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Wet-chemical synthesis of zirconium oxyfluoride

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Zirconium oxyfluoride is used as a catalyst on alumina to produce chlorinated hydrocarbons [1], as a coating material for planar optical waveguides [2], and as an inorganic pigment to produce a pink or purple color in ceramic materials [3]. One reason it is not more widely used is because zirconium oxyfluoride is difficult to produce. It has been deposited by ion-beam techniques [4] and by using hydrogen fluoride gas [5–7]. The former method involves precision vacuum equipment and gases not amenable to high production rates, while the latter involves gases that are highly corrosive and caustic. To overcome these limitations, a less expensive and more environmentally friendly method for producing zirconium oxyfluoride is desired to expand its usefulness.

In this letter, we describe a wet-chemical technique for synthesizing zirconium oxyfluoride. We started by making a zirconium oxyfluoride precursor in solution and driving off the solvent. To form a coating, the dried powder was mixed in a different solvent to make a coating solution. The solution was deposited onto a substrate by dipping or spinning. In order to trap fluorine in the coating, it was fired rapidly with a scanned laser beam. Development of the precursor solutions was monitored by differential scanning calorimetry (DSC) and nuclear magnetic resonance (NMR) spectroscopy. Coating composition was examined by scanning Auger microscopy (SAM) and X-ray diffraction (XRD).

The zirconium oxyfluoride precursor was made by dissolving zirconium acetate in an excess of trifluoroacetic acid (TFA). The solution was refluxed for several hours to assure complete exchange of the acetate ligands for trifluoroacetate ligands. After the solution was cooled to room temperature, excess TFA and the acetic acid formed from the exchange reaction was removed under vacuum. The remaining zirconium trifluoroacetate powder was dissolved in methanol to produce a coating solution. Coatings were deposited typically by spinning onto silicon wafers and quartz windows at 3000 rpm for 30 s. The coating solution was passed through a 0.2 micron filter before deposition.

The wet gel coatings were dried at 100 °C for 15 min. Some coatings were fired in a furnace under air, flowing nitrogen, flowing sulfur hexafluoride (400 cm^3/min) in nitrogen gas, or forming gas (3.5% H_2/Ar). Filtered dry nitrogen was used for an inert atmosphere. Sulfur hexafluoride was added as a non-corrosive fluorinating agent. Forming gas was used to produce an inert reducing atmosphere. All of these atmospheres were employed to prevent complete oxidation of the zirconium. Firing temperatures were 400 and 600 °C with a heating rate of 10 °C/min. Before firing, samples were placed in a tube furnace which was sealed, evacuated and purged (3×) with the process gas. After the firing cycle, samples were allowed to cool in the sealed furnace under the flowing process gas.

Other coatings were fired with a scanned carbon dioxide laser, which produced localized surface heating due to absorption of the radiation by the coating/substrate [8, 9]. The primary difference between furnace-firing and laser-firing is that heating occurs in milliseconds with the laser as opposed to minutes [10–12]. Typical laser firing parameters were 2.0 W (continuous mode) and 2.5 cm/s scan speed with a 430 micron beam diameter ($1/e^2$). Using the laser heating modeling in Ref. [12], these parameters produced a peak temperature of 560 °C, with a duration of 40 ms above 280 °C.

In synthesizing the zirconium oxyfluoride precursor, trifluoroacetate completely replaced the acetate ligands on the zirconium ions. After the reacted solution was dried and dissolved in a deuterated solvent, ^{19}F NMR revealed a—76.51 ppm shift due to the CF_3 group (Fig. 1), where pure trifluoroacetic acid produced a shift of—76.57 ppm. Using ^{1}H NMR, no protons were found in the zirconium trifluoroacetate solution except for those associated with the 99.5% $CDCl_3$ solvent (7.24 ppm), indicating that no acetate ligands remained. The replacement of acetate ligands with trifluoroacetate was important since it was the source of fluorine for the zirconium oxyfluoride coatings.

Upon heating the dried zirconium trifluoroacetate powder to 600 °C at 10 °C/min under nitrogen, two exothermic peaks were produced (Fig. 2). The first, at 300 °C, coincided with a large loss in weight of the sample. This exotherm was attributed to the burnout of organic species. The second and smaller peak at 450 °C was assigned to crystallization of the material.

Different firing temperatures and atmospheres were employed to vary the balance of fluorine and oxygen in the fired material. According to XRD, none of the coatings fired in the furnace, regardless of atmosphere, were fluorinated. Even at temperatures as low as 400 °C, all of the coatings were tetragonal zirconium dioxide

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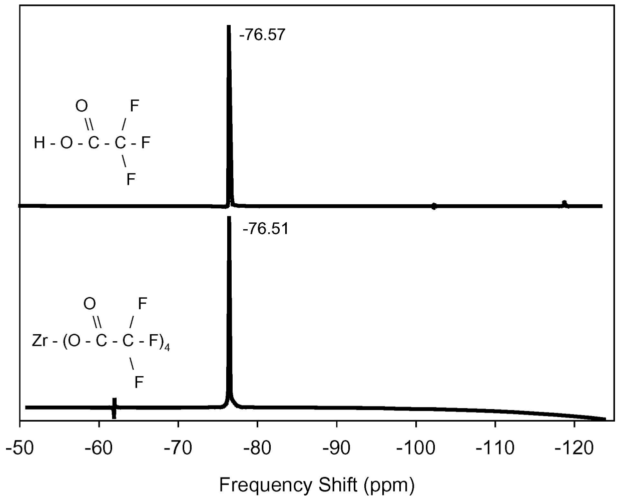

Figure 1 ^{19}F NMR spectra of our zirconium trifluoroacetate powder (bottom) and trifluoro-acetate (top) for comparison (both were dissolved in deuterated chloroform). Our powder produced a similar peak shift that indicated full conversion of zirconium acetate to zirconium trifluoroacetate.

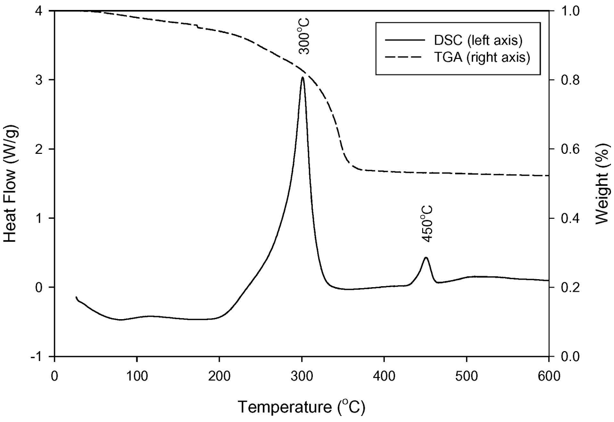

Figure 2 Thermal analysis of our zirconium trifluoroacetate powder heated under nitrogen at 10 °C/min. The exotherm at 300 °C corresponded to organic burnout, while the exotherm at 450 °C was due to crystallization of the powder.

(zirconia). At higher temperatures, some of the coatings were a mix of tetragonal and monoclinic zirconia, while others had completely transformed to the higher temperature monoclinic phase. A representative sampling of these spectra is shown in Fig. 3. Only the laser-fired coating exhibited a spectrum that matched that of a zirconium oxyfluoride phase, Zr(O, F)$_{2.706}$. The crystalline peaks in this spectrum (Fig. 4) matched the reported phase after deconvolution of the large amorphous peak that was due to the silica substrate. The subscript on the mixed anions indicated a composition containing approximately 52% fluorine and 48% oxygen.

Elemental analysis with SAM confirmed the XRD findings. The coatings fired in the furnace, regardless of atmosphere, contained no fluorine, with one small exception. The coating fired under SF$_6$ had a trace of fluorine on the surface, which disappeared after even minor sputtering. The fluorine was adsorbed on the surface, but not incorporated into the structure of the coating. On the other hand, a significant amount of fluorine was found in the laser-fired coating, and was not attributed solely to surface absorbed species. Fig. 5 shows an Auger survey spectrum indicating the presence of Zr, O, F, and C. The carbon is most likely surface contamination or a small amount of residual organics from the wet chemical deposition. Sputter profiling was attempted to determine the distribution of fluorine as a function of depth; however, charge build-up in the sample prevented accurate measurements from being made.

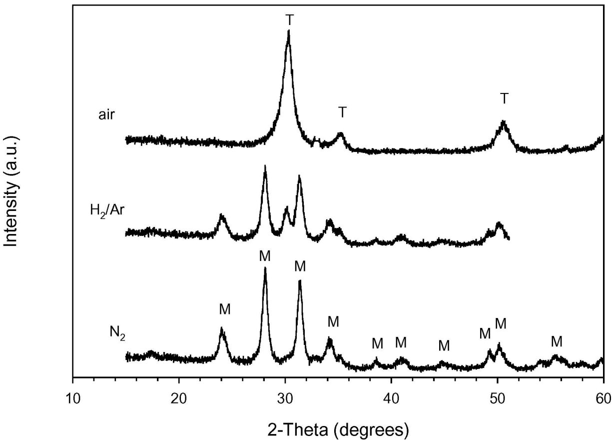

Figure 3 X-ray diffraction spectra of coatings heated to 600 °C in air (top), forming gas (middle), and dry nitrogen (bottom). The letters indicate the phase to which the peaks are attributed (M = monoclinic ZrO$_2$, T = tetragonal ZrO$_2$).

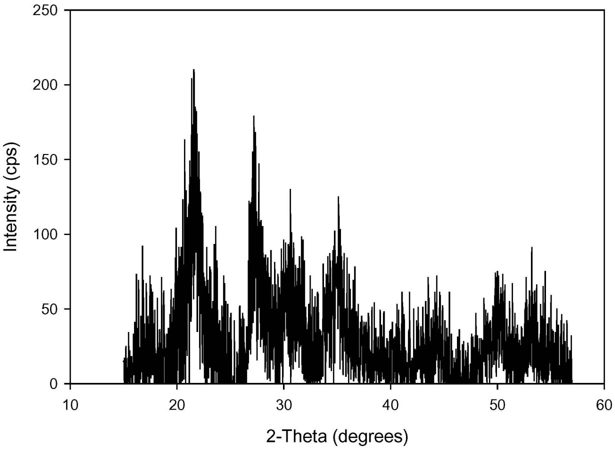

Figure 4 X-ray diffraction spectrum of a laser-fired coating that indicated formation of zirconium oxyfluoride.

In order to quantify the composition of the laser-fired zirconium oxyfluoride, Auger sensitivity factors were determined through the use of similar standards. As a starting point, the literature value for zirconium was used. Next, zirconium dioxide (ZrO$_2$) was measured, and the sensitivity factor for oxygen was adjusted to produce an oxygen-to-zirconium ratio (O/Zr) of 2. Likewise, zirconium fluoride (ZrF$_4$) was probed, and the sensitivity factor for fluorine was adjusted to yield a fluorine-to-zirconium ratio (F/Zr) of 4. With these sensitivity factors, the calculated composition from the spectrum in Fig. 5 was 17.2% zirconium, 13.4% oxygen, and 69.4% fluorine. The compound with this composition would be ZrO$_{0.78}$F$_4$, assuming that all of the anions were bonded to zirconium. It is more likely that all of the detected oxygen bonded to zirconium and only part of the fluorine bonded to the metal ion. In this

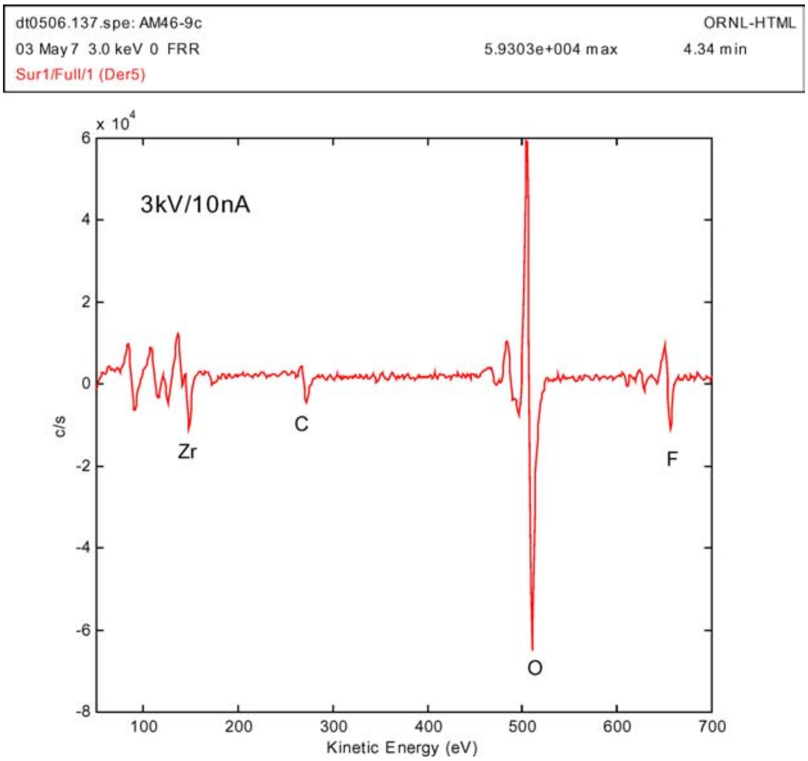

Figure 5 Differentiated Auger survey spectrum of a laser-fired film showing the presence of Zr, O, F, and C. The atomic percents of each species were calculated to be 17.2:13.4:69.4:trace, respectively, using sensitivity factors experimentally determined from similar standards.

case, the compound would be $ZrO_{0.78}F_{2.44}$, in order to maintain charge balance. The rest of the fluorine, which was in excess from the wet coating process, could have been trapped in the glass by the fast laser-firing process along with the small amount of carbon noted in the spectrum (Fig. 5).

The results of this study are similar to those of a similar study involving borosilicate glass [13]. In that study, volatile boron was lost during furnace firing, while it was trapped into the glass film by fast firing with a laser. In the current investigation, it is more likely that the oxidation of zirconium is limited by the short firing time rather than fluorine needing to be trapped, although both mechanisms are possible. Zirconium is a reactive metal and a well-known oxygen getter [14], so much so that it is pyrophoric when the particle size is below 10 microns [15]. It is this property of zirconium that prohibits the easy formation of either zirconium fluoride or oxyfluoride.

In an attempt to repeat the fast-firing experienced by the zirconium oxyfluoride precursor coating heated with the laser, another rapid firing experiment was devised. It was determined [16] that a coated silicon wafer could be heated to 500 °C in approximately 10 s by placing it directly onto an alumina plate that had been preheated to 900 °C. An alumina plate was placed in a box furnace and allowed to equilibrate at 900 °C. The coupon was placed on the preheated plate, and after 10 s, the sample was removed and allowed to cool under ambient conditions. XRD revealed that the coating was monoclinic zirconia. This experiment showed that the crystallization and complete oxidation of the zirconium precursor occurred in less than several seconds.

Many studies have been conducted on the oxidation of zirconium, especially by the nuclear power industry because zirconium has been used in water-cooled nuclear reactors. The constants and rate laws governing the oxidation of zirconium varied from study to study, most of which investigated the long-term oxidation of zirconium. Dawson *et al.* on the other hand, studied the early stages of zirconium oxidation, albeit a bulk study, and found that the oxidation rate was consistent with anion vacancy diffusion [17]. Even Dawson's investigation was insufficient to describe the rate of oxidation in the current study due to the high surface to volume ratio of our films. Furthermore, we were concerned with the formation of the oxide over the fluoride in the presence of both, which is not strictly oxidation in the metallurgical sense. Even so, the fact that zirconium has a high affinity for oxygen is not beneficial for the wet chemical synthesis of zirconium oxyfluoride.

Under the present investigation, we were able to produce zirconium oxyfluoride films by fast firing our wet-chemical precursor with scanned laser irradiation. The firing times were on the order of tens of milliseconds. Formation of a zirconium oxyfluoride phase using conventional furnace firing was problematic due to zirconium's high affinity for oxygen. Zirconia was the only discernable phase even when the films were fired under a reducing atmosphere. For comparison, the firing times were on the order of minutes. Even when furnace firing times were reduced to seconds, zirconia was still the only product. Thus, the two orders of magnitude in time between laser-firing and fast furnace-firing were crucial to the formation of zirconium oxyfluoride.

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