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Catalyst-Enhanced Chemical Vapor Deposition of Yttrium Oxide

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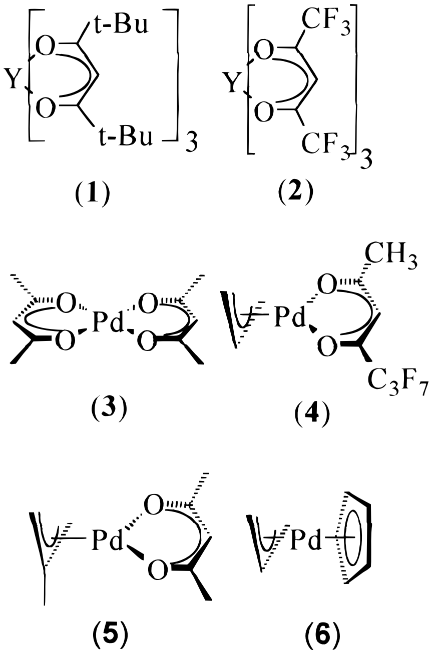
High-quality yttrium oxide thin films can be prepared from [Y(thd)$_3$] (**1**, thd = 2,2,6,6-tetramethyl-3,5-heptanedionato) under mild conditions by the catalyst-enhanced chemical vapor deposition technique using oxygen as carrier gas. Several palladium compounds, such as [Pd(acac)$_2$] (acac = 2,4-pentadionato), [Pd(η^3-C_3H_5)(η^5-C_5H_5)] (C_3H_5 = allyl), and [Pd(η^3-C_4H_7)(acac)] (C_4H_7 = 2-methylallyl), have been used as catalyst precursors. The films of yttria have open, amorphous structures, as characterized using XPS, SEM, EDX, and XRD techniques. The volatile products of the chemical vapor deposition reactions are analyzed and give evidence for the catalytic chemical vapor deposition.

Introduction

Yttrium oxide (Y_2O_3) thin films have potential applications as electronic insulators, optical or magneto-optical materials, protective coatings, and reaction barriers.[1−9] Yttria is also an important component in a wide variety of materials such as yttria-stabilized zirconia (YSZ),[10] yttrium−aluminum or yttrium−indium garnet (YAG or YIG),[11] the perovskite phase $YTiO_3$,[12] and, especially, yttrium-based high conducting temperature superconducting metal oxide materials.[13]

Because of the strategic significance of yttria and yttria-based materials, there has been growing interest in formation of yttria films by using chemical vapor deposition (CVD) methods. The yttrium compounds [Y(thd)$_3$] (thd = 2,2,6,6-tetramethyl-3,5-heptanedionato),[4−7,9] [Y(tmod)$_3$] (tmod = 2,2,7-trimethyl-3,5-octanedionato),[7] [Y(COT)Cp*] (COT = cyclooctatetraenyl, Cp* = η^5-pentamethylcyclopentadienyl),[8] and [YCp$_3$] (Cp = η^5-cyclopentadienyl)[14] have been used as precursors, usually with oxygen as carrier gas. So far, [Y(thd)$_3$] (**1**, Chart 1) is the preferred precursor, based on its good volatility, easy preparation, and excellent air and water stability; the *tert*-butyl substituents are important in providing steric protection and preventing association of the complex through formation of bridging β-diketonate groups.[4−7,9] However, thermal CVD from **1**, which has high thermal stability, requires very high temperatures (>700 °C), and this greatly limits the range of substrates that can be coated. To improve the CVD process, and in particular to lower the minimum CVD temperature, reactive carrier gases such as oxygen are typically used, and plasma enhancement techniques have been developed.[4−6]

Chart 1



We recently gave a preliminary report of a new enhancement method called catalyst-enhanced chemical

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Table 1. Deposition Conditions, Film Composition, and Deposition Rate for Yttrium Oxide Films[a]

prec/cat./subst[d]	T, °C S/P/C[b]	analysis[c]					CVD rate, μm/h
		Y	O	Pd	C	F	
1/no/glass	500/135/−	39	47		6		*e*
1/ **3** /glass	315/135/120	45	48	1	6		0.3
1/ **4** /glass	360/135/40	34	40	8	6	12	0.5
2/ **5** /glass	315/135/20	41	12	0	9	38	0.8
1/ **5**/glass	315/135/20	44	50	1	5		1.3
1/ **5**/glass	360/135/20	45	53	2	0		1.5
1/ **5** /SiO_2	360/135/20	48	52	0	0		1.4
1/ **5** /TiN	360/135/20	48	52	0	0		1.3
1/ **5** /Al	360/135/20	48	52	0	0		1.4
1/ **6**/glass	360/135/0	34	54	1	11		0.4

[a] In all cases, carrier gas was O_2 at 50 mL min^{-1} and the pressure was approximately 1 Torr. [b] Substrate temperature for deposition/temperature for yttrium precursor reservoir/temperature for catalyst reservoir. [c] Analytical data in atom % for yttria films as deposited. Pure yttria should give Y, 40%; O, 60%. [d] Precursor for yttrium/precursor for catalyst/substrate. For precursor structures, see Chart 1. [e] The film is too thin for thickness measurement; 8 atom % silicon was present (see text).

vapor deposition (CECVD), in which a small amount of a catalyst precursor is introduced into the CVD reactor along with the main CVD precursor and, by chemical catalytic enhancement, allows the CVD to be carried out at lower temperature than is possible in its absence.[15] This paper provides details of this research as applied to the CECVD of yttrium oxide films using palladium complexes as catalyst precursors.

Experimental Section

The complexes [Y(thd)$_3$][16] (**1**), [Y(hfac)$_3$][17] (**2**), [Pd(acac)$_2$][18] (**3**), [Pd(η^3-allyl)(fod)][19,20] (**4**), [Pd(η^3-2-methylallyl)(acac)][19,20] (**5**), and [Pd(η^3-allyl)(Cp)][21] (**6**) were prepared according to the literature methods. Complexes [Y(thd)$_3$] and [Pd(η^3-allyl)(Cp)] were purified by sublimation, and other precursors of CVD and catalyst precursors were purified by recrystallization.

The CECVD reactions were carried out using a Pyrex vertical cold-wall reactor under reduced pressure, using dynamic pumping. A sidearm was used to introduce the carrier gas, which was passed through a reservoir containing the catalyst precursor before entering the CVD reactor. The yttrium-containing CVD precursor was present in a reservoir at the base of the reactor. The substrate (glass, SiO_2, Al, TiN, silicon wafer, or Pt/Si) was washed with water and acetone before use and was held near the top of the reactor, where it was heated by a temperature-controlled heating rod. The relative amounts of yttria and palladium precursors delivered were controlled roughly by the temperature of each precursor reservoir; the ratio of yttria:Pd precursor is estimated to range from 10:1 to 500:1 under limiting conditions used (Table 1). The deposition time was usually 1 h and the pressure in the CVD reactor was about 10 Torr.

XPS spectra of yttria films were recorded using the SSL SSX-100 small-spot XPS surface-analysis instrument with a monochromatized Mg Kα X-ray source (1253.6 eV). The surface composition, reported in atom percent from XPS spectra, was determined after sputtering with argon at 4 keV until a constant composition was given. The atom percent values were determined from the peak intensities, corrected for relative sensitivity using the Schofield ratio and summing individual components to 100%. Top and cross section views of films were obtained by SEM using an ISL DS-13 scanning electron microscope. The thickness (and hence the deposition rates) of the films was measured directly from the SEM images and confirmed in some cases by using a Dektak profilometer.

In some CVD experiments, the volatile products were collected using a trap cooled by liquid nitrogen and were then analyzed by GC−MS.

Results and Discussion

CECVD Reactions and Characterization of the Yttrium Oxide Films. Initial experiments on low-pressure CVD of yttria on a glass substrate from the precursor [Y(thd)$_3$] (Chart 1) were carried out in the absence of a catalyst using a vertical cold-wall CVD reactor. No detectable films could be grown from the precursor [Y(thd)$_3$] at a substrate temperature of 500 °C when no carrier gas was used or when the carrier gas was either nitrogen or hydrogen. However, when oxygen was used as the carrier gas, some deposition occurred very slowly at 500 °C. Examination of the surface of the film formed under these conditions by SEM indicates only formation of small islands of yttria (Figure 1a), and analysis by XPS (Table 1) showed the presence of yttria and silica, with some carbon impurity. It is clear that the film is very thin so that silica from the substrate is detectable. These results are fully consistent with literature reports that CVD of yttria from [Y(thd)$_3$] occurs efficiently only at temperatures >700 °C.[4−7] In addition, studies of the thermolysis of [Y(thd)$_3$] in the vapor phase have shown that only partial decomposition to give [Y(thd)$_2$] occurs below 500 °C but that decomposition occurs more easily, at temperatures above 400 °C, in the presence of oxygen.[22] These results provide a reference point for comparison with the CECVD reactions described below, which were carried out using oxygen as carrier gas.

Using the same cold-wall CVD apparatus as above, but with a volatile palladium complex introduced into the CVD reactor with the oxygen carrier gas, it was possible to grow films of yttrium oxide on several different substrates in the temperature range 315−360 °C from the precursor [Y(thd)$_3$]. The conditions are given in Table 1 and are much milder than in any previous thermal CVD study.[4−7] Table 1 also lists analytical data on the films obtained by XPS and growth rates, where measured, obtained from SEM cross sections of the films. When formed under conditions where little palladium was incorporated, the films were colorless and transparent, but they were pale yellow to yellow-brown in samples containing detectable amounts of palladium. The acceleration of film deposition by the palladium complex precursors is remarkable in this CECVD process, so a detailed study was carried out.

First, evidence that codeposition from both palladium and yttrium complex precursors is necessary in order

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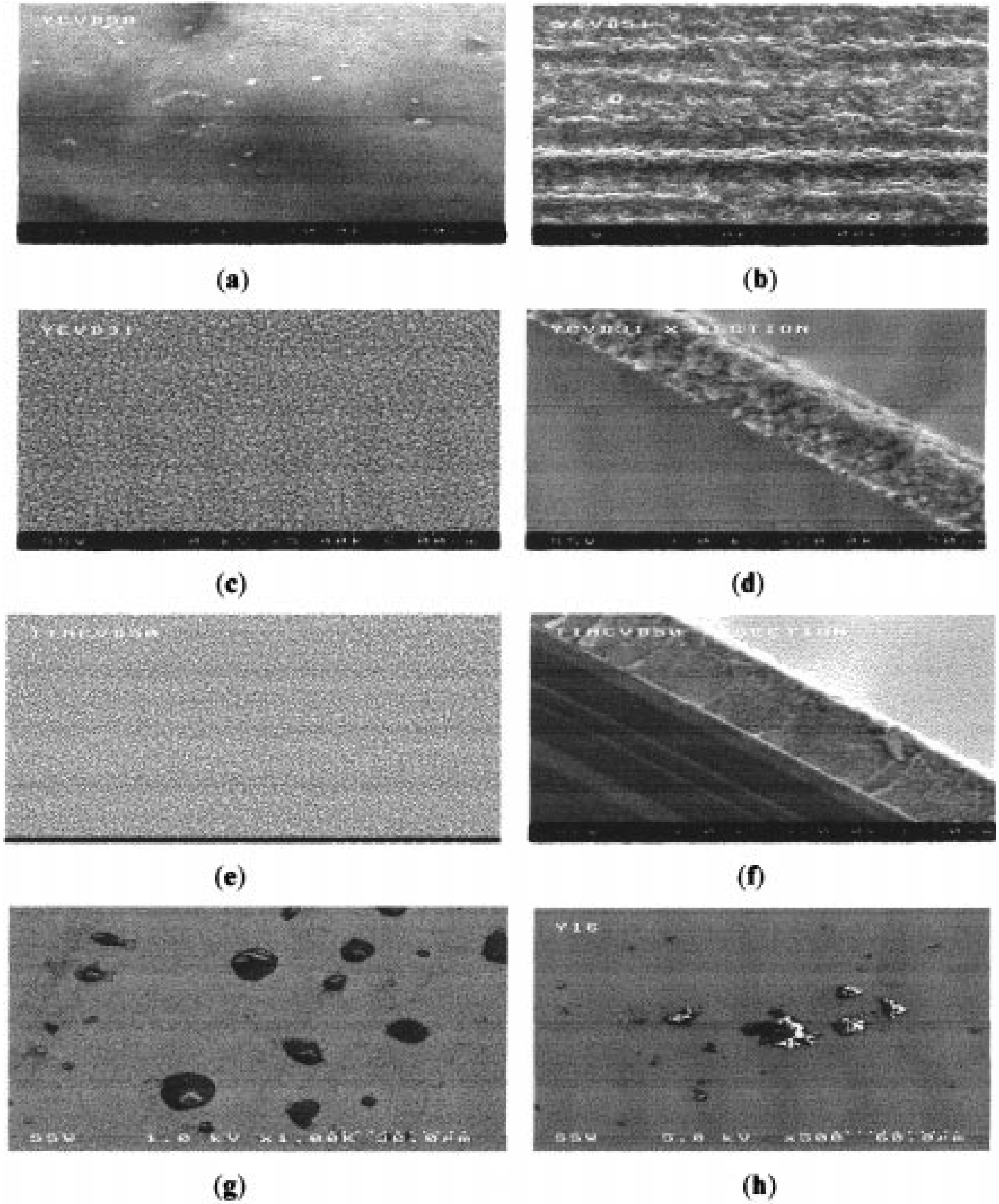

(a) (b) (c) (d) (e) (f) (g) (h)

Figure 1. SEM images of the yttrium oxide thin films grown from [$Y(thd)_3$], with oxygen carrier gas. (a) Film grown at 500 °C with no catalyst. (b) Film grown at 360 °C on aluminum using catalyst **5**. (c and d) Film grown on glass at 315 °C using **5** as catalyst. (e and f) Film grown on TiN at 360 °C using **5** as catalyst. (g) Film grown on glass at 360 °C with **6** as catalyst. (h) Film grown on glass at 315 °C with **3** as catalyst.

to observe CECVD is presented. If the substrate was precoated with palladium metal and then reacted in a separate CVD experiment with an yttrium precursor, the catalytic effect was not observed and no yttria films could be obtained. A weak catalytic effect was, however, observed if palladium was first deposited from **5**, followed immediately by yttria deposition in the same reactor. It is likely that this effect is due to traces of undecomposed palladium precursor still present in the reactor, but this is not easy to prove. It should also be noted that the catalytic effect of complex **5** is much less when using a simple hot-wall reactor, rather than the cold-wall reactor used in most of this research. The problem with the hot-wall reactor is that there is a temperature gradient in the furnace; most of the palladium precursors decompose immediately on entering the reactor to deposit palladium metal on the walls where the temperature is only about 200 °C. This is too low a temperature for CECVD of yttria, so the yttrium precursors pass through the reactor with only little decomposition to yttria in the 350−400 °C zone of the reactor. Hence palladium and yttria are not codeposited and the catalytic effect is much less; a palladium precursor that decomposes only in the temperature range 300−400 °C would probably be effective under these conditions. These observations are consistent with either gas phase or surface catalysis effects.

Several palladium compounds, [Pd(acac)$_2$] (**3**), [Pd(allyl)(fod)] (**4**), [Pd(2-methylallyl)(acac)] (**5**), and [Pd(allyl)(Cp)] (**6**) (Chart 1)[18−20] were tested as catalyst precursors for yttrium oxide thin films. Complex **3** is simplest to prepare, but it is not ideal for this application, because it has lower volatility than the other precursors. As a result, with the simple apparatus used in which catalyst was introduced in a carrier gas stream at close to room temperature, too little catalyst was transported to give a marked catalytic effect; **3** is likely to be a good catalyst using equipment with a heated inlet line to improve transport of the precursor. Complex **6** has good volatility, but the yttria films formed in its presence from [Y(thd)$_3$] precursor contained much higher carbon contamination than with the other catalyst precursors. Although it is well-known that cyclopentadienylmetal complex precursors often give films by CVD processing that are heavily contaminated with carbon, it is somewhat surprising that such small quantities of **6**, which was used only as the catalyst precursor, can lead to significant carbon impurities in the yttria films, even when formed under conditions where the palladium content was too low to be detected by XPS. The fluorine-containing compound **4** is a volatile liquid precursor and gave a good deposition rate when used as a catalyst precursor in CVD from [Y(thd)$_3$], but the yttria films formed contained significant fluoride impurity. These data from both catalyst precursors **4** and **6** show that ligand components from the palladium precursor can be incorporated into the yttria films, strongly suggesting a direct interaction between yttrium and palladium precursors or their decomposition products during film deposition (see later discussion for a possible interpretation). The best yttria films were obtained when complex **5** was used as the catalyst precursor, since pure yttria films were obtained and a high, reproducible deposition rate was found. Typical conditions are given in Table 1.

Of the yttrium-containing precursors tested, [Y(thd)$_3$] was clearly superior. Thus, [Y(hfac)$_3$] gave films containing more fluoride than oxide and also more carbon impurity than in similar experiments with [Y(thd)$_3$] as precursor (Table 1). Clearly, [Y(hfac)$_3$] gives mixed oxide−fluoride phases rather than the desired oxide. This is not surprising given the previous observation that small amounts of a fluorine-containing organopalladium precursor can lead to fluoride impurity in the yttria films, even when the yttrium precursor is fluorine-free. Hence most research was carried out using the precursor [Y(thd)$_3$].

The surface composition of each yttrium oxide thin film was obtained by XPS analysis. The films were sputtered with argon to remove surface impurities prior to analysis, and the observed binding energies were corrected for charging effects, which are considerable with these insulator films, by reference to the C(1s) binding energy at 284.6 eV or, when carbon was absent, to the O(1s) binding energy at 292.5 eV.[23] A typical XPS spectrum for an yttrium oxide film on silica is shown in Figure 2. For this film, only peaks due to yttrium and oxygen are detected by XPS, the palladium and carbon content being too low to detect. It was possible to obtain films with detectable amounts of palladium by increasing the flow of palladium precursor to the reactor. The main Y3d$_{5/2}$ binding energy was at 156.5 eV for pure yttrium oxide films, in good agreement with literature value. For the oxide−fluoride films, the Y3d$_{5/2}$ binding energy increased, closer to the value for pure YF$_3$ at 159.8 eV.[23]

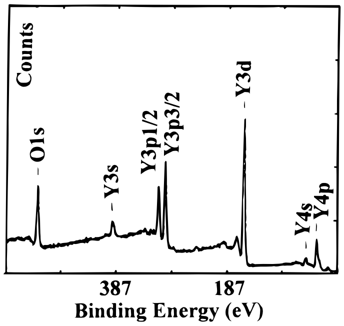

Figure 2. XPS spectrum for yttrium oxide thin film on a silica substrate. The film was grown from [Y(thd)$_3$] with **5** as catalyst precursor at 360 °C.

The XPS analysis (Table 1) shows that the films as deposited are oxygen-deficient, as is commonly observed when oxide films are formed by CVD and not annealed under oxygen.[8] They could be annealed at 500 °C in oxygen and then gave the expected Y:O ratio of 2:3. In the XPS spectra of the initial films, the yttrium 3d peak was broad and not completely resolved. The main Y3d$_{5/2}$ binding energy was at 156.5 eV, but there was a shoulder at lower binding energy (ca. 155 eV), perhaps corresponding to yttrium(II) centers in the oxygen-deficient material. The high-resolution XPS also shows that the O1s signal actually contains more than one component. The main peak is at a binding energy of 529.5 eV and is clearly due to oxide in yttria, and a minor peak at 532 eV is assigned to surface hydroxide, in agreement with literature reports.[7,8,24] There is also a minor peak at lower binding energy (528 eV), and this might be attributed to oxide associated with reduced yttrium centers, since it was absent in annealed films.

Several substrates, such as glass, SiO$_2$, Si, TiN and Al, have been used in this work, and it is possible to grow yttria films on all of them. In all cases, there is excellent adhesion of the yttrium oxide films to the substrate. The substrates do not appear to affect the CVD process greatly, either in terms of purity of the films or growth rates (Table 1). However, there were differences in the film morphologies, as described below.

The morphologies of the formed yttrium oxide thin films are revealed by SEM measurements. Some typical SEM images of the thin films, as either top or cross section views, are displayed in Figure 1. The film formed on aluminum from [Y(thd)$_3$] with catalyst **5** at 360 °C (Figure 1b) has a corrugated appearance with particle sizes around 300 nm. The film grown on glass with compound **5** as the catalyst at 315 °C (Figure 1c,d) is more uniform and the mean particle size is about 200

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nm. The film thickness shown in Figure 1d is 1.3 μm. The film grown on TiN with **5** as catalyst at 360 °C (Figures 1e, 1f) is comprised of smaller particles with a mean size of about 40 nm and has a thickness of 1.3 μm (Figure 1f). All the SEM images in Figure 1b-f show that the films are porous and open, and the particles have no clear edges. XRD analysis shows that the films are amorphous. Annealing under oxygen at 500 °C gave more crystalline yttria, as determined by XRD, but the porous morphology remained. Even though the films are porous, they show excellent adhesion to the substrates, as shown by either tape or scratch tests. It could be argued that the open morphology is a result of gas-phase nucleation, but the strong adhesion suggests that the particles are formed at the surface.

The film obtained from [Y(thd)$_3$] with complex **6** as the catalyst at 360 °C (Figure 1g) contains large black patches (10−30 μm across) on the surface that are shown by EDX analysis to contain mostly carbon. This type of structure may arise from gas-phase decomposition and particle growth, followed by adsorption onto the surface. It is consistent with the presence of a high level of carbon impurity in the film, as determined by XPS analysis. Some surface carbon was also detected by SEM/EDX in the film grown from [Y(thd)$_3$] on glass using complex **3** as catalyst (Figure 1h).

The Mechanism of CECVD. There are several puzzling features about the CECVD process, and it is interesting to consider how it might occur. In the absence of a catalyst, the low-temperature growth of yttrium oxide films on glass gives films having features of layer and island (Strancki−Krastannov) growth,[25] as indicated by the SEM images (Figure 1a), suggesting that yttrium oxide grows on the substrate more easily than on itself. However, when a palladium complex was used as catalyst precursor, the morphology of the yttria films as depicted by SEM (Figure 1b−f) is quite different, having an open, honeycomb structure comprised of many small particles. This is consistent with deposition of very small palladium crystallites which act as centers for catalysis of formation of yttria around them. In the simplest case, a catalytically active particle might be completely surrounded by yttria, and then growth would stop until a new catalytic center is formed. However, under conditions of low palladium complex feed rates, yttria films are still formed and have the same open morphology, even when the palladium concentration in the films is too low to detect by XPS (ca. 0.5%). One possible explanation for this is that the formation of catalytic particles could be reversible and that palladium may then be able to migrate through the yttria {for example by reaction with diketone Htdh, formed as a CVD product, and oxygen to give volatile [Pd(thd)$_2$] and water; massive palladium cannot be transported in this way, however}, but this is not easy to prove. Under conditions of high palladium complex feed rates, the yttria films may contain up to 10% palladium as determined by XPS. The Pd3d$_{5/2}$ binding energy of 335.5 eV clearly shows that palladium is present as the metal (literature BE = 335.0−335.5 eV[23]) rather than an oxide form (PdO has BE = 336.1−336.5 eV[23]), and this is consistent with observations that CVD from the palladium precursors alone under these conditions gives pure palladium metal. No large palladium crystals could be detected by SEM/EDX or by XRD. A similar mechanism involving surface catalysis has been suggested recently to explain the catalysis by fine metal powders of the formation of coiled whiskers or fibers of carbon, silicon carbide, and some transition metal phosphides.[26] A metal-catalyzed process is also indicated by the observations that palladium or platinum precursors give the catalytic effect but nickel and cobalt precursors do not; under oxygen the base metal precursors give the metal oxide rather than the metal, so metal surface catalysis cannot occur.

The possibility was considered that a chemical reaction might occur between the palladium complex and yttrium complex precursors and that this might activate the yttrium complex toward decomposition. Hence, the interaction of [Y(thd)$_3$] and [Pd(η^3-2-methylallyl)(acac)] was examined in CD$_2$Cl$_2$ solution by NMR. A rapid reaction was observed, but this occurred only by exchange of β-diketonate ligands to give an equilibrium with [Y(thd)$_2$(acac)] and [Pd(η^3-2-methylallyl)(thd)]. No exchange of the 2-methylallyl group occurred. Although this reaction could affect the stability of the yttrium precursor to a minor extent, it cannot account for the remarkable catalytic effect observed in CVD. We note also that the presence of a copper(II) β-diketonate actually increases the thermal stability of [Y(thd)$_3$] in an oxygen atmosphere; apparently, the copper complex decomposes at a lower temperature and so depletes the oxygen concentration in the reaction zone.[22b] If this type of ligand exchange can occur under CVD conditions, either in the gas phase or at the substrate surface, it gives a means of fluoride contamination only if the palladium precursor contains fluorine (as observed, Table 1).

Some further insight into the mechanism was obtained by analysis of the condensable volatile products from the CVD reactions by GC−MS in the absence or presence of a catalyst. The volatiles were collected in a liquid nitrogen cooled trap and, after warming to room temperature, the gaseous and liquid fractions were analyzed separately by GC−MS. The gaseous fraction from yttrium oxide CVD from [Y(thd)$_3$] (**1**) with oxygen carrier gas in the absence of a catalyst contained carbon monoxide (35%), carbon dioxide (50%), and $Me_2C{=}CH_2$ (15%), while the liquid fraction contained mostly the free β-diketone 2,2,6,6-tetramethyl-3,5-heptanedione (Htdh, 86%), with many minor organic products, including *t*-BuCOMe and others whose structures were not unambiguously defined by their mass spectra. Water is also present in the liquid fraction, as shown by IR and MS. These results are qualitatively in agreement with earlier studies of decomposition of [Y(thd)$_3$], though more ligand fragments and less diketone were formed under the conditions used previously.[22,27] Carbon mon-

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oxide and 2-methylpropene are formed in a decarbonylation reaction.[22,27] When similar CVD was carried out using the catalyst precursor **5**, the analogous products were carbon dioxide (88%) and $Me_2C{=}CH_2$ (12%) from the gaseous fraction, while the free diketone Htdh and water were the only detectable products in the liquid fraction. No carbon monoxide was detected in the gas phase and no complex mixture of organic compounds was found in the liquid fraction. It has been shown earlier that CVD of palladium metal from **5** under similar conditions gives only carbon dioxide and water as volatile products by complete combustion of the organic ligands, catalyzed by the forming palladium surface. In this reaction, too, it seems that the ligands on palladium are completely oxidized and that the ligand fragments from decomposition of $[Y(thd)_3]$ are also oxidized. These results strongly suggest that much of the decomposition of $[Y(thd)_3]$ occurs at a palladium metal surface, where catalytic combustion of organics can occur efficiently. It is likely that there is also some gas-phase decomposition of $[Y(thd)_3]$ to give the free diketone observed, perhaps by abstraction of a hydrogen atom from one β-diketonate ligand by a second diketonate to give free Htdh. If formed in this way, it would not be subject to palladium-catalyzed oxidation. There is insufficient evidence at this stage to allow a detailed mechanism to be proposed.

Conclusions

In the presence of a palladium complex such as $[Pd(\eta^3$-2-methylallyl)(acac)], the CVD of yttria from the β-diketonate derivative $[Y(thd)_3]$ can be carried out under much milder conditions than in its absence. Conditions have been found which give yttria films with very low impurity levels of either carbon or palladium. This CECVD process may be important in allowing CVD of yttria films to be carried out on thermally sensitive substrates. The very open, porous structures formed could make the palladium-containing films useful as yttria-supported catalysts, though they are disadvantageous in applications in electronics and protective coatings, where dense films are needed. While the mechanism is not clearly defined, the current observations suggest that catalysis occurs at tiny palladium crystallites formed by CVD from the palladium precursor.

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