Chemical Vapor Deposition of Tantalum Oxide from Tetraethoxo(β-diketonato)tantalum(V) Complexes

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The complexes [Ta(OEt)$_4$(β-diketonate)] (β-diketonate = acetylacetonate, **2**; hexafluoroacetylacetonate, **3**; 1,1,1-trifluoroacetylacetonate, **4**; dipivaloylmethanate, **5**; 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionate, **6**) are established as volatile liquid precursors for low-pressure chemical vapor deposition (CVD) of films of tantalum(V) oxide. They give thermal CVD at a slightly lower temperature than the commonly used precursor [{Ta(OEt)$_5$}$_2$], **1**. In all cases, the CVD at 300−450 °C gives amorphous films of Ta_2O_5, which crystallize on annealing at 800 °C under oxygen. Promotion of Ta_2O_5 film formation is established using catalyst-enhanced CVD with a palladium precursor as "catalyst" and the minimum CVD temperature is then reduced to 200 °C.

Introduction

Tantalum oxide, Ta_2O_5, has important applications as a dielectric material in dynamic random access memory (DRAM),[1−3] integrated optical device and thin film capacitors,[4] large scale integrations (LSI's), and electroluminescent devices.[5,6] Other applications include use as corrosion-resistant materials, high-temperature ceramics,[7] antireflection coatings for solar cells,[8] optical waveguides,[9] and solid-state O_2 sensors.[10] Traditional film fabrication techniques have included thermal oxidation,[11] anodic oxidation,[12] reactive sputtering,[13] ion plating,[14] sol−gel processing,[15] and chemical vapor deposition (CVD).[16−19] The most popular precursor for the CVD of films of Ta_2O_5 is the ethoxide [$Ta_2(OEt)_{10}$],[16d−h] but exploratory CVD experiments with [$Ta_2(OMe)_{10}$], [Ta(dpm)$_4$Cl] and [Ta(dpm)$_5$] (where dpm = 2,2,6,6-tetramethyl-3,5-heptanedionato), [TaMe$_3$(OR)$_2$] (where R = C_{2-7} alkyl groups), [Ta(NMe$_2$)$_5$], and [TaF$_5$] as precursors have also been carried out, some using photochemical or plasma enhancement methods to reduce the temperature required for CVD.[16−19] In addition, perovskites containing tantalum, such as $SrBi_2Ta_2O_9$, are potentially useful as ferroelectric computer memories.[16i]

Most simple tantalum alkoxides such as tantalum(V) ethoxide adopt binuclear structures [$Ta_2(OR)_8(\mu$-$OR)_2$], with two bridging alkoxide ligands, in order for the tantalum(V) centers to attain octahedral coordination, and evaporation occurs only after dissociation to monomers [Ta(OR)$_5$].[16] It was considered that mononuclear tantalum complexes [Ta(OR)$_4$(β-diketonate)][20,21] might have improved volatility and so constitute a useful new class of precursors for CVD of tantalum

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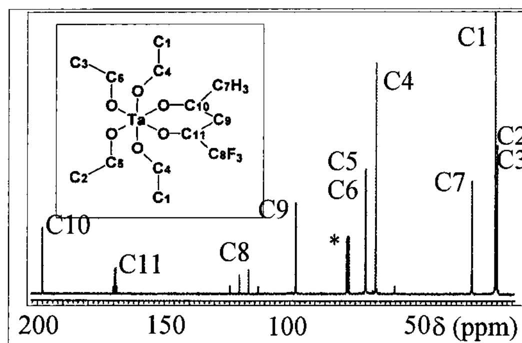
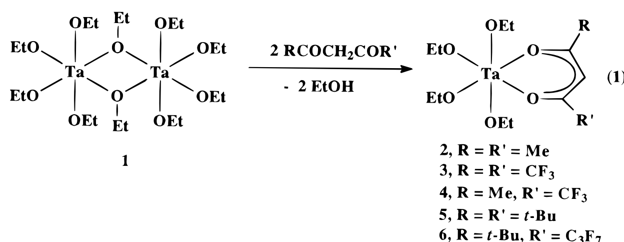


Figure 1. The ^{13}C NMR spectrum of precursor **4**. Assignments are given and the peak marked * is due to solvent CD_2Cl_2.

oxide. In addition, the presence of the chelating β-diketonate might reduce the moisture sensitivity compared to the simple alkoxide derivatives. This paper reports that the complexes [Ta(OEt)$_4$(β-diketonate)] are useful as liquid precursors for CVD of Ta_2O_5.

Results and Discussion

Precursor Synthesis. The synthetic method is illustrated in eq 1, involving the reaction of [Ta$_2$(OEt)$_{10}$], **1**, with the required β-diketone, gave the products [Ta(OEt)$_4$(β-diketonate)], **2**–**6**, in good yields. In most cases, the reactions were carried out in refluxing tetrahydrofuran, but the reaction with hexafluoroacetylacetone to give **3** was carried out at −78 °C since the reaction at room temperature or higher gave a complex mixture of products. The products were easily isolated by evaporation of solvent and ethanol byproduct under vacuum and were purified by vacuum distillation. All were isolated as pale yellow liquids and were stored under vacuum or in an atmosphere of dry nitrogen. They are all hydrolyzed slowly by water.



Characterization of Precursors. The new complexes were readily characterized by their spectroscopic properties. The electron impact mass spectra did not give an intense parent ion, but all gave a major ion peak due to [Ta(OEt)$_3$(β-diketonate)]$^+$, arising from fragmentation of one ethoxy group. The IR spectra of each complex gave bands due to ν(C=O) = 1680 cm^{-1} and ν(C=C) = 1560 cm^{-1}, indicative of the presence of the β-diketonate ligand.

The structures were defined clearly by the NMR spectra as illustrated for one of the less symmetrical complexes **4**, for which the NMR labeling scheme and the ^{13}C NMR spectra are shown in Figure 1. Complete data are listed in the Experimental Section. The ^{13}C-{^1H} NMR spectrum of **4** contained six resonances for the ethoxy carbon atoms, three for the CH_3 groups at δ = 18.1, 17.8, and 17.9, and three for the CH_2 groups at δ = 65.8, 69.81, and 69.83 (peaks due to C^2,C^3 and C,$^5C^6$ are not resolved in Figure 1 but are resolved in expanded spectra), each in a 2:1:1 ratio as expected. All other peaks are clearly resolved in Figure 1, and the carbon atoms C^8 and C^{11} appear as 1:3:3:1 quartets due to coupling to three fluorine atoms of the C^8F_3 group. The ^1H NMR spectrum of **4** contained three triplet resonances for the methyl protons and three quartet resonances for the methylene protons of the three different types of ethoxo ligands at δ = 1.05, 1.25, and 1.27 ppm and δ = 4.10, 4.57, and 4.59, each in a 2:1:1 ratio. The methylene protons $C^4H^aH^b$ are expected to be diastereotopic but appeared as a single quartet presumably because the chemical shifts are accidentally degenerate. Characteristic resonances for the β-diketonate ligand were observed at $\delta(CH_3)$ = 2.20 and δ(CH) = 5.88. These NMR data clearly demonstrate the octahedral, rigid structures of the precursor complexes.

Table 1. Thermogravimetric (TGA) Data for the Precursors

precursor	res. obsd^a	res. calcd^a	T range/°C^b
[{Ta(OEt)$_5$}$_2$], **1**	9	54	160–210
[Ta(OEt)$_4$(acac)], **2**	14	48	90–370
[Ta(OEt)$_4$(hfac)], **3**	58	39	75–370
[Ta(OEt)$_4$(tfac)], **4**	48	43	100–250
[Ta(OEt)$_4$(dpm)], **5**	30	41	80–230
[Ta(OEt)$_4$(fod)], **6**	33	34	120–215

^{a} Residue observed (%) and residue calculated (%) on the basis that the residue is pure Ta_2O_5. ^{b} Temperature range over which the reported weight loss was observed.

Volatility Studies. The new complexes could all be purified by vacuum distillation at 60–70 °C at 0.01 Torr, but they were not sufficiently stable to be distilled at atmospheric pressure. Some further study on the stability and volatility was carried out by using thermogravimetric analysis (TGA), and data are summarized in Table 1.

The TGA experiments were carried out at atmospheric pressure under a dry nitrogen atmosphere to prevent hydrolysis or oxidation by air. It can be seen from Table 1 that all the complexes leave an involatile residue in the TGA experiment, shown to be mostly tantalum oxide, and Table 1 gives the percent residue observed and calculated if the residue were pure Ta_2O_5. The compounds fall into three groups. Compounds **1**, **2**, and **5** leave a significantly lower residual mass than expected if complete decomposition to Ta_2O_5 occurs, indicating that partial evaporation occurs along with decomposition. Complex **6** leaves a residual mass within experimental error of that expected for decomposition to Ta_2O_5, while complexes **3** and **4** leave a higher mass, suggesting that the tantalum oxide formed also contains residual organic impurities.

Chemical Vapor Deposition (CVD). Films of Ta_2O_5 were grown from precursors (**1**–**6**) using a cold-wall vertical CVD reactor which has been described elsewhere.[22] Typically, films were grown on TiN(100) or Pt(111), as films on a silicon wafer, with the substrate temperature in the range 300–450 °C and the precursor reservoir at 60–100 °C using oxygen carrier gas at a pressure of 1 Torr. In most cases, the films formed were strongly adherent and uniform, with the exceptions being films grown from the precursor **1** at 300–400 °C

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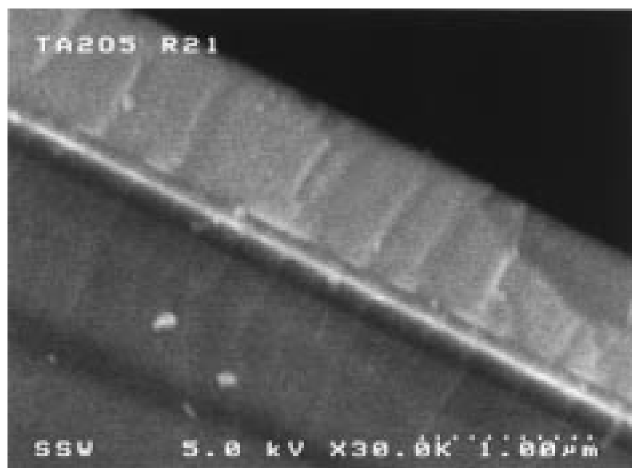

Figure 2. Cross sectional SEM micrograph of a film of Ta_2O_5 grown on TiN at 300 °C from precursor **5**. The top layer is the Ta_2O_5 (0.55 μm), and the next layer is TiN (0.25 μm). The top view shows a flat surface with no detectable structure by SEM.

which were easily delaminated by scratching. All films were analyzed by XPS, and selected films were also characterized by SEM and XRD. Further details are given below.

Rate of Deposition. A comparison of the rates of film deposition on the substrate TiN(100) was made as a function of the precursor, using a standard set of CVD conditions. The precursor temperature was 80 °C, the substrate temperature was 300 °C, and the carrier gas was oxygen at a flow rate of 50 mL min^{-1}. The growth rates in μm h^{-1} under these conditions were **1**, 0.0; **2**, 0.30; **3**, 0.25; **4**, 0.67; **5**, 0.28; and **6**, 0.54 as measured from SEM cross sections of deposited films (Figure 2). Note that the thickness of the film grown from the conventional precursor **1** was too thin to measure, whereas all the β-diketonate complexes **2**−**6** gave reasonable growth rates. The less symmetrical complexes **4** and **6** gave the highest growth rates, but the range is only modest. Complex **1** is less volatile than the other complexes and also appears to require a higher substrate temperature for efficient CVD. In an experiment in which the precursor reservoir for CVD using **1** was 120 °C and the TiN substrate temperature was 450 °C, the deposition rate of Ta_2O_5 was 0.99 μm h^{-1}. Complexes **2**−**6** thus have a clear advantage over **1** for giving CVD under milder conditions.

Characterization of Films and Film Purity. All films grown were characterized by X-ray photoelectron spectroscopy (XPS), and selected films were characterized by SEM, XRD, and electrical studies. XPS spectra of films that were formed using the CVD technique were compared with the reference Ta_2O_5 film grown by anodic oxidation of tantalum metal (Ta $4f_{7/2}$ peak at 26.1 eV; O 1s at 530.5 eV), with thin films grown from the traditional Ta_2O_5 CVD precursor [Ta(OEt)$_5$] (Ta $4f_{7/2}$ = 26.6 ± 0.2 eV; O 1s = 531.0 ± 0.5 eV), and with literature data for bulk Ta_2O_5 (Ta $4f_{7/2}$ = 26.8 eV).[23] In the films grown from the precursors **2**−**6**, the corresponding values were Ta $4f_{7/2}$ = 26.5 ± 0.2 and O 1s = 531.0 ± 0.5 eV. Comparisons of the binding energies of the Ta $4f_{7/2}$ peaks indicate the formation of Ta_2O_5 in each case. It is difficult to measure precise binding energies for these thin films due to charging effects; calibration was made using the graphitic carbon impurity peak at C 1s = 285.0 eV.

Table 2. XPS Analytical Data for Selected Films of Tantalum Oxide

conditions[a]	BE/eV[b]	O/Ta[c]	%C[d]
	Ta $4f_{7/2}$/O 1s		
1/100/Pt/450/N	26.4/530.4	2.1	8
1/100/TiN/450/N	26.4/531.2	2.3	10
2/60/Pt/300/N	26.4/531.3	2.0	6
2/60/TiN/300/N	26.4/531.5	1.9	8
2/100/Pt/450/N	26.5/531.5	2.0	5
2/100/TiN/450/N	26.4/531.5	1.9	7
3/60/Pt/300/N	26.4/531.3	2.1	2
3/60/TiN/300/N	26.4/531.5	2.1	5
4/60/Pt/300/N	26.4/531.2	2.1	8
4/60/TiN/300/N	26.1/530.8	1.9	8
4/100/Pt/450/N	26.5/531.5	2.3	7
4/100/TiN/450/N	26.5/531.5	2.0	8
5/60/Pt/300/N	26.5/531.2	2.2	3
5/60/TiN/300/N	26.3/530.8	2.0	4
5/60/Pt/450/N	26.3/531.2	2.0	2
5/60/TiN/450/N	26.4/531.1	1.9	3
6/60/Pt/300/N	26.4/531.2	2.0	8
6/60/TiN/300/N	26.0/530.8	2.0	8
1/120/Pt/250/Y	26.5/531.5	2.2	8
1/120/TiN/250/Y	26.5/531.5	2.0	10
2/80/Pt/200/Y	26.5/531.3	2.0	5
2/80/TiN/200/Y	26.5/531.2	2.0	6
2/80/TiN/300/Y	26.3/531.3	1.9	6
3/80/Pt/200/Y	26.5/531.5	2.3	3
3/80/TiN/200/Y	26.5/531.5	2.2	2
4/80/Pt/200/Y	26.3/531.2	2.0	5
4/80/TiN/200/Y	26.2/531.2	2.0	6
5/80/Pt/200/Y	26.5/531.5	2.1	3
5/80/TiN/200/Y	26.5/531.5	2.2	5
6/80/Pt/200/Y	26.1/531.0	2.0	9
6/80/Pt/300/Y	26.4/531.5	2.0	9
6/80/TiN/200/Y	26.4/531.5	2.0	8

[a] Precursor number/precursor temperature (°C)/substrate/substrate temperature (°C)/catalyst present (Y) or absent (N). In all cases reported, the carrier gas was oxygen at a flow rate of 50 mL min^{-1}. [b] Binding energy for Ta $4f_{7/2}$ or O 1s peak in XPS. [c] Oxygen:tantalum 1 atom ratio. [d] Atom % of total carbon impurity.

Tantalum oxide films are quickly contaminated with carbon (apparently hydrocarbon) on exposure to the atmosphere, and it is therefore difficult to find the carbon impurity level arising directly from the CVD process. Table 2 gives XPS analytical data for selected films of Ta_2O_5 grown on TiN(100) and Pt(111) substrates, after 2 min of sputtering to remove adventitious surface carbon. The same analytical procedure was used for a sample of a film of Ta_2O_5 grown by anodic oxidation in a "carbon-free" environment, and it gave a carbon content of 7 at. %, in the same range as the films grown by CVD (Table 2). The carbon contents listed are therefore upper limits on the impurities introduced in the actual CVD process. However, some carbon impurity does appear to arise from the CVD as shown by more detailed analysis of the C 1s peak. At high resolution, the C 1s impurity peak for tantalum oxide films grown using oxygen carrier gas resolved into three components at 285.0 eV (graphitic carbon), with weaker peaks at 286.4 eV (C−O, similar to values in organic alcohols)[24] and 288.3 eV (C=O, similar to values in ketones).[24] The higher binding energy peaks were much weaker or

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absent in films grown under the same conditions but using carrier gas nitrogen or hydrogen and were also absent in the film grown by anodic oxidation. These impurity peaks therefore arise from carbon introduced during the CVD process whereas the graphitic carbon is probably largely due to contamination following exposure of the films to air. For CVD under hydrogen, a minor carbon peak was observed at 283 eV and is tentatively assigned to carbide. In most cases (Table 2), there was little difference in carbon contamination for films grown on TiN(100) or Pt(111) surfaces, so the catalytically active platinum surface does not affect the growth.[25] In a few films formed from precursor **1**, study of the films by SEM showed the presence of carbon particles on the surface of the film. These black clusters are not unprecedented and have been reported to be caused by incomplete thermal decomposition of the precursor,[16h] perhaps indicating significant gas-phase decomposition and nucleation under these conditions.[27b]

No fluorine was detected by XPS in any of the films. Therefore, the CF_3 or C_3F_7 groups present in the precursors **3**, **4**, and **6** do not lead to detectable fluorine incorporation into the films.

Effect of Carrier Gas. In CVD experiments using $[Ta(OEt)_5]$ as precursor, Oehrlein[11a] has shown that Ta_2O_5 deposited in the presence of dry oxygen favors formation of smooth, defect free surfaces. When wet oxygen or wet argon was used to aid the deposition, films with a great density of pinholes were formed. These surface defects cause early breakdown in the electrical properties of the films, particularly to a high leakage current. Kimura et al.[26] showed that the addition of water to the carrier gas contributes to the pinhole growth observed for Ta_2O_5 films annealed below 600 °C. The as-deposited films are typically oxygen-deficient but give the expected O:Ta ratio of 2.5 after annealing under oxygen at 600 °C.

To study the effect on the formation of Ta_2O_5 films, as a function of carrier gas and of the precursor, CVD reactions were carried out using a Pt(111) substrate heated to 300 °C, the precursor reservoir at 80 °C, and a carrier gas flow rate of 50 mL min^{-1}. Under these conditions the precursor **1** failed to give useful films, but data were obtained using each precursor **2**−**6**. For all precursors, the as-deposited films grown with oxygen carrier gas gave O:Ta ratio of 2.0 ± 0.1 while this ratio was 1.1 ± 0.2 for films grown using nitrogen or hydrogen as carrier gas. In all cases, annealing under oxygen at 600−800 °C for 4 h gave O:Ta = 2.5 as expected for Ta_2O_5. There was no major color change on annealing. The level of carbon impurity in the films was low in all cases but was lowest on average in films grown using hydrogen carrier gas (Table 2). It is likely that hydrogen can react with intermediates to give free alcohol and β-diketone by hydrogen atom donation, as observed in several related CVD processes.[27] In the present case, the difference in carbon impurity level is modest and CVD under oxygen has the advantage of giving films with less oxygen deficiency.

Effect of Substrate and Annealing the Film. For electrical applications, postdeposition annealing in an oxidizing atmosphere after Ta_2O_5 deposition is needed to reduce the leakage current of the resulting samples, arising from defect states in the Ta_2O_5 films. Annealing the sample in air or oxygen improves the ratio of oxygen to tantalum and reduces the oxygen vacancies in the oxide.[28]

While as-deposited films of tantalum oxide were amorphous by XRD, annealing under oxygen for 4 h at 600−800 °C of Ta_2O_5 films grown on a platinum substrate gave crystalline films, identified as δ-Ta_2O_5 (Figure 3).[29] In previous studies, δ-Ta_2O_5 was obtained by CVD on silicon,[3] but β-Ta_2O_5 was obtained by CVD on silicon dioxide.[30] For the films grown on platinum-(111), the film was oriented preferentially in the ⟨100⟩ plane so the growth was not epitaxial but may still be determined by matching with the substrate lattice.[29]

The activation energy for surface diffusion in Ta_2O_5 has been reported as 0.74 eV, and the effective temperature for the onset of nucleation of crystallites in Ta_2O_5 is 264.5 °C. Hence the presence of some crystalline character might be expected for films grown at 300 °C or higher. However, no crystalline character could be detected either by XRD or SEM in these films when grown either on platinum or on titanium nitride at 300−450 °C.

Electrical Properties. Electrical measurements were carried out on films of Ta_2O_5 grown from the precursor **4** on Pt(111) or TiN(100) at 300 °C using oxygen carrier gas. The film thickness was determined to be 1 μm by TEM measurement, and results were averaged for three measurements on each capacitor. The dielectric constant at 1 MHz was 27 ± 1 or 25 ± 4 for films on Pt or TiN, respectively, in the range found for Ta_2O_5 of 25−30.[32] The electrical measurements on the TiN(100) substrate were difficult since TiN provides a poor contact with the top electrode used in the measurements and the reproducibility was poorer than for the measurements on Pt(111). Measurements were made for films on TiN grown at temperatures from 300 to 450 °C, but no significant change was observed.

Catalyst-Enhanced CVD. A number of enhancement methods have been developed for CVD processes, and among them is catalyst-enhanced CVD (CECVD), in which co-deposition of a catalytically active metal

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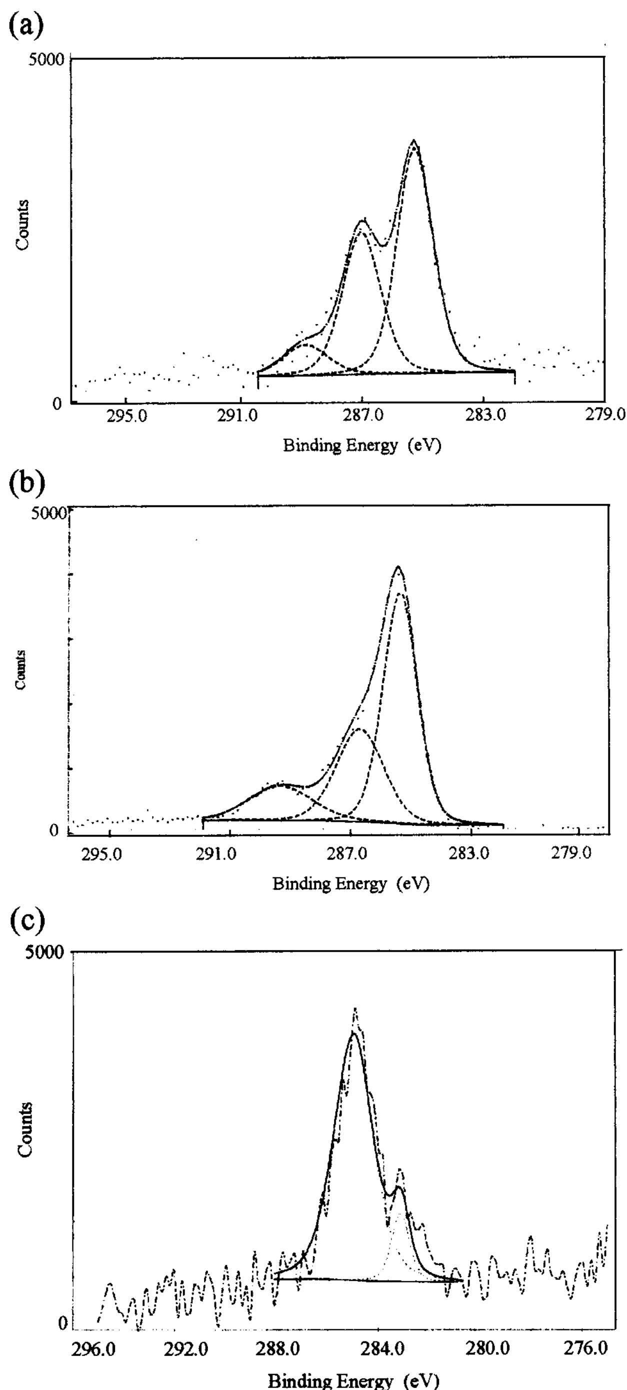

Figure 3. Carbon 1s peaks in the XPS spectra of tantalum oxide films: (a) using oxygen carrier gas; (b) using nitrogen carrier gas; (c) using hydrogen carrier gas. Note the decrease in higher binding energy peaks due to C=O and C−O groups on going from (a) to (b) and appearance of a lower binding energy peak, tentatively assigned to carbide, in (c).

such as palladium can enhance the CVD of other materials.[33] The basis is that palladium is a highly active catalyst for hydrogenation and oxidation and also yields a very active surface for CVD.[25,33,34] The complex [Pd(η^3-2-methylallyl)(acac)], **7**, (acac = acetylacetonate) is particularly useful for catalyst- enhanced CVD and was used in the following experiments.[33]

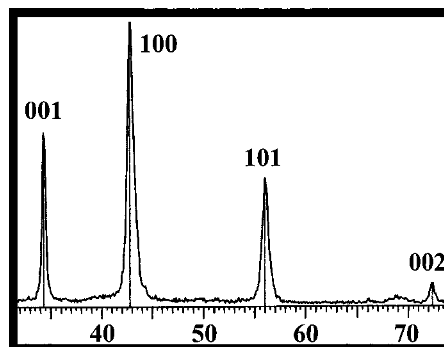

Figure 4. XRD of a film of Ta_2O_5 grown from **4** on Pt(111) at 300 °C and then annealed at 800 °C under oxygen for 4 h. Angles 2Θ are given for chromium Kα radiation and for a randomly oriented film the intensities of the (001) and (100) peaks would be equal.

Films of Ta_2O_5 were grown as before but with the addition of the precursor **7**, which was delivered to the substrate through a separate inlet using nitrogen carrier gas at ambient temperature. Prior seeding of the substrate with palladium followed by thermal CVD of the tantalum precursors showed no catalytic effect, thus showing that the co-deposition is important. For each precursor **1**−**6**, films of Ta_2O_5 could be grown using oxygen as the main carrier gas at 200 °C on either Pt(111) or TiN(100) by CECVD whereas temperatures of at least 300 or 350 °C were required for simple CVD using **2**−**6** or **1**, respectively, as described above. The morphology of the films as studied by SEM and electrical properties were the same as in thermal CVD, and the palladium content of the films was too low to detect by XPS (<0.5%). The catalyst effect is similar to that observed previously, but the observation of formation of dense films of Ta_2O_5 in this case differs from the case of CECVD of yttria or zirconia which yields porous films.[33]

Mechanistic Studies. The volatile products from CVD of Ta_2O_5 on TiN(100) at 350 °C using oxygen carrier gas and the precursor [Ta(OEt)$_4$(acac)], **2**, were collected in a liquid nitrogen cooled trap and analyzed by FTIR and GC-MS. The products identified were H_2O, CO_2, EtOH, and $MeCOCH_2COMe$ along with numerous unidentified organics. The observation of CO_2 and H_2O indicates that exhaustive oxidation of organic fragments occurs in the oxygen carrier gas under these conditions.[35,36] The same products were observed in CECVD in the presence of the precursor **7**, but under these conditions, traces of acetaldehyde, 2-methylpropene, and diethyl ether were also detected. The 2-methylpropene is presumably derived from the 2-methylallyl substitu-

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ent of **7**, while the acetaldehyde may be derived from a β-elimination reaction of an ethoxytantalum group. Since the major products are formed by combustion of the organics in both cases, it is difficult to draw conclusions about the primary steps in CVD.

Conclusions

The complexes $[Ta(OEt)_4(\beta\text{-diketonate})]$, **2**–**6**, are shown to be good precursors for CVD of films of tantalum(V) oxide and give thermal CVD at slightly lower temperature than the commonly used precursor $[\{Ta(OEt)_5\}_2]$, **1**. In all cases, the CVD gives amorphous films of Ta_2O_5, which crystallize on annealing to 600–800 °C under oxygen for about 4 h. Promotion of film formation is established using CECVD with a palladium precursor as “catalyst” and the minimum CVD temperature is then reduced to 200 °C.

Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere by using a glovebox and/or standard Schlenk techniques. All solvents were dried and degassed prior to use. ^1H, $^{13}C\{^1H\}$, and $^{19}F\{^1H\}$ spectra were recorded using a Varian Gemini 300 MHz NMR spectrometer and are referenced to TMS or $CFCl_3$. Infrared spectra were measured using a Perkin-Elmer System 2000 FT-IR spectrometer. All mass spectra were recorded using a Finnigan MAT 8200 spectrometer. The thermogravimetric analysis (TGA) was carried out using a Perkin-Elmer TGA7 instrument. Film analysis was carried out by X-ray photoelectron spectroscopy (XPS) using a Surface Science Laboratory Model SSX-100 small spot X-ray photoelectron spectrometer with a monochromatized Al Kα photon source. Samples were studied before and after a 2 min sputter period. Sputtering removes surface carbon but also causes partial reduction of Ta(V). Scanning electron microscopy (SEM) analysis was carried out using a Hitachi S-4500 field emission scanning electron microscope, and transmission electron microscopy (TEM) images were obtained using a Phillips CM 20 STEM microscope. X-ray diffraction (XRD) patterns were collected with a 12 kW Rigaku Rotaflex model RV-200B with a chromium rotating anode and a Rigaku goniometer with a thin film attachment. Electrical characterization was carried out by depositing gold (Au) top electrodes by vacuum evaporation in an Edwards E306 evaporator onto the CVD films. Each electrode measured 430 μm in diameter, giving a capacitor area of $A = 1.4 \times 10^{-7}$ m^2. Since the films covered the entire substrate, no direct contact to the bottom was made. As a result, two capacitors were tested in series using an LCR meter (Hewlett-Packard 4284A). Gas chromatographic–mass spectrometric (GC-MS) studies were carried out using a Varian 3400 gas chromatograph equipped with a DB5 column and a Finnigan MAT 8200 mass spectrometer.

Preparation of Complexes. *[Ta(OEt)4(hfac)], **3**.* 1,1,1,6,6,6-Hexafluoro-2,4-pentanedione (0.348 mL, 2.46 mmol) (hfac) was added to a stirred solution of $[Ta(OEt)_5]$ (0.648 mL, 2.46 mmol) in THF (5 mL) cooled to −78 °C. The mixture was stirred for 8 h, and the solvent was removed in vacuo to give a light yellow liquid in 61% yield. NMR in $CDCl_3$: $\delta(^1H) = 1.01$ [t, $^3J_{HH} = 7$ Hz, 6H, CH_3CH_2O]; 1.19 [t, $^3J_{HH} = 7$ Hz, 6H, CH_3CH_2O]; 4.07 [q, $^3J_{HH} = 7$ Hz, 4H, CH_3CH_2O]; 4.56 [q, $^3J_{HH} = 7$ Hz, 4H, CH_3CH_2O]; 6.17 [s, 1H, OCCHCO); $\delta(^{13}C) = 18.20$ [CH_3CH_2O]; 18.84 [CH_3CH_2O]; 66.75 [CH_3CH_2O]; 70.97 [CH_3CH_2O]; 92.05 [OCCHCO]; 116.82 [q, $^1J_{CF} = 284$ Hz, $OCCF_3$]; 177.55 [q, $^2J_{CF} = 36$ Hz, $OCCF_3$); $\delta(^{19}F) = -76.80$ [s, $OCCF_3$). MS: m/z calcd for $Ta(OEt)_3(hfac) = 523.04$; found 523.04. Calculated mass M, $[Ta(OEt)_4(hfac)] = 568.08$ amu: 523.04 $[M - OEt]^+$; 497.0 $[M - OEt - HCCH]^+$; 443.0 $[C_8F_4H_{10}O_5Ta]^+$; 361.1 $[C_6F_2H_6O_4Ta]^+$; 335.0 $[C_4F_2H_4O_4Ta]^+$; 267.0 $[CF_2H_4O_2Ta]^+$; 217.0 $[H_4O_2Ta]^+$.

*[Ta(OEt)4(tfac)], **4**.* To a stirred solution of $[Ta(OEt)_5]$ (0.641 mL, 2.46 mmol) in CH_2Cl_2 (10 mL) was added 1,1,1-trifluoro-2,4-pentanedione (0.299 mL, 2.46 mmol). The yellow solution was allowed to stir at room temperature for 3 h. The solvent was removed in vacuo along with the ethanol byproduct, leaving the product as a pale yellow liquid, which was purified by distillation under vacuum at 65 °C/0.1 Torr. Yield: 86%. NMR in $CDCl_3$: $\delta(^1H) = 1.05$ [t, $^3J_{HH} = 7$ Hz, 6H, CH_3CH_2O]; 1.23 [t, $^3J_{HH} = 7$ Hz, 3H, CH_3CH_2O]; 1.27 [t, $^3J_{HH} = 7$ Hz, 3H, CH_3CH_2O]; 2.23 [s, 3H, $COCH_3$]; 4.08 [q, $^3J_{HH} = 7$ Hz, 4H, CH_3CH_2O]; 4.57 [q, $^3J_{HH} = 7$ Hz, 2H, CH_3CH_2O]; 4.59 [q, $^3J_{HH} = 7$ Hz, 2H, CH_3CH_2O]; 5.88 [s, 1H, OCCHCO]; $\delta(^{13}C) = 17.82$ (CH_3CH_2O]; 17.93 [CH_3CH_2O]; 18.10 [CH_3CH_2O]; 27.94 [$OCCH_3$]; 65.81 [OCH_2CH_3]; 69.81 [OCH_2CH_3]; 69.88 [OCH_2CH_3]; 97.61 [OCCHCO]; 117.85 [q, $^1J_{CF}$= 283 Hz, CF_3]; 169.38 [q, $^2J_{CF}$=34 Hz, $OCCF_3$]; 198.07 [$OCCH_3$); d(^{19}F) −75.86 [s, CF_3). MS: m/z calcd for exact mass calculation $[Ta(OEt)_3(tfac)] = 469.06$; found 469.06. Calculated mass M, $[Ta(OEt)_4(tfac)] = 514.06$ amu: 499.1 $[M - CH_3)^+$; 469.06 $[M - OEt]^+$; 424.0 $[M - OEt - OEt]^+$; 361.1 $[C_7H_{13}O_4FTa]^+$; 314 $[C_6H_{13}O_3Ta]^+$; 273 $[C_4H_{12}O_2Ta]^+$; 183 $[TaH_2]^+$; 139 $[C_4F_3H_3O_2]^+$.

*[Ta(OEt)4(dpm)], **5**.* To a stirred solution of $[Ta(OEt)_5]$ (0.641 mL, 2.46 mmol) in THF (10 mL) was added 2,2,6,6-tetramethyl-3,5-heptanedione (0.513 mL, 2.46 mmol). The mixture was refluxed for 4 h. After removal of the solvent and the alcohol byproduct in vacuo, the viscous yellow liquid was purified by vacuum distillation and obtained in 82% yield. NMR in $CDCl_3$: $\delta(^1H) = 0.94$ [t, $^3J_{HH} = 7$ Hz, 6H, CH_3CH_2O]; 1.09 [s, 18H, $C(CH_3)_3$]; 1.19 [t, $^3J_{HH} = 7$ Hz, 6H, CH_3CH_2O]; 3.95 [q, $^3J_{HH} = 7$ Hz, 4H, CH_3CH_2O]; 4.49 [q, $^3J_{HH} = 7$ Hz, 4H, CH_3CH_2O]; 5.75 [s, 1H, OCCHCO); $\delta(^{13}C) = 18.22$ [OCH_2CH_3]; 18.86 [OCH_2CH_3]; 27.86 [$C(CH_3)_3$]; 40.48 [$C(CH_3)_3$]; 64.74 [OCH_2CH_3]; 68.34 [OCH_2CH_3]; 92.71 [OCCHCO]; 199.53 [OCCHCO). MS: m/z calcd for $Ta(OEt)_3(dpm) = 499.18$; found 499.18. Calculated mass M, $[Ta(OEt)_4(dpm)] = 544.0$ amu. Obsd: 499.18 $[M - OEt]^+$; 454.0 $[M - OEt - OEt]^+$; 443.1 $[C_{13}H_{26}O_5Ta]^+$; 361.1 $[C_8H_{20}O_4Ta]^+$; 305.0 $[C_4H_{12}O_4Ta]^+$; 277.0 $[C_2H_8O_4Ta]^+$; 249.0 $[H_4O_4Ta]^+$.

*[Ta(OEt)4(fod)], **6**.* To a stirred solution of $[Ta(OEt)_5]$ (0.641 mL, 2.46 mmol) dissolved in THF (10 mL) was added 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionate (0.570 mL, 2.46 mmol), and the resulting mixture was refluxed for 3 h. Removal of solvent by evaporation and purification of the resulting product gave a yellow liquid in 74% yield. NMR in $CDCl_3$: $\delta(^1H)$ 1.06 [t, $^3J_{HH} = 7$ Hz, 6H, CH_3CH_2O]; 1.11 [s, 9H, $C(CH_3)_3$]; 1.26 [t, $^3J_{HH} = 7$ Hz, 3H, CH_3CH_2O]; 1.29 [t, $^3J_{HH} = 7$ Hz, 3H, CH_3CH_2O]; 4.06 [q, $^3J_{HH} = 7$ Hz, 2H, CH_3CH_2O]; 4.07 [q, $^3J_{HH} = 7$ Hz, 2H, CH_3CH_2O]; 4.58 [q, $^3J_{HH} = 7$ Hz., 2H, CH_3CH_2O]; 4.62 [q, $^3J_{HH} = 7$ Hz, 2H, CH_3CH_2O]; 6.09 [s, 1H, OCCHCO); $\delta(^{13}C)$ 17.91 [CH_3CH_2O]; 18.44 [CH_3CH_2O]; 18.84 [CH_3CH_2O]; 27.56 [$C(CH_3)_3$]; 42.09 [$C(CH_3)_3$]; 65.68 [CH_3CH_2O]; 69.61 [CH_3CH_2O]; 69.84 [CH_3CH_2O]; 95.00 [OCCHCO]; 109.88 [t, $^1J_{CF} = 267$ Hz, $CF_2CF_2CF_3$),111.18 [t, $^1J_{CF} = 261$ Hz, $CF_2CF_2CF_3$]; 118.13 [q, $^1J_{CF} = 290$ Hz, $CF_2CF_2CF_3$); $\delta(^{19}F)$ −126.50 [s, $CF_2CF_2CF_3$]; −119.67 [q, $^3J_{F-F} = 9$ Hz, $CF_2CF_2CF_3$]; −80.80 [t, $^3J_{F-F} = 9.4$ Hz, $CF_2CF_2CF_3$). MS: m/z calcd for $Ta(OEt)_3(fod) = 611.11$; found 611.11. Calculated mass M, $[Ta(OEt)_4(fod)] = 656.149$ amu: 611.11 $[M - OEt]^+$; 566.1 $[M - OEt - OEt]^+$; 499.1 $[C_{13}F_4H_{22}O_4Ta]^+$; 469.0 $[C_{11}F_4H_{16}O_4Ta]^+$; 443.0 $[C_9F_4H_{14}O_4Ta]^+$; 361.1 $[C_9H_8O_4Ta]^+$; 335.1 $[C_4H_{10}O_4Ta]^+$; 245.0 $[TaO_4)^+$; 169 $[C_3F_7]^+$.

Chemical Vapor Deposition Procedure. CVD was carried out using a vertical cold-wall reactor under reduced pressure with dynamic pumping. A sidearm allowed introduction of carrier gas. The substrate was heated by using a temperature-controlled heating rod. Deposition times were typically 2 h. In CECVD experiments, the catalyst precursor [Pd(2-methylallyl)(acac)] was introduced to the reactor from a second sidearm, using nitrogen carrier gas. Specific conditions are listed in the text and Table 2.

After deposition, thermal annealing under oxygen of some of the films was carried out at 800 °C by using a tube furnace; typically samples were heated for 4 h in a slow oxygen stream.

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