Catalyst Enhanced Chemical Vapor Deposition: Effects on Chemical Vapor Deposition Temperature and Film Purity

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A number of enhancement methods have been developed for chemical vapor deposition (CVD) processes, and these may serve either to lower the temperature of the CVD process, thus allowing films to be grown on thermally sensitive substrates, or to improve the purity of the deposited films. Common enhancement methods include the use of reactive carrier gases, photochemical irradiation using standard UV sources, lasers or synchrotron radiation, ion beams, and plasmas.[1,2] It is also well-known that some CVD processes in which catalytically active metals are deposited may be autocatalytic and that seeding a surface with an active metal may promote selective CVD on the seeded areas, particularly if a reactive carrier gas such as hydrogen or oxygen is also used.[1−5] It is thought that the catalytically active metal acts as a reactive site for adsorption and dissociation of the CVD precursor and, in the presence of a reactive carrier gas oxygen or hydrogen, greatly facilitates removal of ligand fragments from the surface by catalytic oxidation or reduction, respectively.[1−5] In turn, this regenerates a clean surface for further precursor adsorption and decomposition. If this interpretation is correct, it seemed possible that catalysis of the CVD of a noncatalytic material might occur by co-deposition (rather than pre-deposition as in the prior literature described above) of a catalytically active material. Such a process could be termed catalyst-enhanced chemical vapor deposition (CECVD). This paper demonstrates that CECVD using a palladium precursor is possible and that it can be effective either in lowering the temperature of CVD of films of yttria or zirconia from their β-diketonate precursors or in reducing carbon impurities in CVD films of cobalt alloys formed from an alkyne complex precursor.

Previous studies have shown that CVD of palladium can be enhanced by use of either hydrogen or oxygen as reactive carrier gases and can be very surface-selective.[4,5] In addition, it is known that palladium is a highly active catalyst for both hydrogenation and oxidation and that it yields a very active surface for CVD of other metals.[5,6] Palladium was therefore chosen as the catalyst component for CECVD, and although

several precursors have been shown to have catalytic activity, the complexes [Pd(η^3-2-methylallyl)(acac)] (**1**, acac = acetylacetonate)[4] and [Pd(hfac)$_2$] (**2**, hfac = hexafluoroacetylacetonate)[5] have been shown to be particularly useful for CECVD under oxidative or reductive conditions, respectively.
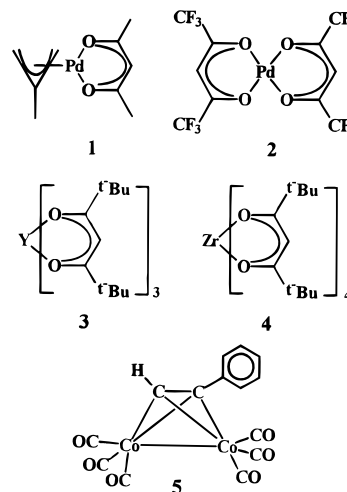
Yttria (Y$_2$O$_3$) and zirconia (ZrO$_2$) are important as advanced materials or components of more complex oxide materials; thus, there has been much interest in CVD of thin films of these compounds.[7] The complexes [Y(thd)$_3$] (**3**) and [Zr(thd)$_4$] (**4**, thd = 2,2,6,6-tetramethyl-3,5-heptanedionate) are good precursors for yttria and zirconia thin films based on their good volatilities, ease of preparation, and storage (they are stable to moist air).[6] However, because they have high thermal stabilities, the CVD processes must be carried out using very high deposition temperatures. When vertical cold-wall CVD reactor was used,[4] reasonable growth rates of yttria or zirconia were obtained only at 700 °C using oxygen as the carrier gas, and the minimum temperature at which CVD was observed was 500 °C. However, in the presence of low concentrations of the palladium precursor **1** in the oxygen carrier gas, yttria or zirconia films could be grown from the CVD precursors **3** or **4** at temperatures from 300−360 °C. The deposition conditions, data from surface analysis of the films and, when measured, the deposition rates are listed in Table 1. It is clear that under the optimum conditions, no carbon impurities are detected and, most remarkably, that the palladium content is often too low to be detected by XPS analysis. The use of oxygen as reactive carrier gas was essential, and no useful films were formed using either nitrogen or hydrogen as the carrier gas at temperatures as high as 500 °C. The films could be grown on several substrates, including glass, silicon, silicon oxide, aluminum, titanium nitride, and platinum, and the films show excellent adhesion in all cases. At a CVD temperature of 360 °C, the growth rates for selected yttria and zirconia films were 1.25 and 0.5 μm/h, respectively. Palladium-free films are transparent and colorless but pale yellow or pale brown films were formed if palladium contamination was detectable. SEM images (Supporting Information) of the yttria and zirconia films show that, except for those formed on aluminum, they are very uniform with an open, amorphous structure. The particle sizes ranged from 40 to 300 nm depending on the substrate used. The smoothest

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Table 1.   Deposition Conditions,[a] Film Composition, and Deposition Rates for Yttria and Zirconia Thin Films

source materials (precursor/catalyst/substrate)	T (°C)[b]	film composition (atom %)[c]			CVD rate (μm/h)
		Y or Zr	O	C	
Y(thd)$_3$/**1**[d]/glass	315/135/20	44.2	50.1	4.9	1.25
Y(thd)$_3$/**1**/glass	360/135/20	44.6	53.6	0	
Y(thd)$_3$/**1**/SiO$_2$	360/135/20	48.5	51.5	0	
Y(thd)$_3$/**1**/TiN	360/135/20	47.6	52.4	0	1.25
Y(thd)$_3$/**1**/Al	360/135/20	47.8	52.2	0	
Zr(thd)$_4$/**1**/glass	360/160/20	45.2	54.8	0	
Zr(thd)$_4$/**1**/glass	300/170/20	38.9	61.1	0	
Zr(thd)$_4$/**1**/TiN	360/165/20	41.0	59.0	0	0.5
Zr(thd)$_4$/**1**/Si	360/170/20	44.9	55.1	0	
Zr(thd)$_4$/**1**/SiO$_2$	360/165/20	43.5	56.5	0	

[a] In all cases: carrier gas O$_2$ at 50 mL/min; pressure 1 Torr; Pd content is undetectably low. [b] Deposition temperature/temperature for precursor reservoir/temperature for catalyst reservoir. [c] Analytical values obtained after argon sputtering. The theoretical values are 40.0% yttrium and 33.3% zirconium, respectively; note that the films are somewhat oxygen-deficient, as expected when formed by CVD and not annealed under oxygen. [d] Compound **1** is [Pd(2−methylallyl)(acac)].

films were found on TiN substrates, while the films on aluminum were comprised of large particles (ca. 300 nm) with many cracks and cavities. Other palladium precursors which showed catalytic activity include [Pd(η^3-allyl)(fod)], [Pd(η^3-allyl)(hfac)], and [Pd(acac)$_2$], (fod = 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionate), but best results were given by complex **1**. For example, the problem of fluorine contamination of the oxide films was observed when using the fluorine-containing precursors. Prior seeding of the substrate with palladium followed by thermal CVD of yttria or zirconia under the same conditions as used in CECVD did not give good films; the co-deposition is clearly important.

During the CVD of cobalt metal thin films,[8] serious carbon contamination is found if [Co$_2$(CO)$_6$(PhC≡CH)] (**5**) is used as the CVD precursor even when using a hydrogen carrier gas.[9] The problem appears to be due to the presence of the phenyl group, which is often difficult to remove cleanly in CVD;[1b] the precursor [Co$_2$(CO)$_6$(*t*-BuC≡CH)] gives pure cobalt films under the same conditions.[9] Since palladium metal is a well-known heterogeneous catalyst for hydrogenation,[6] it seemed possible that co-deposition of palladium with cobalt using a hydrogen carrier gas might give carbon-free metal films even from the normally poor precursor **5**. In this experiment, [Pd(hfac)$_2$] (**2**) is introduced into the CVD reactor together with [Co$_2$(CO)$_6$-(PhC≡CH)] (**5**) by separate inlets, and the amount of **2** introduced is controlled by adjusting the relative hydrogen carrier gas flow rates and the reservoir temperature of the palladium precursor. The CVD substrate is held at a temperature of 250 °C. It was shown that if 0−3% Pd is present in the final film, there is no significant effect on the carbon content (ca. 37%) of the film; however, the carbon impurity then decreases in an approximately linear fashion with palladium content and no carbon is detected if 9% or more palladium is present in the Co/Pd alloy film (Supporting Information). In

this case, the CECVD cannot be used to prepare pure cobalt films but can be used to easily prepare cobalt−palladium alloys that are free of carbon contamination and have potential applications as magneto-optical materials. The palladium precursor **2** is preferred for this CECVD process since **1** is not stable in the presence of hydrogen.

The CECVD of pure Co/Pd films can be explained by the catalytic properties of the palladium metal, which can hydrogenate the carbon (from decomposition of the phenyl group in the phenyl acetylene) into volatile hydrocarbon.[6,9] It seems that there is a minimum palladium content in the forming Co/Pd alloy film which is needed to allow this catalytic effect. However, it is not so clear how the CECVD of yttria and zirconia occurs, since the catalytic effect is observed even when the resulting films contain undetectably low concentrations of palladium.[10] Further research on the mechanistic aspects is required, but this work clearly establishes the phenomenon of catalyst-enhanced CVD and shows how it can be used either to decrease the temperature required for a thermal CVD process or to reduce carbon contamination in CVD films. It may be expected that several other metals may exhibit catalytic effects similar to those observed here using palladium, and further studies are in progress.

Supporting Information Available: Figures 1 (SEM micrographs of yttria (**a**, top view, and **b**, cross section) and zirconia (**c**, top view, and **d**, cross section) films grown on TiN) and 2 (relationship between amount of carbon impurity and palladium (in atomic percentage) in the Co/Pd thin films) (2 pages). See any current masthead page for ordering and Internet access instructions.

JA971588L

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(10) Preliminary work indicates significant differences in the organic products formed with and without a palladium catalyst. For example, in CVD of yttria, the β-diketone was always formed but, in the absence of Pd, CO was a major product (from decarbonylation of the β-diketone), whereas in the presence of Pd, CO was not observed and CO$_2$ was formed in high yield, suggesting catalytic oxidation by Pd crystallites.