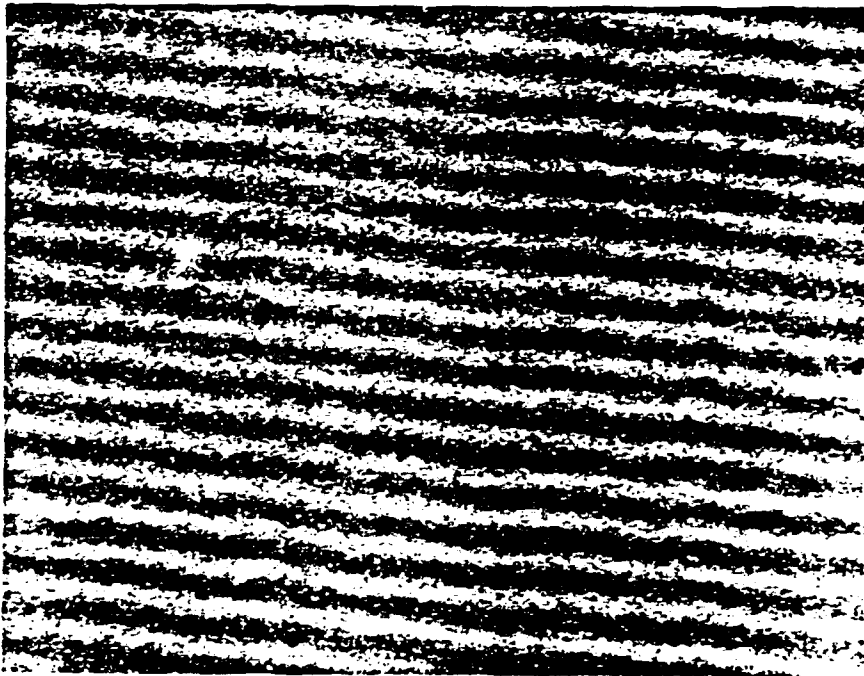
200 nm

Figure 2c



100 nm

Figure 3



300 nm