Chemical Vapor Deposition of Iridium, Platinum, Rhodium and Palladium

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This article reviews the progress in the chemical vapor deposition of iridium, platinum, rhodium and palladium metals. In the course of the last decade the number of articles on CVD of this group of metals has increased significantly. A wide variety of metal organic complexes have been investigated as potential precursors and appreciable results have been obtained. However, some aspects such as low deposition rates and impurity incorporation into the films still remain as concerns in this area. The representative results on CVD of these metals are presented according to the type of metal organic complexes used.

1. Introduction

Chemical vapor deposition (CVD) of noble metals has a great significance for practical applications in electronics, protective coating and catalyst industries.[1–4] The potentiality of applications is due to the valuable combination of the intrinsic properties of these metals, including high thermal/chemical stability, high electrical conductivity and catalytic activity. Thick enough coatings of fully dense morphology are essential to offer an effective corrosion/oxidation protection. On the other hand, high-purity deposits of controllable and reproducible uniform thickness or particle size are required to perform adequately in device or catalyst applications. The success of CVD strongly depends on the availability of suitable precursors having high volatility, thermal stability and clean decomposition. Most of the precursors employed in CVD of noble metals are metal organic complexes. Many of these complexes have been specifically synthesized to fulfill the demands of a given CVD process. Excellent comprehensive reviews describing the synthesis and characterization of a wide variety of metal organic complexes with the possibility to be used in CVD have been reported.[5–10] A great effort has been made in developing viable technologies for CVD of iridium, platinum, rhodium and palladium. Thus, a considerable number of publications report results on new and existing complexes used in CVD and the quality of the deposits obtained. Here, an overview of the available literature on CVD of iridium, platinum, rhodium and palladium metals is presented. The CVD operating conditions and their effects on the purity of the deposits and the deposition rates achieved by each specific chemical complex are discussed.

2. Chemical Vapor Deposition of Iridium

CVD of iridium is of interest to prepare oxidation protective coatings on structural graphite for temperatures above 1773 K because of the compatibility of iridium with carbon materials (*i.e.* no carbide formation). CVD of iridium is also attractive to prepare contacts and offers excellent

potential for producing radiation damage-free electrodes with a high degree of conformal coverage. We have shown that iridium and platinum electrode films can be epitaxially grown by CVD. Table 1 indicates the variety of chemical complexes that have been used to yield iridium, platinum, rhodium and palladium deposits by CVD. The CVD operating conditions for iridium and the quality of the deposits are given in Table 2.

2.1 Iridium halides

CVD of iridium was early investigated to prepare iridium coatings on graphite for oxidation protection by using iridium halides such as $IrCl_3$, $IrCl_4$, $IrBr_3$ and IrF_6. Iridium coatings prepared by hydrogen reduction of iridium halides were typically of high-purity; however, the deposition temperature needed to be relatively high, above 973 K.[11] The use of $IrCl_3$ and CO provided deposition rates about 7.05×10^{-2} nm·s⁻¹.[12] A more volatile molecule such as the ethyl-alcohol (C_2H_5OH) led much higher deposition rates, up to 1.22 nm·s⁻¹. Although IrF_6 was advantageous to attain even higher deposition rates of about 3.33 nm·s⁻¹, it attacked the graphite substrate and caused rough, pitted or powdery deposits.[11–13] Fluoridation of iridium powder to form IrF_6, seemed to be a better route to produce thick (30–70 μm thick) and non-porous coatings on graphite and metallic substrates.[14] Nevertheless, the high temperature required for deposition and the problems originated by the corrosive action of iridium halides made them unattractive as precursors for CVD of iridium.

2.2 β-diketonate iridium complexes

Metal β-diketonate complexes are recognized as prospect CVD precursors because of their advantageous combination of thermal stability and volatility. Iridium acetylacetonate, $Ir(acac)_3$, exhibits the highest thermal stability among the acetylacetonates of the platinum group metals.[5] Conveniently, it sublimes without significant decomposition at 453–473 K[15] and then it decomposes in an oxygen atmosphere above 525 K.[6] Thus, $Ir(acac)_3$ has become one of the most common complexes for CVD of iridium (see Table 2). The thermal properties of $Ir(acac)_3$ have been published.[5,6,16] Thick iridium coatings (about 50 μm thick) for oxidation protection have been achieved at comparatively high deposition rates up to 6.94 nm·s⁻¹.[16] Nevertheless, one significant

Table 1   Chemical complexes employed in CVD of iridium, platinum, rhodium and palladium.

	Iridium	Platinum	Rhodium	Palladium
metal halides	$IrCl_3$			$PdCl_2$
	$IrCl_4$			
	$IrBr_3$			
	IrF_6			
metal β-diketonates	$Ir(acac)_3$	$Pt(acac)_2$	$Rh(acac)_3$	$Pd(acac)_2$
	$(acac)Ir(1,5\text{-}COD)$	$Pt(hfac)_2$	$Rh(tfac)_3$	$Pd(hfac)_2$
	$(hfac)Ir(1,5\text{-}COD)$	$[PtMe_3(acac)]_2$		
	$(thd)Ir(1,5\text{-}COD)$			
carbonyl complexes	$[Ir(\mu\text{-}SC(CH_3)_3)(CO)_2]_2$	$Pt(CO)_2Cl_2$	$Rh_2Cl_2(CO)_4$	
		$(MeCp)Pt(CO)$	$(acac)Rh(CO)_2$	
			$(thd)Rh(CO)_2$	
			$(hfac)Rh(CO)_2$	
allyl complexes	$Ir(allyl)_3$	$Pt(allyl)_2$	$Rh(allyl)_3$	$Pd(allyl)_2$
		$CpPt(allyl)$	$Rh(allyl)(CO)_2$	$Pd(Me\ allyl)_2$
				$CpPd(allyl)$
				$Pd(allyl)(acac)$
				$Pd(allyl)(hfac)$
				$Pd(Me\ allyl)(hfac)$
				$Pd(Me\ allyl)(acac)$
cyclopentadienyl complexes		$(Cp)PtMe_3$	$(Cp)Rh(CO)_2$	
		$(MeCp)PtMe_3$		
cyclooctadienyl complexes	$(Cp)Ir(1,5\text{-}COD)$	$(1,5\text{-}COD)PtMe_2$	$(Cp)Rh(1,5\text{-}COD)$	
	$(MeCp)Ir(1,5\text{-}COD)$	$(1,5\text{-}COD)PtMe(Cp)$		
	$[Ir(methoxide)(1,5\text{-}COD)]_2$	$(1,5\text{-}COD)PtMeCl$		
	$[Ir(acetate)(1,5\text{-}COD)]_2$	$(1,5\text{-}COD)PtMe(allyl)$		
	$(keim)Ir(1,5\text{-}COD)$			
	$(hfda)Ir(1,5\text{-}COD)$			
	$(amak)Ir(1,5\text{-}COD)$			
alkyl complexes		$PtMe_2(MeNC)_2$		$PdMe_2(PMe_3)_2$
		$PtMe(allyl)(MeNC)_2$		$PdMe_2(PEt_3)_2$
		$PtMe(vinyl)(MeNC)_2$		$PdMe_2(tmeda)$
		$PtMe(t\text{-}BuC{\equiv}C)(MeNC)_2$		
metal carboxylate				$Pd(acetate)_2$
metal phosphines		$Pt(PF_3)_4$	$[Rh(PF_3)_2Cl]_2$	
ethylene complexes	$CpIr(C_2H_4)_2$		$CpRh(C_2H_4)_2$	$Pd(C_2H_4)_2$

acac = acetylacetonate = $C_5H_7O_2$
hfac = hexafluoroacetylacetonate = $C_5HO_2F_6$
thd = tetramethylheptanedionate = $C_{10}H_{20}O_4$
1,5-COD = 1,5 cyclooctadienyl = C_8H_{12}
Me = methyl = CH_3
allyl = η^3-C_3H_5
Cp = cyclopentadienyl = η^5-C_5H_5
acetate = $C_2H_3O_2$
methoxide = CH_3O
keim, hfda, amak = fluorinated amino alcohol ligands
t-BuC$\equiv$C = tert-butylethynyl = C_6H_9
Et = ethyl = C_2H_5
PEt_3 = triethyl-phosphine = $(C_2H_5)_3P$
PMe_3 = trimethyl-phosphine = $(CH_3)_3P$
tmeda = tetramethylethylenediamine = $C_6H_{12}N_2H_2$
vinyl = C_2H_4

Table 2 CVD operating conditions for iridium.

Chemical complex	Activation	Substrate temperature/K	Gas present	Impurities	Deposition rate /nm·s^{-1}	Ref.
IrCl$_3$, IrCl$_4$, IrBr$_3$	thermal	1073–1273	Ar	high-purity		[12]
IrCl$_3$, IrCl$_4$, IrBr$_3$		973	H$_2$	"		[12]
IrCl$_3$			CO–H$_2$O	"	7.05×10^{-2}	
IrCl$_3$			CO–H$_2$–C$_2$H$_5$OH	"	1.22	
IrF$_6$		1073	Ar, H$_2$	"	3.33	[14]
Ir(acac)$_3$	thermal	973	vacuum, Ar	C (% not specified)	6.94	
		673–873	O$_2$	C- and O-free	2–5×10^{-2}	[17], [19]–[21]
		643–823	H$_2$			[24]
(acac)Ir(1,5-COD)	thermal	873	H$_2$	1 mass%C and O		[25]
(thd)Ir(1,5-COD)	thermal	623	H$_2$		6.9×10^{-2}	[26]
(hfac)Ir(1,5-COD)	thermal	523–623	H$_2$		2.5×10^{-1}	[27]
[Ir(μ-SC(CH$_3$)$_3$)(CO)$_2$]$_2$	thermal	423–723	H$_2$	1 mass%S (>673 K)		[28]
Ir(allyl)$_3$	thermal	373	H$_2$	<2 mass%O		[30]
			vacuum	13–17 mass%C	2.8×10^{-2}	[31]
			H plasma	<3 mass%C	1.7×10^{-3}	[31]
(Cp)Ir(1,5-COD)	thermal	973			1.7×10^{-1}	[12]
		393	H$_2$	<1 mass%C	2.7×10^{-3}	[32]
		543	O$_2$	<1 mass%C, O	7.0×10^{-3}	[32]
		863	vacuum	80 mass%C		[32]
(MeCp)Ir(1,5-COD)	thermal	393	H$_2$	<1 mass%C	2.5×10^{-2}	[32]–[33], [35]
		523–973	O$_2$	<1 mass%C, O	1–7×10^{-2}	[32]–[33], [35],[37]
		953	vacuum	82–87 mass%C	2.5×10^{-1}	[32]–[33]
		550–723 (direct liquid injection)	O$_2$	high-purity	1.17	[34], [36]
[Ir(acetate)(1,5-COD)]$_2$	thermal	523	vacuum	<1 mass%C, O	8×10^{-3}	[32]
[Ir(methoxide)(1,5-COD)]$_2$	thermal	873	H$_2$	90–95 mass%Ir		[25]
(keim)Ir(1,5-COD)	thermal	623–673	O$_2$	<2 mass%O		[40]
(hfda)Ir(1,5-COD)	thermal	623–673	O$_2$	<2 mass%O		[40]
(amak)Ir(1,5-COD)	thermal	623–673	O$_2$	<2 mass%O		[40]
CpIr(C$_2$H$_4$)$_2$	laser	room temp	H$_2$, He	<1 mass%C		[41]

drawback is the carbon contamination arising from the decomposition of the acac ligand, leading to porous coatings when exposing to air at high temperatures.

We have investigated the CVD of iridium using Ir(acac)$_3$ complex, with particular attention on the effect of oxygen gas addition on the morphology and purity of the films.[17] Iridium films prepared without oxygen addition invariably contained carbon. TEM observations revealed that the films consisted of iridium clusters (1–4 nm in diameter) surrounded by amorphous carbon. The carbon content was estimated to be about 20 mass%C. As a practical application, it was found that this kind of films (iridium-carbon nano-composite) exhibit excellent electric and catalytic performance as electrodes for zirconia solid electrolytes, particularly, at temperatures below 873 K.[18] The electrical conductivity associated to the electrode/electrolyte interface was superior to that showed by conventional platinum paste electrodes. This behavior could be attributed to the favorable high surface area and enhanced catalytic activity exhibited by the small clusters.

On the other hand, the addition of oxygen was effective to suppress carbon incorporation into iridium films prepared from Ir(acac)$_3$.[19] Thus, high-purity films with no detectable

signals of carbon or oxygen could be obtained by controlling the oxygen flow rate to avoid formation of IrO$_2$. As a result of the oxygen presence, lower deposition temperatures were attained, although deposition rates were inevitably low (0.02–0.05 nm·s^{-1}), for temperatures higher than 823 K. Additionally, it was demonstrated that high-purity films can be grown in epitaxial mode on MgO and α-Al$_2$O$_3$ single-crystal substrates.[20] Then, epitaxially grown iridium films on α-Al$_2$O$_3$ were successfully utilized as intermediate electrodes for epitaxial growth of AlN films for electronic device applications.[21] Iridium films have been investigated also as electrical contacts to oxide high-temperature superconductors and protective coatings for the anodes in the electrolysis of seawater.[22,23]

It has been confirmed that the addition of oxygen reduces considerably the carbon contamination and improves the film morphology. High-purity iridium films (<1 mass%C, O) were obtained by introducing oxygen during the film growth, maintaining the precursor at 453 K.[15] Hydrogen gas has been used to a lesser extent as a reactive gas for Ir(acac)$_3$.[23,24] Therefore, it is difficult to assess the effect of hydrogen on the level of carbon impurity in films prepared from Ir(acac)$_3$.

Mixed ligand β-diketonate complexes such as (acac)Ir(1,5-

COD) and (thd)Ir(1,5-COD) are able to produce high-purity iridium films (about 1 mass%C and O) by using hydrogen as a reactive gas.[25,26] Particularly, the (thd)Ir(1,5-COD) complex yields deposition rates about 6.9×10^{-2} nm·s^{-1}, in spite of its lower volatility.[26] In contrast, (hfac)Ir(1,5-COD) provides much higher deposition rates of about 0.25 nm·s^{-1} by heating the complex at 333–338 K.[27] Mixed ligand β-diketonates are feasible CVD precursors because they exhibit high volatility and stability in air and are easy to handle. Complexes containing hfac and thd groups sublime favorably without decomposition at 333–343 K and 7.2 Pa, while complexes containing acac ligands melt with undesirable decomposition.[25-27]

In conclusion, high-quality iridium films can be obtained using this group of complexes, specially Ir(acac)$_3$, although its potential application is limited due to the low deposition rate obtained to date.

2.3 Carbonyl iridium complex

The tetracarbonyl bis(μ-SC(2-methyl-2-propane-thiolato))diiridium complex, [Ir(μ-SC(CH$_3$)$_3$)(CO)$_2$]$_2$, has a melting point of 401 K and its decomposition starts around 433 K under helium or hydrogen atmospheres.[28] This complex, stable in air and moisture, can produce high-purity films (1 mass%S) at 723 K by adding hydrogen gas and heating the complex at 383 K. Carbon-supported iridium catalysts have been prepared using this carbonyl complex.[29]

2.4 Allyl iridium complex

Iridium allyl, Ir(allyl)$_3$, is the only complex containing the allyl ligand that has been investigated for iridium deposition. The decomposition of Ir(allyl)$_3$ in vacuum produced amorphous iridium films containing considerable carbon impurity (13–17 mass%C). The addition of hydrogen gas yielded carbon-free iridium films with only traces of oxygen impurity (<2 mass%O); nevertheless, films exhibited an amorphous nature.[30] Alternatively, the use of hydrogen plasma resulted in the formation of crystalline films with a low carbon content (<3 mass%C).[31] Deposition rates varied from 2.8×10^{-2} nm·s^{-1} in vacuum to 1.7×10^{-3} nm·s^{-1} in hydrogen plasma.

2.5 Cyclooctadienyl iridium complexes

(Cp)Ir(1,5-COD) is an air stable complex with a melting point of 398–401 K and vapor pressure about 1.4 Pa at 383 K. The lowest temperatures for iridium deposition (373–393 K) have been achieved by decomposition of (Cp)Ir(1,5-COD) along with Ir(allyl)$_3$ and (MeCp)Ir(1,5-COD) complexes in a hydrogen containing atmosphere (see Table 2). The decomposition of (Cp)Ir(1,5-COD) in the presence of hydrogen or oxygen may produce iridium films of high-purity (<1 mass%C) and a favorable crystalline nature but it yields low deposition rates (about 2.7×10^{-3} nm·s^{-1}).[32] The decomposition of this complex in vacuum generates films with significantly high carbon content (80 mass%C).[32] Uniform and homogeneous iridium films prepared from (Cp)Ir(1,5-COD) with comparatively higher deposition rates (1.7×10^{-1} nm·s^{-1}) have been reported. However, no information on the use of a reactive gas and the consequent impurity contents was given.[12]

The decomposition of (MeCp)Ir(1,5-COD) complex occurs above 673 K and its vapor pressure is about 11–40 Pa at 353–393 K.[33] This complex has a low melting point (325 K),[34] which allows its use as a liquid source for CVD. Liquid delivery of precursor is advantageous to provide a constant overall gas flow rate that can lead to high deposition rates. The (MeCp)Ir(1,5-COD) complex was able to produce high-purity iridium films (<1 mass%C, O) by adding either hydrogen or oxygen as reactive gases.[32-35] However, without a reactive gas, the films contained a considerable high carbon content (80–87 mass%C).[32,33] Conventional delivery of (MeCp)Ir(1,5-COD) from the heated solid or liquid complex accounted for deposition rates about 10^{-2} nm·s^{-1}.[32,33,35] On the other hand, direct liquid injection yields higher deposition rates (up to 1.17 nm·s^{-1}).[34] Tetrahydrofuran or toluene can be used as solvents of (MeCp)Ir(1,5-COD) complex for direct liquid injection.[34-36] Direct liquid injection may produce highly (111)-oriented iridium films on SiO$_2$/Si(100) substrates.[37] Decomposition studies in a direct liquid injection CVD process revealed that the reaction temperature of (MeCp)Ir(1,5-COD) decreased from 760 K to below 465 K in the presence of oxygen gas.[37] Because of its attractive properties, decomposition of (MeCp)Ir(1,5-COD) in the absence of oxygen has been additionally studied to clarify the surface reactions that take place on a rhodium surface.[37-39]

[Ir(acetate)(1,5-COD)]$_2$ is the only one complex reported to yield high-purity iridium films (<1 mass%C or O) without the need of a reactive gas (either hydrogen or oxygen).[32] In spite of its clean decomposition, this complex inevitably produced low deposition rates (2.2×10^{-3} nm·s^{-1}), probably because of its relative low volatility (vapor pressure about 10 Pa at 398 K) compared with other iridium (1,5-COD)-complexes. In contrast, [Ir(methoxide)(1,5-COD)]$_2$ requires hydrogen gas to produce iridium films of moderate purity (90–95 mass%Ir).[25]

Cyclooctadienyl complexes, named (keim)Ir(1,5-COD), (hfda)Ir(1,5-COD) and (amak)Ir(1,5-COD), were synthesized by introducing fluorinated ligands (keim)H, (hfda)H and (amak)H to improve volatility and make them attractive for CVD of iridium.[40] Differing only slightly in their molecular structure, these three complexes sublimed without decomposition at 323–333 K under 26.6 Pa. The first two complexes were found to be air-stable. Thermogravimetric studies indicated that complex containing the (keim)H ligand (m.p. 390 K) exhibit the highest volatility, followed by (amak)H (m.p. 400 K) and (hfda)H (m.p. 384 K). All three complexes were able to produce crystalline and pure iridium films containing no detectable carbon, nitrogen or fluorine impurities by the assistance of oxygen gas. The oxygen contamination was determined to be about 2 mass%O. The assistance of hydrogen for decomposition of the (hfda)Ir(1,5-COD) complex resulted in films highly contaminated with carbon (41 mass%C).[40]

2.6 Ethylene iridium complex

Laser CVD of iridium has been further explored by using the air-stable CpIr(C$_2$H$_4$)$_2$ complex. High-purity iridium films (<1 mass%C) could be obtained at room temperature and atmospheric pressure by employing an XeCl excimer

laser. A laser beam of about 1 cm in diameter was perpendicular to the substrate surface. Helium and hydrogen were used as carrier and reactive gas, respectively.[41]

In summary, Ir(acac)$_3$ and (MeCp)Ir(1,5-COD) seem to be the most suitable precursors for the conventional CVD of iridium. These stable complexes lead to high-quality deposits at comparatively high deposition rates among iridium complexes. The CpIr(C$_2$H$_4$)$_2$ complex may be a suitable precursor in laser CVD for applications requiring selective deposition.

3. Chemical Vapor Deposition of Platinum

CVD of platinum has been extensively studied for processing platinum silicide Ohmic and Schottky diode contacts to silicon using almost exclusively conventional activated processes. Moreover, CVD of platinum has become a promising alternative route to prepare catalysts because its ability to produce fine particles. Platinum catalysts prepared in a fluidized-bed CVD reactor are promising for hydrocarbon conversion applications. In addition, we have demonstrated that platinum fine particles produced by CVD exhibit excellent electrochemical properties to be considered in solid electrolyte devices. Table 3 displays the CVD operating conditions and quality of platinum deposits.

3.1 β-diketonate platinum complexes

Platinum acetylacetonate, Pt(acac)$_2$, could be one of the first complexes employed in CVD of platinum. The decomposition temperature of this air-stable and commercially available complex is about 510 K[5,42] and its vapor pressure is approximately 0.5 kPa at 483 K.[5,16] Platinum films prepared from Pt(acac)$_2$ may contain considerable carbon impurity (50 mass%C).[43] We have shown that oxygen is effective to avoid carbon incorporation into the films prepared from Pt(acac)$_2$; platinum films of high-purity and an attractive epitaxial or oriented nature can be grown by an appropriate addition of oxygen.[19-21,44] Epitaxial platinum films on insulating substrates are of interest in device processing to achieve epitaxial growth of functional ceramic over-layers as well as in fundamental conductivity studies. Epitaxial platinum films grown by CVD effectively promoted the epitaxial growth of AlN over-layers.[21]

Evaporation and deposition studies of Pt(acac)$_2$ indicated that the activation energy for deposition of platinum in an argon atmosphere is about 204 kJ·mol^{-1}. A different activation energy value about 56 kJ·mol^{-1}, was determined for the deposition on a platinum pre-coated substrate.[45] Under similar argon atmosphere conditions, consistent activation energies for a reaction-controlled regime about 200 kJ·mol^{-1} at temperatures below 743 K and for a diffusion-controlled regime about 60 kJ·mol^{-1} at higher temperatures were calculated.[20] The study of the rate-limited mechanisms in CVD may allow an appropriate selection of the deposition temperature needed to obtain high deposition rates.

Platinum films prepared in an argon atmosphere contain carbon and show a porous morphology as preferred for electrodes to zirconia solid electrolytes. Conductivity measurements revealed that platinum-carbon films processed by CVD exhibit superior electrode performance than conven-

tional platinum-paste electrodes.[46] Indeed, an oxygen sensor employing yttria-stabilized zirconia coated with platinum-carbon films prepared from Pt(acac)$_2$ allowed for reliable measurements of oxygen activity in amber glasses.[47] The use of hydrogen to assist decomposition of Pt(acac)$_2$ indicates that films invariably contain carbon (16 mass%C) and oxygen (4 mass%O) impurities.[48]

Laser CVD of platinum has been undertaken by using two platinum complexes, platinum hexafluoroacetylacetonate, Pt(hfac)$_2$ and cyclopentadienyltrimethyl platinum, CpPtMe$_3$ (see Table 3). The Pt(hfac)$_2$ complex has been employed to study extensively the photolytic laser CVD of platinum.[49-51] Photolytic decomposition of the complex was observed on the laser power range from 10^2 to 10^7 kW·m^{-2}. The transition from initial photolytic to pyrolytic decomposition was identified at intensities higher than 50×10^4 kW·m^{-2}. Deposition rates as high as 10 nm·s^{-1} were achieved by pyrolytic decomposition, while lower deposition rates of about $10^{-2} - 1$ nm·s^{-1} were promoted by photolytic decomposition of Pt(hfac)$_2$. Both photolytic and pyrolytic decomposition yielded platinum deposits containing about 4 mass%C and O. The vapor pressure of Pt(hfac)$_2$ as a function of temperature was reported.[51]

On the other hand, thermal decomposition of the platinum β-diketonate complex, [PtMe$_3$(acac)]$_2$, in vacuum yielded platinum films with a significant carbon content (30 mass%C). The carbon impurity was reduced to 6 mass%C by adding hydrogen.[7,52,53]

3.2 Carbonyl platinum complexes

Two carbonyl complexes, Pt(CO)$_2$Cl$_2$ and (MeCp)Pt(CO), have been explored for CVD of platinum. Thermal decomposition of Pt(CO)$_2$Cl$_2$ in an hydrogen atmosphere led to high-purity platinum films (99.6 mass%Pt).[43] However, one of the significant disadvantages of this complex is its inevitably decomposition to the nonvolatile PtCl$_2$ chloride, which makes it unattractive for CVD. The (MeCp)Pt(CO) complex produces platinum films with carbon and oxygen impurities (4 mass%C and 3 mass%O) in spite of hydrogen assistance.[52,53] In the absence of a reactive gas, impurities are much higher.

3.3 Allyl platinum complexes

In spite of their air-sensitivity, allyl complexes of the platinum group metals have been investigated for CVD due to their high vapor pressures; Pt(allyl)$_2$ 1.3×10^{-2} Pa at 298 K; Ir(allyl)$_3$ 1.3 Pa at 298 K; Rh(allyl)$_3$ 1.3 Pa at 298 K and Pd(allyl)$_2$ 1.3×10^{-2} Pa at 298 K. Particularly, the Pt(allyl)$_2$ complex has been reported to yield high quality and carbon-free platinum films; however, it is not clear if a reactive gas was used.[54,55] Alternatively, the allyl derivative CpPt(allyl) produces, in vacuum, platinum films containing high carbon and oxygen impurities (38 mass%C and 2 mass%O).[52,53]

3.4 Cyclopentadienyl platinum complexes

Contrasting with other platinum complexes, cyclopentadienyltrimethyl platinum, (Cp)PtMe$_3$, and (methylcyclopentadienyl)trimethyl platinum, (MeCp)PtMe$_3$, have been widely used in the CVD of platinum (see Table 3). Complexes

Table 3   CVD operating conditions for platinum.

Chemical complex	Activation	Substrate temperature/K	Gas present	Impurities	Deposition rate /nm·s^{-1}	Ref.
Pt(acac)$_2$	thermal	773–873	CO_2	50 mass%C	1.67×10^{-2}–1.67×10^{-1}	[43]
		523–773	O_2	C- and O-free	1×10^{-1}–3×10^{-1}	[19]–[21], [44]
		553–823	H_2	16 mass%C, 4 mass%O		[23], [48]
Pt(hfac)$_2$	laser			4 mass%C, O	10 pyrolytic $10^{-2} - 1$ photolytic	[49]–[51]
[PtMe$_3$(acac)]$_2$	thermal	473–523	vacuum	30 mass%C, 4 mass%O		[7], [52]–[53]
		373–423	H_2	6 mass%C, 5 mass%O		
Pt(CO)$_2$Cl$_2$	thermal	573–758	H_2	99.6 mass%Pt	8.3×10^{-2}	[43]
(MeCp)Pt (CO)	thermal	508	vacuum	27 mass%C, 2 mass%O		[52]–[53]
		408	H_2	4 mass%C, 3 mass%O		
Pt(allyl)$_2$	thermal	523		C-free		[54]–[55]
CpPt(allyl)	thermal	473–523	vacuum	38 mass%C, 2 mass%O		[52]–[53]
		373–423	H_2	5 mass%C		
(Cp)PtMe$_3$	thermal	453	H_2	<1 mass%C, O		[30], [56]–[58],
	thermal	523	vacuum	25 mass%C, 1 mass%O		[52]–[53], [55]
	laser	room temp.	H_2/vacuum	3.5 mass%C/20 mass%C	1.6×10^{-1}	[59]
(MeCp)PtMe$_3$	thermal	393	H_2	<1 mass%C, O		[30], [56], [58]
		573–723	O_2	C-free		[60]–[61]
		473–673	O_2	C, O (% not specified)		[62]–[63]
(1,5-COD)PtMe$_2$	thermal	523	vacuum	10 mass%C, 4 mass%O		[52]–[53]
		373–423	H_2	4 mass%C, 2 mass%O		
(1,5-COD)PtMe(Cp)	thermal	523	vacuum	19 mass%C, 4 mass%O		[52]–[53]
		373–423	H_2	5 mass%C		
(1,5-COD)PtMeCl	thermal	523	vacuum	25 mass%C, 5 mass%O		[53]
		373–423	H_2	9 mass%C, 3 mass%O		
(1,5-COD)PtMe(allyl)	thermal	523	vacuum	37 mass%C, 2 mass%O		[52]
		373–423	H_2	4 mass%C, 2 mass%O		
PtMe$_2$(MeNC)$_2$	thermal	523	vacuum	11 mass%C and O-free	1.6×10^{-1}	[52]–[53]
		373–423	H_2	5 mass%C, O-free		
PtMe(allyl)(MeNC)$_2$	thermal	473–523	vacuum	10 mass%C, 4 mass%O		[52]
			H_2	4 mass%C, O-free		
PtMe(vinyl)(MeNC)$_2$	thermal	473–523	vacuum	28 mass%C, O-free		[52]
			H_2	15 mass%C, 3 mass%O		
PtMe(t-BuC≡C)(MeNC)$_2$	thermal	473–523	vacuum	31 mass%C, 13 mass%O		[52]
			H_2	21 mass%C, 9 mass%O		
Pt(PF$_3$)$_4$	thermal	453–573	H_2 (10^5 Pa)	residual P (% not specified)	8.3×10^{-2}–1.6×10^{-1}	[43], [67], [70]
			H_2 (10^{-3} Pa)	high purity		[68]–[69]

containing the cyclopentadienyl group exhibit high volatility and chemical stability. For instance, the vapor pressure of (Cp)PtMe$_3$ at 373 K has been estimated to be about 0.54 kPa. The vapor pressure as a function of temperature for (Cp)PtMe$_3$ and (MeCp)PtMe$_3$ are reported.[1]

Thermal decomposition of both (Cp)PtMe$_3$ and (MeCp)PtMe$_3$ complexes may produce high-purity platinum films (<1 mass%C and O) in the presence of hydrogen at low temperatures (about 453 K or 393 K, respectively).[30,56–58] However, decomposition of (Cp)PtMe$_3$ in vacuum led to platinum films with a considerable amount of carbon (25 mass%C).[52,53] On the other hand, laser CVD of platinum using the (Cp)PtMe$_3$ complex promoted film formation at room temperature and atmospheric pressure.[59] It resulted in amorphous and microcrystalline platinum films of moderate purity (3.5 mass%C) even with the assistance of hydrogen gas.

The effect of oxygen to assist decomposition of (MeCp)PtMe$_3$ is not clear. The use of oxygen is reported to be successful in yielding high-purity platinum films,[60,61] whilst platinum films containing carbon and oxygen impurities despite several explored O_2/Ar ratios, are also reported.[62,63] Nevertheless, irrespective of the effect of oxygen on contaminants, higher temperatures (573–723 K) were required for deposition than those needed with hydrogen gas.[60,62,63] Particularly, high-purity platinum films prepared from (MeCp)PtMe$_3$ in an oxygen containing atmosphere on silicon substrates showed great promise as bottom electrodes for ferroelectric thin films because of their excellent conformal coverage and blocking effect for the diffusion of oxygen and silicon.[61]

3.5 Platinum complexes containing cyclooctadienyl (1,5-COD) and methyl (Me) ligands

Platinum complexes containing cyclooctadienyl and methyl ligands such as (1,5-COD)PtMe$_2$, (1,5-COD)PtMe(Cp), (1,5-COD)PtMeCl and (1,5-COD)PtMe(allyl) have been characterized and evaluated for CVD of platinum.[52,53] In the absence of a reactive gas, all these complexes yielded platinum films containing considerable carbon (10–37 mass%C) and oxygen (2–5 mass%O) impurities. The presence of hydrogen moderately improved the film purity (4–9 mass%C and 0–3 mass%O). Among these complexes, (1,5-COD)PtMe(allyl) produced the most contaminated films in the absence of hydrogen. The (1,5-COD)PtMe$_2$ complex has been employed to prepare catalysts in a specially designed fluidize-bed CVD reactor. Porous silica particles were maintained in a bubbling fluidization regime by contacting them with a gas mixture containing helium, hydrogen and complex vapors. The method resulted in the formation of pure and small palladium particles about 3 nm in size on the surface of the silica support.[64,65] As CVD allows the formation of fine particles due to homogeneous gas phase reactions of the precursors, it has become a novel alternative route to prepare catalysts.

3.6 Platinum complexes containing methyl (Me) and methyl-cyanide (MeNC)$_2$ ligands

In order to explore parameters such as volatility and thermal stability, several platinum complexes involving methyl and methyl-cyanide ligands have been further investigated, including PtMe$_2$(MeNC)$_2$, PtMe(allyl)(MeNC)$_2$, PtMe(vinyl)(MeNC)$_2$ and PtMe(t-BuC≡C)(MeNC)$_2$ complexes.[52] All the films prepared from these complexes without a reactive gas showed the presence of carbon and often oxygen impurities along with a coarse surface morphology (see Table 3). Carbon impurities in the films were found to arise partly from the methyl-platinum (MePt) group, which formed during decomposition of the complexes.[52,66] Specifically, the PtMe$_2$(MeNC)$_2$ complex produced high-purity platinum films with no detectable impurities by supplying an appropriate addition of hydrogen. Due to the interest in the PtMe$_2$(MeNC)$_2$ complex as a CVD precursor, its vapor pressure as a function of temperature has been investigated.[52]

3.7 Phospine platinum complex

The Pt(PF$_3$)$_4$ complex, a stable liquid in dry air, is attractive for CVD because of its high vapor pressure (about 2.2 kPa at 273 K). A wide range of pressures (10^{-3} to 10^5 Pa) have been explored in CVD experiments using this complex.[43,67–69] Under a hydrogen atmosphere, Pt(PF$_3$)$_4$ yields adherent, uniform and smooth platinum films with phosphorous contamination concentrated in the outer layer (about 5 nm) and at the interface between the film and the silicon substrate.[43,67,70] More recent studies have shown that, under high vacuum conditions (3×10^{-3} Pa) and the assistance of hydrogen, this liquid complex produced high-purity-platinum films with a high degree of conformal coverage.[68,69]

Finally, it can be concluded that Pt(acac)$_2$, (MeCp)PtMe$_3$ and Pt(PF$_3$)$_4$ are appropriate precursors for the conventional CVD of platinum. Nevertheless, the deposition rate still remains low as required for CVD processes used in microelectronics and large-area coatings, which most often has to be greater than 1.7 nm·s^{-1}.

4. Chemical Vapor Deposition of Rhodium

Continuous or patterned films and small particles of rhodium have been prepared by CVD because of their relevance in electronics, optics and catalysis. Conventional thermal and assisted CVD processes have been more frequently studied for rhodium than for the other metals of this group. The CVD of rhodium has been achieved exclusively by using metal organic complexes. The CVD operating conditions and quality of rhodium deposits are presented in Table 4.

4.1 β-diketonate rhodium complexes

Rhodium β-diketonates have been employed for CVD of rhodium due to their favorable thermal stability and high vapor pressure. Rhodium acetylacetonate, Rh(acac)$_3$, is one of this type of complexes employed to prepare oxidation resistant coatings. However, rhodium films reached thickness of only some tens of nanometers.[16] The vapor pressure of Rh(acac)$_3$ is about 0.5 kPa at 498 K. Rhodium trifluoroacetylacetonate, Rh(tfac)$_3$, is other complex of this type, which may produce pure and adherent rhodium films by the assistance of hydrogen gas.[71] The complexes containing the acac ligand are thermally more stable than those containing tfac.[5,6,16]

4.2 Carbonyl rhodium complexes

Small rhodium particles (1 to 3 nm in size) synthesized in a special fluidized-bed CVD reactor have been applied as the active phase of SiO$_2$ supported catalysts.[72–74] Two rhodium carbonyl complexes (rhodium carbonyl chloride, Rh$_2$Cl$_2$(CO)$_4$ and rhodium carbonyl acetylacetonate, (acac)Rh(CO)$_2$) and one rhodium allyl complex, (Rh(allyl)$_3$), provided high thermal stability for this task in helium and helium/hydrogen atmospheres. These complexes reached vapor pressures from 6.7 to 10.8 Pa at 313–328 K. The catalysts prepared by CVD render good catalytic activities in the hydrogenation of alkenes and benzene.

As regard to the rhodium particles prepared from Rh$_2$Cl$_2$(CO)$_4$ complex, they exhibited no carbon but chlorine contamination.[72–74] The chlorine impurity was decreased from 23 to 1.5 mass%Cl by addition of hydrogen. The Rh$_2$Cl$_2$(CO)$_4$ complex was further employed to prepare rhodium catalysts on a different support material (TiO$_2$).[75] In this case, the nature and chemistry of the rhodium species deposited on TiO$_2$ were studied; Rh(CO)$_2$ species derived from the dissociative adsorption of Rh$_2$Cl$_2$(CO)$_4$ were found to be in an adsorbed surface layer.[76,77] Additionally, it was shown that hydride-rhodium species were generated in the gas phase due to the reaction between this complex and hydrogen.[78]

On the other hand, rhodium particles prepared from the (acac)Rh(CO)$_2$ complex showed high carbon contents (14 mass%C) even with the assistance of hydrogen gas.[72–74] Consistently, rhodium thin films containing carbon and oxygen impurities were further reported from the thermal

Table 4 CVD operating conditions for rhodium.

Chemical complex	Activation	Substrate temperature/K	Gas present	Impurities	Deposition rate /nm·s^{-1}	Ref.
Rh(acac)$_3$	thermal					[16]
Rh(tfac)$_3$	thermal	523	H$_2$			[71]
Rh$_2$Cl$_2$(CO)$_4$	thermal	353–373	He/H$_2$, H$_2$	1.5 mass%Cl		[72]–[74]
(acac)Rh(CO)$_2$	thermal	373–773	H$_2$	14 mass%C		[72]–[74], [79]
	plasma	423	H$_2$	98 mass%Rh		[81]
	laser	338–368	vacuum	C (% not specified)		[80]
(thd)Rh(CO)$_2$	laser	346–356	vacuum	C (% not specified)		[80]
(hfac)Rh(CO)$_2$	laser	283–328	vacuum	C (% not specified)		[80]
Rh(allyl)$_3$	thermal	353–523	vacuum	14 mass%C	4.2×10^{-2}	[30]–[31], [72]–[74], [82]
		393	H$_2$	<7 mass%C, 2 mass%O		[30], [72]–[74], [82]
		523	H plasma	<3 mass%C	5×10^{-3}	[31]
Rh(allyl)(CO)$_2$	thermal	453	H$_2$	6 mass%C	5.5×10^{-1}	[82]
		453	vacuum	40 mass%C, 12 mass%O		
(Cp)Rh(CO)$_2$	thermal	453	H$_2$	7 mass%C, 4 mass%O	5.5×10^{-1}	[82]
		453	vacuum	20 mass%C, 5 mass%O		
(Cp)Rh(1,5-COD)	thermal	543	H$_2$	3 mass%C	5.5×10^{-1}	[82]
		503	vacuum	19 mass%C		
[Rh(PF$_3$)$_2$Cl]$_2$	electric field		vacuum			[83]
CpRh(C$_2$H$_4$)$_2$	laser	273	He, H$_2$	1 mass%C		[84]

decomposition of (acac)Rh(CO)$_2$ at 473–773 K under ultra-high vacuum (9.3×10^{-7} Pa).[79] The amount of impurities was higher in the initial deposition stage on a silicon surface than on a growing surface. The initial impurity was greatly reduced by using a TiO$_2$ over-layer on silicon. This suggested a direct interaction of complex molecules with the reactive silicon surface. Alternatively, laser CVD of rhodium using the same complex resulted again in carbon contaminated deposits. An argon laser operating between 60 and 390 mW was employed to prepare rhodium stripes (widths up to 600 µm and heights over 5 µm). The level of carbon contamination was not specified.[80]

Plasma enhanced CVD using the (acac)Rh(CO)$_2$ complex and the assistance of hydrogen resulted in rhodium films of acceptable purity (98 mass%Rh), although films thicker than 30–50 nm showed wrinkles and microcracks.[81]

Two additional carbonyl complexes (rhodium carbonyl tetramethyl heptanedionate, (thd)Rh(CO)$_2$, and rhodium carbonyl hexafluoroacetylacetonate, (hfac)Rh(CO)$_2$), were employed for the deposition of rhodium stripes by laser CVD.[80] Rhodium strips deposited from the (thd)Rh(CO)$_2$ complex showed again significant carbon contamination. Rhodium strips prepared from (hfac)Rh(CO)$_2$ were much purer than those from (acac)Rh(CO)$_2$. The higher volatility of the latter complex allowed deposition to take place at 283–328 K. Stripes deposited from the (hfac)Rh(CO)$_2$ had resistivities about 3 times higher than that of bulk rhodium, while strips prepared from (acac)Rh(CO)$_2$ and (thd)Rh(CO)$_2$ exhibit higher resistivities, ranging from 25 to 50 times higher than the corresponding to the bulk material. Thus, (hfac)Rh(CO)$_2$ could be considered, in particular, an adequate carbonyl complex for laser CVD of rhodium among the three complexes mentioned.

4.3 Allyl rhodium complexes

Rhodium allyl, Rh(allyl)$_3$, is one of the most investigated complex for deposition of rhodium. The decomposition of Rh(allyl)$_3$ without assistance of hydrogen resulted in amorphous rhodium films contaminated with carbon (about 14 mass%C).[30,31,72–74,82] Additionally, the results coincide in the beneficial effect of hydrogen to reduce contamination (4 mass%C, <2 mass%O).[30,72–74,82] Specifically, the use of hydrogen plasma for the decomposition of Rh(allyl)$_3$ promoted the formation of pure and crystalline rhodium films (<3 mass%C) at growth rates of about 5×10^{-3} nm·s^{-1}.[31]

The Rh(allyl)(CO)$_2$ complex has been explored for the deposition of rhodium in a lesser extent. The thermal decomposition of this complex in hydrogen produced rhodium films containing about 6 mass%C. Under these conditions, films grew at rates about 5.5×10^{-1} nm·s^{-1} on silicon substrates. Without hydrogen, the carbon content in the films increased substantially up to 40 mass%C.[82]

4.4 Cyclopentadienyl rhodium complexes

Rhodium films prepared from dicarbonylcyclopentadienyl rhodium, (Cp)Rh(CO)$_2$, and cyclooctadienecyclopentadienyl rhodium, (Cp)Rh(1,5-COD), in vacuum (0.14–1.4 Pa) were inevitably contaminated with carbon (about 20 mass%C). However, the presence of hydrogen reasonably decreased the level of carbon to about 3–7 mass%C and reduced the temperature required for deposition from 543 to 503 K, particularly for the (Cp)Rh(1,5-COD) complex.[82]

4.5 Other rhodium complexes

The [Rh(PF$_3$)$_2$Cl]$_2$ complex has been used to prepare rhodium lines and dots at nanometric scale on gold or silicon surfaces by local decomposition of gaseous molecules under

a scanning tunneling microscope tip. The gaseous molecules were dissociated by a high electric field (about 10^9 V·m^{-1}) within the tip-sample gap.[83]

On the other hand, laser CVD of rhodium films using the gaseous $CpRh(C_2H_4)_2$ complex was carried out in both helium and hydrogen atmospheres at room temperature and atmospheric pressure. The films contained less than 1 mass%C and seemed to be crystalline in some extent.[84]

It can be said that the rhodium complexes studied in conventional CVD produce deposits of only moderate purity even with the assistance of a reactive gas. Higher temperatures promote the organic ligand decomposition, resulting in carbon and oxygen incorporation. The role of the reactive gas is to avoid the incorporation of carbon and oxygen containing fragments. Since the temperature and the gas composition are the main factors for purity control, a search for appropriate operating conditions may allow the preparation of high-purity films from the same complexes.

5. Chemical Vapor Deposition of Palladium

An increasing number of publications on CVD of palladium have been recently published. Small particles and films of palladium or palladium-based alloys are of interest in inorganic membranes for hydrogen permeation, catalysts and microelectronic devices. The CVD operating conditions and quality of palladium deposits are listed in Table 5.

5.1 Palladium chloride

Unlike the variety of metal organic complexes of palladium, $PdCl_2$ is the unique halide compound employed as a CVD palladium precursor. Sublimation of $PdCl_2$ at 673–723 K and the subsequent hydrogen reduction of chloride vapors at 723–773 K led to palladium deposits inside a porous top layer of α-alumina (pore size about 150 nm)[85] or γ-alumina (pore size 3–6 nm)[86] for catalytic membrane applications. Deposition of palladium inside γ-alumina pores was achieved by introducing $PdCl_2$ and hydrogen from opposite sides of a ceramic support. The nature of CVD provides the opportunity to reach the internal and external surfaces of porous substrates.

5.2 β-diketonate palladium complexes

Palladium acetylacetonate, $Pd(acac)_2$, is one of the palladium complexes that has been widely investigated for the preparation of catalytic materials by CVD.[87–92] For instance, a uniform distribution of palladium inside γ-alumina pores (3–6 nm in diameter) was completed by decomposition of $Pd(acac)_2$ without assistance of a reactive gas.[90] In this case, palladium could be in the form of ultrafine particles as suggested by the broadening of its XRD reflections. The presence of hydrogen led to smooth and reflective palladium films exclusively on the surface of the γ-alumina.[90] Hydrogen has been preferably used as the reactive gas to assist the decomposition of $Pd(acac)_2$. Its effectiveness to avoid carbon or oxygen impurities arising

Table 5   CVD operating conditions for palladium.

Chemical complex	Activation	Substrate temperature/K	Gas present	Impurities	Deposition rate /nm·s^{-1}	Ref.
$PdCl_2$	thermal	723–773	H_2			[85]–[86]
$Pd(acac)_2$	thermal	523–573	vacuum	high C (% not specified)		[90]–[91]
		623–673	H_2	C- and O-free		[87], [92]
$Pd(hfac)_2$	thermal	353–473	H_2	<1 mass%C, O and F	1.6–7.0	[95]–[98]
		523	H_2	20–40 mass%C		[101]
		498–648	vacuum	high C (% not specified)		[100]
$Pd(allyl)_2$	thermal	523	vacuum	<1 mass%C		[55]
$Pd(Me\ allyl)_2$	thermal	523	vacuum	<1 mass%C		[55]
$CpPd(allyl)$	thermal	523	vacuum	5 mass%C		[55]
	thermal	303–333	H_2	high purity		[102]
	plasma	298–393	H_2 plasma/O_2 plasma	70 mass%Pd/>99 mass%Pd		[103]
	laser	298	vacuum	50 mass%C	2.2×10^{-1}	[104]–[105]
$Pd(allyl)(hfac)$	thermal	303–333	H_2,	high purity		[65]–[64], [102]
		603–643	O_2	>99 mass%Pd	1.9×10^{-2}–1.1×10^{-1}	[91], [108]
$Pd(Me\ allyl)(hfac)$	thermal	603–643	O_2	>99 mass%Pd	1.9×10^{-2}–1.1×10^{-1}	[108]
$Pd(Me\ allyl)(acac)$	thermal	603–643	O_2	>99 mass%Pd		[108]
$PdMe_2(PMe_3)_2$	thermal	403–573	vacuum	12 mass%C		[110]
		403–573	H_2	C-free, 12 mass%P		[110]
$PdMe_2(PEt_3)_2$	thermal	403–573	vacuum	9 mass%C		[110]
		403–573	H_2	C-free, 10 mass%P		[110]
$PdMe_2(tmeda)$	thermal	403–573	vacuum	10–13 mass%C		[110]
			H_2	11 mass%C		[110]
$Pd(acetate)_2$	thermal	573–673	vacuum			[111]–[112]
$Pd(C_2H_4)_2$	thermal					[6]

from Pd(acac)$_2$ was proved by obtaining pure palladium films consisting of agglomerated crystallites smaller than 100 nm on the surface of porous α-alumina disks (pore size: 150 nm).[92]

Some efforts have been devoted to improve the performance of supported catalytic materials by preparing palladium-based alloy films. Thus, palladium-nickel alloy films were prepared on porous α-alumina disks and porous α-alumina disks coated with γ-alumina top-layer by using metal acetylacetonate complexes.[92,93] The pore sizes of the α-alumina and γ-alumina were 150 and 4 nm, respectively. The complexes were mixed and packed in a glass tube for evaporation. Hydrogen and the complex vapors were introduced from opposite sides of the porous alumina disks to attain a counter-diffusion process. Deposition led to porous films on α-alumina disks contrasting with bright continuous films on the top-layer γ-alumina. Porous palladium-nickel films, consisting of particles around 300 nm in size, showed superior sensitivity to hydrogen and better resistance to hydrogen brittlement than bright films.

The palladium hexafluoroacetylacetonato complex, Pd(hfac)$_2$, is stable in air up to 503 K and has a vapor pressure of approximately 0.14 kPa at 333 K.[94] The selective deposition of palladium has been investigated due to its particular relevance in microelectronic devices. High-purity palladium films (<1 mass%C, O and F) could be prepared on several substrates (glass, silicon, copper, tungsten, aluminum, nickel) from Pd(hfac)$_2$ in the presence of hydrogen.[95–98] Under vacuum and without the assistance of hydrogen, palladium films were selectively deposited only on copper substrates.[95] Surface reaction studies suggested that selective deposition on copper was accomplished by reaction of the Pd(hfac)$_2$ complex to produce Cu(hfac)$_2$ and metallic palladium.[96,97] Alternatively, high deposition rates of interest for electronic applications (1.6–7.0 nm·s^{-1}) were achieved by decomposition of Pd(hfac)$_2$ at 353–473 K under reduced pressures in the presence of hydrogen.[99]

The Pd(hfac)$_2$ complex has been additionally employed to deposit palladium inside the porous top-layer of α-alumina (pore size 60–400 nm) supports for catalytic membranes intended for the reduction of nitrate in drinking water. The deposits consisted of palladium particles (7–11 nm in size) and carbon, obtained without the assistance of a reactive gas.[100] On the other hand, binary Pd–Cu or Pd–Sn catalytic membranes were prepared from Pd(hfac)$_2$ at 523 K using hydrogen as a carrier and reactive gas. In spite of hydrogen presence, significant carbon content was found in the deposits (20–40 mass%C).[101]

5.3 Allyl palladium complexes

The palladium allyl complexes, Pd(allyl)$_2$ and Pd(Me allyl)$_2$, are able to produce high-purity palladium films containing less than 1 mass%C without the assistance of a reactive gas, even though both complexes exhibit disadvantageous thermal instability at room temperature and air sensitivity.[55]

The cyclopentadienylallyl palladium complex, (Cp)Pd(allyl), is moderately stable in air and has a vapor pressure about 2.9 Pa at 298 K. It has been investigated for palladium deposition in thermal and activated CVD processes. Thermal

decomposition yielded amorphous palladium films (up to 2 μm thick) contaminated with carbon (5 mass%C).[55] The use of hydrogen led to crystalline palladium films with low levels of carbon.[102]

Decomposition of (Cp)Pd(allyl) in an argon plasma CVD process at room temperature resulted in the formation of thin palladium films (10 to 300 nm thick) with a low metallic content (about 70 mass%Pd). By increasing the deposition temperature to 393 K, the palladium films reached high-purity (>99 mass%Pd), however, it caused an inevitable decrease in the deposition rate.[103]

Photochemical decomposition of (Cp)Pd(allyl) using a mercury lamp at about 15 W·m^{-2} resulted in films consisting of palladium particles (100 nm in diameter) in an organic polymer matrix. Polymerization of organic ligands during photodecomposition might form the polymeric matrix. Auger results showed that the films consisted almost entirely of palladium and carbon (about 50 mass%C).[104] Laser CVD of palladium patterns (20 μm × 20 μm) at room temperature from (Cp)Pd(allyl) provided deposition rates about 2.2×10^{-1} nm·s^{-1}.[105]

The (Cp)Pd(allyl) complex has been additionally employed to prepare catalysts by CVD.[64,106,107] Pd/Y-zeolite catalysts were prepared by introducing the vapor phase of this complex inside the Y-zeolite cavities and subsequent decomposition to metal particles by heating at 773 K in hydrogen. These catalysts were active in the methylcyclopentane conversion at 573 K.[106] Pd/SiO$_2$ catalysts were further prepared from (Cp)Pd(allyl) in a fluidized-bed CVD reactor. This method allows the preparation of highly dispersed palladium aggregates (5–25 nm in size) with high activity both in alkene hydrogenation and alcohol hydrocarbonylation.[64] Recently, palladium and palladium-nickel alloy membranes were prepared on nickel-stainless steel or γ-alumina/α-alumina porous supports.[107]

The Pd(allyl)(hfac) complex is able to produce either palladium films or particles of high-purity with the assistance of hydrogen.[64,65,102] The use of oxygen is also effective to achieve high-purity palladium films (>99 mass%Pd) from this complex.[91,108] On the other hand, Pd(Me allyl)(hfac) and Pd(Me allyl)(acac) may also produce high-purity palladium films but exclusively with the assistance of oxygen gas.[108] Films prepared in hydrogen containing atmosphere or in vacuum show significant carbon contamination (15–40 mass%C). Pd(allyl)(hfac), Pd(Me allyl)(hfac) and Pd(Me allyl)(acac) show sufficient stability and volatility, which lead to deposition rates from 1.9×10^{-2} to 1.1×10^{-1} nm·s^{-1}.[108,109] Specifically, Pd(allyl)(acac) was unable to produce palladium deposits because it decomposes at ambient conditions.

5.4 Palladium complexes containing methyl (Me) ligand

Thermal decomposition of PdMe$_2$(PMe$_3$)$_2$ and PdMe$_2$(PEt$_3$)$_2$ complexes in the presence of hydrogen may produce palladium films with no carbon contamination, but with significant phosphorus impurity (10–12 mass%P). Without the assistance of a reactive gas, these two complexes besides PdMe$_2$(tmeda), produce palladium films contaminated with carbon (9–13 mass%C).[110] Methane, ethane and ethylene were detected as volatile products from the decom-

position of these three complexes.

5.5 Other palladium complexes

Two additional complexes, $Pd(acetate)_2$ and $Pd(C_2H_4)_2$, have been investigated for the deposition of palladium. The $Pd(acetate)_2$ complex was employed to prepare palladium layers about 4.4 μm thick on the porous surface of α-alumina support tubes.[111] Palladium deposits filled the pores (about 150 nm in size) near the top surface of the tubes thus forming palladium membranes. These membranes were resistant to hydrogen embrittlement and sulfur and chlorine poisoning. The $Pd(C_2H_4)_2$ complex was reported to be stable only in an ethylene atmosphere.[6] Additionally, Pd–Ag alloy films were obtained by mixing $Pd(acetate)_2$ and $Ag(acetate)$.[112] $Pd(acetate)_2$ started to decompose at about 493 K.

Several palladium complexes may produce high-purity films with the assitance of a reactive gas. Except $Pd(hfac)_2$, palladium complexes yield low deposition rates.

6. Summary

The remarkable increase in publications over the last decade demonstrates the interest in CVD of noble metals. A few iridium, platinum, rhodium or palladium complexes exhibit a favorable combination of stability, volatility and clean decomposition. The use of hydrogen or oxygen as reactive gases is essential to reduce contaminants. For this group of metals, the deposition rates are typically low to be of interest for industrial application. However, high-quality deposits have been achieved, particularly in the case of epitaxial films. Potential applications have emerged from the production of fine particles by CVD, namely catalysts and electrocatalytic electrodes. The use of auxiliary energy sources such as plasma or laser to assist CVD is a viable route to increase deposition rates, although the deposition is confined to small areas. The understanding of the surface reaction mechanisms may allow design of new complexes or modification of operating conditions to provide high deposition rates.

Acknowledgment

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