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REVIEW

Organochromium precursors for low-temperature OMCVD of chromium-based coatings

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Many organochromium compounds have been used as volatile chromium sources to prepare chromium-based coatings by chemical vapor deposition. Chromium carbides, nitrides, oxides and alloys have been deposited on different substrates at low temperature (<500 °C). Organochromium precursors are reviewed and some of their drawbacks are discussed. They are classified according to the nature of the chromium–ligand bonds (carbonyls, amides, arenes or alkyls). Furthermore, experimental results obtained in the same apparatus for a series of representative precursors are reported to discuss, with literature data, how the ligand affects the composition and the structure of the films.

Keywords: Organochromium, coating, thin film, chemical vapor deposition

INTRODUCTION

The increasing interest in low-temperature chemical vapor deposition (CVD) processes promotes research on the use of organometallic (OM) compounds. For electronic components, low-temperature processes are required at each stage of their fabrication to avoid interdiffusion at the interfaces and subsequent, degradation of their properties. Hard metallurgical coatings, albeit refractory materials, also have to be prepared at low temperature to minimize problems related to dimensional variations and structural changes in the base material. Chromium-based coatings have numerous applications and most of them have been successfully prepared by OMCVD. For instance, chromium carbide[1-3] and chromium metal[4] are prepared as contact and interconnect materials for electronic components, CrSi and CrNi[5] as resistor material, Cr_2O_3 is deposited as selective absorber coating for photothermal energy conversion,[6] CrO_2 as ferromagnetic film for information storage[7] and chromium alloys, such as CrNi[8] and CrV,[9] are used as underlayers to improve adherence of hard coatings on steel substrates. The tremendous resistance to corrosion of chromium films is well known. The chromium carbides, Cr_3C_2, $Cr_{23}C_6$ and chiefly Cr_7C_3,[10] are attractive protective hard refractory coatings because of their good wear and corrosion resistance in agressive media. Chromium nitride exhibits both promising wear and corrosion resistance, and tribological properties, for applications in the nuclear industry.[11, 12]

Although much progress has been made in identifying suitable precursors for CVD of transition-metal films,[13] one of the drawbacks of OMCVD is contamination of the deposit by carbon derived from the ligands. The thermal decomposition of organometallic compounds can occur by numerous mechanisms and a crucial problem is to control this carbon incorporation. Consequently, as demands made on the deposition methods become more stringent, particular emphasis is placed on the choice of the precursor molecule. The nature of the ligand and the type of metal–ligand bonds determine and control the chemical reactions which convert the precursor to the thin film. However, we do not yet know which ligands are useful and which are deleterious for the growth of pure chromium metal or of a particular phase.

In this paper, organochromium compounds used as chromium sources in OMCVD are reviewed in order to attempt to afford a further insight into the above-mentioned questions. Although the ideal properties required of a precursor limit the choice, many organochromium

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compounds have been used. They are classified according to the nature of the chromium–ligand bonds.

2 CHROMIUM CARBONYL COMPOUNDS

2.1 Chromium hexacarbonyl

$Cr(CO)_6$ was the first organochromium compound used for low-temperature chromium deposition.[14] Its thermal decomposition has been less intensively studied than that of $M(CO)_6$ (M = Mo, W), probably because chromium is more reactive toward carbon monoxide (CO) than molybdenum and tungsten. Its pyrolysis has been performed from 250 to 710 °C and a high level of contamination by oxygen and carbon has been found (Table 1). The carbon incorporation originates both from the disproportionation reaction and the dissociative chemisorption of CO on the growing film. Occurrence of reaction [1] is limited either under low pressure[6, 14–16] or using high total flow rate,[17] since in both cases CO groups are rapidly removed from the reaction zone. Likewise, cold-wall reactors are generally used to minimize homogeneous decomposition of carbonyls.[14–18] The presence of additional reagents in the gas phase, e.g. water,[14] hydrogen sulfide[15] or carbon dioxide,[17] is also a reported solution. Hydrogen, which frequently favors the removal of carbon in other CVD processes, seems inefficient.[14] This is consistent with our recent results and will be briefly discussed in the last section. Without additive reagents, coatings are typically described as a mixture of Cr, Cr_3C_2 and Cr_2O_3, the proportion of which depends on the experimental conditions.

$$2CO \rightarrow CO_2 + C \qquad [1]$$

Table 1. Chromium-based coatings prepared by OMCVD using $Cr(CO)_6$[a]

Deposition temp. (°C)	Carrier gas/ add. reagent	Substrate	Deposited phases	Ref.
400–600	H_2	Steel	Cr + carbide	14
300	He	Steel	$Cr + CrC_{1-x} + Cr_2O_3 + C$	19
300	H_2	SiC fiber	Cr_2O_3	16
250–650	H_2/H_2S	Steel	$Cr + Cr_3C_2 + Cr_2O_3$	15
288–371	N_2/CO_2	Steel	Cr metal	17
300–450	Ar/O_2	Steel	Cr_2O_3	6
120–230	$H_2/Ni(CO)_4$	Steel	NiCr	8
710	H_2	GaAs	Cr-doped GaAs	18

[a] Chromium carbide, chromium oxide and pure chromium metal have been deposited using this precursor. Photo- and plasma-assisted CVD data are not included.

Deposition in a hot-wall reactor, under a helium atmosphere and reduced pressure, leads to multiphased coatings. Their characterization, by methods including XPS, TEM and grazing X-ray analyses, gives evidence for a mixture of an original metastable cubic CrC_{1-x} phase, Cr_2O_3, free carbon and a small amount of chromium metal.[19, 20] A thorough examination of these literature data shows that the decarbonylation process at the surface is not quantitative and probably the dissociative chemisorption of CO [21] is predominantly responsible for the film contamination. Surface studies indicate that while desorption of undissociated CO is complete above 127 °C, dissociated CO species persist above 727 °C [22]. Furthermore, thermal decomposition under vacuum of $Cr(CO)_6$ by laser heating results in a lower incorporation of impurities[23]. This supports the assumption that CO desorption is strongly favored over dissociation at higher temperature. Then, $Cr(CO)_6$ undergoes a sufficiently clean decomposition around 710 °C to be used as a chromium source to dope GaAs layers, in a deposition process well known for its stringent purity requirements [18]. Photo-assisted CVD using $Cr(CO)_6$ is also an expanding field but it is beyond the scope of this review; see for example Ref. 24.

2.2 Tricarbonyl(arene)chromium and related complexes

Many tricarbonylchromium(arene) complexes have been used as chromium sources in OMCVD (Table 2). These complexes are of particular interest for mechanistic studies because they have structural features of both $Cr(CO)_6$ and bis(arene)chromium compounds. It has been reported that the carbon content in the film can be controlled for a given temperature by selecting suitable arene ligands. However, in addition to discrepancies, literature data reveal that the film composition varies with the deposition temperature over a relatively wide range so that no reli-

Table 2 Tricarbonyl(arene)chromium compounds[a] used as chromium sources in OMCVD

$(CO)_3Cr[arene]$[b]	Deposition temp. (°C)	C content (wt %)	Ref.
$[\eta^6\text{-}C_6H_6]$	300–375	4–7	25
o-$[\eta^6\text{-}C_6H_4Me_2]$	350–400	5–7	25
m-$[\eta^6\text{-}C_6H_4Me_2]$	400	5	25
p-$[\eta^6\text{-}C_6H_4Me_2]$	275–350	2	25
$[\eta^6\text{-}C_6H_3Me_3]$	300–375	6–11	25, 26
$[\eta^6\text{-}C_6H_5(NH_2)]$	400–700	0.5–10	26
$[\eta^6\text{-}C_6H_5(NMe_2)]$	275–400	5	25, 26
$[\eta^6\text{-}C_6H_5(OMe_2)]$	300	4–5	25
$[\eta^6\text{-}C_6H_4(C_4H_8)]$	275–400	2–11	25
$[\eta^6\text{-}C_6H_2(C_4H_8)_2]$	375–450	3–9	25
$[(\eta^6\text{-}C_7H_8)Cr(CO)_3]$[c]	300–600	9–12	27
$[(\eta^5\text{-}C_5H_5)CrH(CO)_3]$[c]	330–473	12	28

[a] Some related complexes of this family are also included.
[b] The structure of the arene ligand is reported in this column.
[c] Complexes with a related structure.

able correlation can be found between the carbon content of the film and the arene structure. Chromium carbide films are grown at temperature as low as 275 °C.[25] At higher temperatures, the carbon level is relatively high; the films are described as mixtures of $Cr_{23}C_6$ and free carbon, and they contain up to 8 wt % oxygen in the form Cr_2O_3, due probably to dissociation of carbonyl groups.[26]

The mechanism of decomposition of (cycloheptatriene)tricarbonylchromium, $(C_7H_8)Cr(CO)_3$, has been investigated. Chromium films grown in the temperature range 300–600 °C contain 9–12 wt % carbon and up to 4 wt % oxygen. From ^{13}C labeling experiments, Truex *et al.* have shown that the majority of incorporated carbon (>85%) originates from the cycloheptatriene ring.[27] Reactions involving CO ligands, including reaction [1], have a minor contribution to the growth mechanism. The reactivity of π-arene ligands seems to be greater than that of carbonyls for the formation of chromium carbide coatings. Amorphous films with an atomic ratio Cr : C = 1.5 : 1 are deposited between 330 and 473 °C from the related complex $CpCr(CO)_3H$ ($Cp = C_5H_5$). The oxygen level decreases from 17 to 2.5 at. % by increasing the temperature in the above-mentioned range. Hydrogen does not alter significantly the film composition. From gas-phase analyses, it is assumed that most of the carbon deposited originates also from decomposition of the cyclopentadienyl ring rather than of carbonyl groups.[28]

3 CHROMIUM COMPOUNDS WITH Cr–O–C OR Cr–N–C BONDS

In this section the term 'organometallic', which denotes compounds containing metal–carbon bonds, is extended to metal complexes which feature metal–oxygen–carbon or metal–nitrogen–carbon bonds. Alkoxide or acetylacetonate complexes have been employed in CVD processes to deposit many metal oxides. By hydrogen reduction, they are also potential precursors to pure transition-metal films. Nevertheless, there are a few published reports for the chromium derivatives. Trifluoroacetylacetonatechromium, $Cr(C_5H_4O_2F_3)_3$, was selected to attempt to prepare composite ceramic materials by simultaneous deposition of an SiC matrix and a dispersed Cr_3C_2 phase. However, in agreement with a thermodynamic prediction, the large quantity of carbon present in this molecule causes carbon to deposit in the system.[29]

Dialkylamides of transition elements which feature M–N bonds are very attractive single sources for deposition of transition-metal nitrides. For instance, TiN is claimed to have been deposited from $Ti(NMe_2)_4$ but films are heavily contaminated with carbon[30] and addition of NH_3 is required for a good quality of film.[31, 32] Amorphous chromium carbonitride films are deposited under low pressure (40 Pa) from the chromium amide, $Cr[N(iPr)_2]_3$. The composition of films deposited at 330 °C is $Cr_{0.56}C_{0.29}N_{0.13}$ and the nitrogen content slightly decreases to 9 at. % at 473 °C. Evidence for a mixture of chromium carbide, nitride and free carbon has been found.[28]

The fact that a pure chromium nitride phase is not obtained is in good agreement with thermodynamic analyses performed in our laboratory. Indeed, by contrast with calculations performed for high temperature (~1100 °C), the calculated isothermal section of the Cr–N–C system at 527 °C reveals that free carbon is thermodynamically stable with both the solid solution $Cr_2(N, C)$ and the CrN phase.[33] Consequently, the large quantity of carbon brought into the gas phase by the organochromium precursor induces a carbon contamination of the film. Moreover, a complex equilibrium calculation using a computer program based on the minimization of the Gibbs energy of the whole system has been performed to predict the composition of the deposit, using different organochromium precursors and deposition conditions.[34, 35] At 527 °C, the chemical system $Cr(NEt_2)_4/H_2/He$ should lead to the CrN phase

Table 3 Typical results, including deposition temperature and film characterization, on the deposition of chromium-based coatings using representative organochromium precursors[a]

Precursor	$\bar{D}$(Cr–L) (kJ mol^{-1})	Deposition temp. (°C)	C content[b] (wt %)	XRD/TEM results[c]	Free C[d] (%)	Ref.
$Cr(CO)_6$	107.0	300	12.9[e]	CrC_{1-x} + oxides	50	19, 20
$Cr(C_6H_6)_2$	165.1	527	12.4	$Cr_7C_3 + Cr_3C_2$	29	20, 35
$Cr[C_6H_5(iPr)]_2$	160.1	510	13.0	Cr_7C_3	38	38
$Cr(C_5H_5)_2$	283.4	630	9.8	$Cr_7C_3 + Cr_3C_2 + Cr_{23}C_6$	34	20
$Cr(tBu)_4$	—	128	20.8[f]	Amorphous	50	39
$Cr(CH_2CMe_3)_4$	—	355	17.5[g]	$CrC_{1-x} + Cr_2O_3$	90	40
$Cr(CH_2SiMe_3)_4$	—	495	27.5[h]	Amorphous	>50	41

[a] Samples were prepared in the same low-pressure CVD apparatus: carrier gas, helium; total pressure, 300–2500 Pa; total flow rate, 300 sccm for $Cr(CO)_6$ and 100–150 sccm for the other precursors. [b] EPMA analyses. [c] Only the identified crystalline phases are reported. [d] XPS analyses. [e] Contains also 9.3 wt % O. [f] XPS data; contains also 2.6 wt % O. [g] AES data; contains also 18.5 wt % O. [h] AES data; contains also 13.5 wt % Si and 2.5 wt % O.

only under atmospheric pressure, and removal of free carbon would be possible only for a gas-phase ratio $H_2/Cr(NEt_2)_4 > 100$. Decreasing the total pressure would give successively $Cr_2(N, C)$ and then Cr_3C_2 around 100 Pa, both phases being contaminated by free carbon, even for high values of the ratio $H_2/Cr(NEt_2)_4$.[34] This is consistent with results reported for $Ti(NMe_2)_4$,[30–32] and $Cr[N(iPr)_2]_3$.[28] Furthermore, this explains why for the deposition of CrN by OMCVD we have not retained the single-source route. Taking account of these calculations, we have preferred to use separate gas streams of $Cr(C_6H_6)_2$ and NH_3 (or N_2H_4) as sources of chromium and nitrogen, respectively, since CrN low-pressure CVD processes require a large excess of the nitrogen source.[33–36]

4 BIS(CYCLOPENTADIENYL)-CHROMIUM AND RELATED SUBSTITUTED COMPOUNDS

To avoid oxygen contamination of films, oxygen-containing ligands must be excluded. With this purpose in mind, hydrocarbon ligands are preferred. Bis(cyclopentadienyl)metal compounds have been explored as potential CVD precursors but literature on chromocene is scarce. Besides a patent which briefly mentions its use,[37] our data seem to be the only report.[20] Under reduced pressure (300 Pa), deposition of a crystalline metallic coating requires the substrate temperature to be raised to 630 °C. The higher temperature range of deposition found for chromocene compared with bis(η^6-arene)chromium compounds or carbonyl derivatives can be predicted from the higher value of the chromium–ligand mean bond strength (Table 3). Characterizations give evidence for a mixture of the three stable chromium carbide phases contaminated by free carbon. The total carbon level (9.8 wt %) is significantly lower than in films prepared from bis(η^6-arene)chromium derivatives (~12.5 wt %). Pure chromium metal films cannot be obtained with this precursor due to side decomposition reactions of the cyclopentadienyl ring. In spite of this, it is also used as a chromium source for the doping of semiconductors prepared by vapor-phase epitaxy.[42]

To our knowledge, alkyl-substituted cyclopentadienylchromium derivatives have never been tried as chromium sources. However, due to their lower melting points, they can be attractive liquid precursors for chromium carbide deposition [m.p. of $Cr(\eta^5\text{-}C_5H_5)_2 = 173$ °C whereas $Cr(\eta^5\text{-}C_5H_4Me)_2 = 35$ °C].

5 BIS(ARENE)CHROMIUM DERIVATIVES

Table 4 gives a list of π-bonded bis(arene)chromium compounds previously proposed as potential chromium sources, including deposition temperature and data on film composition.[1, 2, 25, 26, 38, 43–63] The feasibility of chromium deposition from such precursors was first demonstrated in 1962 using bis(cumene)chromium, $Cr[C_6H_5iPr)]_2$.[43] Relatively few investigations have been performed on the simpler compound of this family, the bis(benzene)chromium, $Cr(C_6H_6)_2$.[26, 44–47] However, according to thermodynamic analyses and its lower C:Cr atomic ratio, it is a better candidate for deposition of chromium-based materials which should not contain carbon, such as CrN.[20, 35] By contrast, much work has been reported on bis(alkylbenzene)chromium compounds.[1, 2, 26, 38, 43, 48–63]

In these sandwich chromium (0) complexes, the chromium–arene mean bond strength is not significantly different for chromium–benzene and chromium–alkylbenzene π-bonds (Table 3). Consequently, thermal decomposition of these bis(arene)chromium complexes occurs in the same temperature range (300–550 °C) to yield chromium carbide films, regardless of the nature of the alkyl substituent bound to the benzene ring. Previously, thermal decomposition of $Cr(C_6H_6)_2$ was claimed to give pure chromium metal,[45] but this was never confirmed.[20, 26, 35, 46] A common feature of these arene precursors is that amorphous films are formed between 300 and 500 °C while crystalline chromium carbides are grown at higher temperature.[38, 55] As shown in Table 4, the composition and heterogeneous structure of the films depend strongly on experimental conditions. They are successively described as a mixture of chromium metal, $Cr_{23}C_6$ and carbon,[26] chromium metal, Cr_7C_3 and Cr_3C_2,[43] Cr_7C_3 and free carbon,[56] chromium metal supersaturated with carbon[60] or pure chromium metal.[61] Although the incorporated carbon is assumed to originate from cleavage of the aliphatic side-chain[48] and the carbon level in the film has been found to increase with accumulation of alkyl substituents on the benzene ring,[26] it is now accepted that the carbon incorporation is due to side-reactions involving catalytic dehydrogenation of aromatic hydrocarbons formed. This is supported by our results[20, 35, 38] which show that, under similar deposition conditions, the carbon content in films deposited using $Cr(C_6H_6)_2$ and $Cr[C_6H_5(i\text{-}Pr)]_2$ is not significantly different (Table 3). Furthermore, kinetic studies have shown that alkyl substituents on the benzene ring did not affect in the kinetic parameters.[47, 51, 52] The process would be autocatalyzed by chromium atoms at the moment of their liberation and would be weakly dependent on the temperature, leading to a constant carbon incorporation over the deposition temperature range.[38] Pure chromium metal films (~0.1 wt %C) can then be obtained by addition of hexachlorobenzene to the gas phase to inhibit decomposition side-reactions of aromatic hydrocarbons.[55] Pyrolysis of bis(arene)chromium iodides leads also to very low carbon contamination, probably because a disproportionation reaction plays a major role in the growth mechanism.[26, 64]

Table 4 Bis(arene)chromium compounds used for the deposition of chromium carbide films by OMCVD[a]

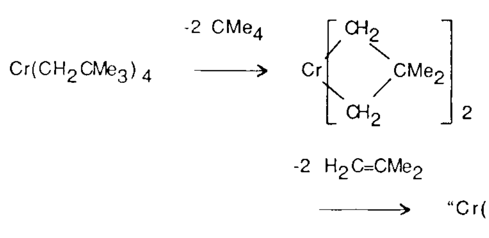
$Cr(arene)_2$	Deposition temp. (°C)	C content (wt %)	Identified phases	Ref.
$Cr(C_6H_6)_2$	300	0	Cr metal	45
	400–700	0.5–10	$Cr + Cr_{23}C_6 + C$	26
	500	1–8	$Cr_{23}C_6 + Cr_7C_3$	46
	527	12.4	$Cr_7C_3 + Cr_3C_2 + C$	20, 35
$Cr(C_6H_5Me)_2$	400–700	0.5–10	$Cr + Cr_{23}C_6 + C$	26
$Cr(C_6H_4Me_2)_2$	400–700	0.5–10	$Cr + Cr_{23}C_6 + C$	26
$Cr(C_6H_3Me_3)_2$	400–700	0.5–10	$Cr + Cr_{23}C_6 + C$	26
$Cr(C_6H_5Et)_2$	450–700	0.7–6	$Cr + Cr_{23}C_6 + C$	26, 48–54
	300–475	0.1	Cr	55
$Cr(C_6H_5Et)(C_6H_4Et_2)$	280–400	—	Mechanisms	56–59
$Cr(C_6H_5C_6H_5)_2$	400–700	0.5–10	$Cr + Cr_{23}C_6 + C$	25
$Cr[C_6H_5(iPr)]_2$	300–325	—	Cr	61
	350	8	$Cr + Cr_7C_3 + Cr_3C_2$	43
	325–520	7.5–12	$Cr + C$	1, 2, 60
	325–550	11–13	$Cr_7C_3 + C$	10, 20, 25 38, 62, 63

[a] Only the identified phases are reported.

6 TETRA-ALKYLCHROMIUM COMPOUNDS

Tetra-alkylchromium complexes usually undergo decomposition under or around room temperature. However, we have recently shown that if the β-decomposition route is blocked or hindered using appropriate ligands, these complexes become suitable precursors for OMCVD.[39–41] Then amorphous chromium carbide films are deposited in the exceptionally low temperature range 100–150 °C using tetra-*tert*-butylchromium, $Cr(tBu)_4$.[39] The films contain a large amount of carbon (~20 wt %C) when they are deposited under an inert or hydrogen atmosphere. This carbon is incorporated in two forms: carbidic and free C (~50%). However, it is noteworthy result that a very low carbon incorporation is found when deposition is performed under dynamic vacuum, without any carrier gas.[39] Tetraneopentylchromium, $Cr(CH_2CMe_3)_4$, has also been successfully used to prepare microcrystalline metallic films in the temperature range 250–350 °C.[28,40] A common feature of these homoleptic chromium alkyls is that a relatively large amount of carbon is incorporated in the film when the deposition experiments are conducted under the usual CVD conditions, i.e. using a stream of carrier gas (Table 3).

Both the higher thermodynamic stability of $Cr(CH_2SiMe_3)_4$ and the lower kinetic lability of the ligand $—CH_2SiMe_3$ results in a significant increase of the deposition temperature range (450–515 °C).[41] In contrast with $Cr(tBu)_4$, both $Cr(CH_2CMe_3)_4$ and $Cr(CH_2SiMe_3)_4$ are characterized by the absence of β-hydrogen. Thus, the Cr–C cleavage and the ligand removal presumably occur by the cyclometallation process:



[2]

In the case of the chromium neopentyl derivative, the release of isobutene in the second part of reaction [2] generates a nutrient species, $[Cr(CH_2)_2]$, for the growth of chromium carbide films. Nevertheless, using $Cr(CH_2SiMe_3)_4$, the formation of the transient silalkene analogue of isobutene ($H_2C{=}SiMe_2$) is improbable because of its low stability. As a result, fragmentation of the methylsilyl ligand can occur after the first step, leading to silicon and carbon incorporation in the film.[41]

7 CONCLUDING REMARKS

Many organochromium compounds have been used to deposit chromium-based coatings by CVD at low temperature. For instance, chromium carbide films are prepared below 500 °C whereas the industrial CVD process from chromium halides works at 1050 °C. However, selection of a more suitable precursor to deposit a particular phase is still difficult because of discrepancies in the literature data. The composition and structure of the films depend on experimental conditions which are sometimes only partially reported. The choice will depend both on the process requirements (pressure and temperature ranges) and the nature of the coating. For instance, to avoid oxygen contamination of the films, oxygen-containing ligands will be definitively excluded.

Using carbonyl or bis(arene)chromium compounds, pure chromium metal films are prepared by addition to the gas phase of further reagents. With most of the reviewed precursors, the carbon incorporation results from decomposition side-reactions of the ligand or hydrocarbon formed. Interestingly, deposition under dynamic vacuum, without any carrier gas, leads to very low carbon contamination of the films, e.g. $Cr(CO)_6$[23] and $Cr(tBu)_4$.[39] Furthermore, the inefficiency of hydrogen to reduce the carbon level in the film has been frequently mentioned.[14,28,39–41] Collision-induced dissociative chemisorption[65] serves to explain such observations. Chromium is not a Fischer–Tropsch-active metal; i.e. in contrast with Pt, Co, Ni, etc., it is not able to catalyze the hydrogenolysis of CO to hydrocarbon and water, or the methanation of surface carbon in the presence of hydrogen. In such cases, the carrier gas molecules may promote the surface decomposition of some of the ligands or of hydrocarbons formed, interfering with their removal, which is more efficient under vacuum. CVD mechanisms are complex and further investigations are required to overcome the problem of impurity incorporation in the film.

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