

# Iridium coatings grown by metal–organic chemical vapor deposition in a hot-wall CVD reactor

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## Abstract

Deposition of uniform coatings on relatively large size and/or complex shaped pieces require generally isothermal rather than cold-wall chemical vapor deposition (CVD) reactor. After a review of the state-of-the-art of Ir CVD processes aiming the selection of the starting materials, Ir thin films were deposited on W substrates by thermal decomposition of Ir(COD)(MeCp) either in presence of H<sub>2</sub> or O<sub>2</sub>. The growth was carried out in a horizontal hot-wall metal–organic chemical vapor deposition reactor under reduced pressure and low temperature (573–673 K). Using this CVD reactor the process is more difficult to control using H<sub>2</sub> rather than O<sub>2</sub> as co-reagent. The purity, the microstructure, the growth rate and the thickness uniformity depend on the deposition conditions. Oxygen avoids carbon incorporation in the layers and enhances significantly the growth rate. However, co-deposition of Ir and IrO<sub>2</sub> was observed using a high excess of O<sub>2</sub>. Polycrystalline, compact, untextured and pure Ir coatings were deposited with a satisfactory thickness uniformity over a length of approximately 15 cm and with a typical thickness of 1–2 μm. These coatings have attractive properties to be used as oxidation barriers at high temperature. Optimal deposition conditions were found using the trends predicted by a kinetic model simulating the growth rate along the CVD reactor. A good thickness uniformity along the reactor requires a very short residence time of the reactive species. As a result, the conversion rate is low leading to a poor efficiency of the process.

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**Keywords:** Chemical vapor deposition; Iridium coatings; Kinetic model

## 1. Introduction

Iridium deposition has been extensively investigated for microelectronics applications as electrode material in high-density memory devices and ferroelectric capacitors [1,2]. Ir is a noble, FCC metal with a small unit cell dimension, a high melting point (2727 K) and chemical stability. Owing to these properties, it acts as a good diffusion barrier to oxygen. As a result, Ir has a great interest as protective coating due to its good resistance against corrosion and oxidation at high temperature [3–5]. Chemical vapor deposition (CVD) technique has attractive advantages for growth of Ir thin films such as good conformal coverage on patterned or rough surfaces owing to the high throwing power of gaseous reagents and a good ability for large-scale production. CVD is particularly well adapted to uniform

deposition on complex shaped base material with a relatively high growth rate. Furthermore the use of metal–organic precursors permits decreasing significantly the deposition temperature. However, noble metal films deposited by metal–organic chemical vapor deposition (MOCVD) often contain carbon as impurity originating from the thermal decomposition of the organic ligands. Addition of a co-reagent in the gas phase is generally achieved to eliminate carbon impurity.

Various organometallic compounds of Ir have been studied as Ir sources for MOCVD process [6,7]. Depending on the constraints of the process, most of these precursors have advantages and drawbacks that are briefly discussed in the next section. For industrial development, an MOCVD process must produce reproducible films with uniform thickness over large substrate area, at high growth rate and high output. A high growth rate in a relatively large CVD reactor requires a sufficient and constant vapor phase delivery rate. This can be achieved, for instance, using direct liquid injection of the precursor [8,9]. However, due to the high reactiv-

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ity of the Ir precursors, it is difficult to obtain a good uniformity of the thickness along the reactor.

In this paper, the thickness uniformity over relatively large substrate area is addressed. We report the deposition of high-purity Ir films on W plates 10 cm long using Ir(COD)(MeCp) either in presence of H<sub>2</sub> or O<sub>2</sub> as co-reagent. The influence of the reactive gas phase on the purity and the thickness uniformity is discussed. A simple kinetic model was used to determine the optimal deposition conditions leading to a satisfactory thickness uniformity of the Ir films along the reactor.

## 2. State-of-the-art of CVD of Ir

Due to the attractive potentiality of Ir thin films, many molecular compounds have been investigated as precursors for CVD processes. They can be classified in different families depending on the type of ligands bonded to the metal. Ir(III) halides were the first compounds used as Ir sources [10,11]. They have a low volatility and decompose at high temperature, typically  $T > 1090$  K. They generate a corrosive atmosphere that is generally harmful for the substrates. A co-reagent such as H<sub>2</sub> has been used to improve the purity of the films while CO, a very toxic gas, has been proposed to increase the growth rate [10]. Due to these drawbacks, metal–organic compounds are preferred.

Ir(III) anionic chelates are frequently used to deposit Ir by MOCVD. The organic groups are bonded to the metal by Ir–O bonds. The first representative of this family is iridium *tris*-acetylacetonate, Ir(acac)<sub>3</sub>. It has been extensively used in CVD [1,3,4,12–23]. The reason is likely because it is an air-stable compound and the cheapest metal–organic precursor rather than for its great potentiality to produce high quality films. Indeed, films with heterogeneous structures [12] and high levels of O and C contamination have been reported [13,14,16–19,24]. The presence of H<sub>2</sub> [1,12,20,21,25] or O<sub>2</sub> [13,14,16–18,23,25] as co-reagent is necessary to deposit thin films with a high purity. Iridium(III) hexafluoroacetylacetonate, Ir(hfa)<sub>3</sub>, has a better volatility than Ir(acac)<sub>3</sub> but a similar behavior in CVD [22].

For a better control of the C elimination and to avoid O incorporation in the layers, complexes containing only Ir–C bonds (without oxygen) have been investigated [8,9,26–33]. These compounds decompose at low temperature and the organic groups are generally cleanly eliminated leading to high-purity films. However, due to the low temperature, the layers are frequently amorphous [26–29]. Under very low pressure C contamination was reported [29,31]. For this reason, even with this type of precursors, the presence of H<sub>2</sub> [26–31] or O<sub>2</sub> [9,31–33] is recommended. We found in this family Ir( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)<sub>3</sub> [26–29], Ir(Cp)(C<sub>2</sub>H<sub>4</sub>)<sub>2</sub> [30], Ir(COD)(Cp) [31], and Ir(COD)(MeCp) [8,9,31–33]. The low melting point (312 K) of this last precursor

permits its use as liquid source near room temperature [8,31]. Interestingly, it is soluble in common organic solvents and has been used in a direct liquid injection CVD process [9,32,33].

The last type of precursors consists of mixed Ir(I) complexes containing anionic chelate bonded to Ir by oxygen and neutral hydrocarbon ligands. For instance, the following precursors have been investigated: Ir(COD)(acac) [2,34], [Ir(COD)( $\mu$ -OOCH)]<sub>2</sub> [34], [Ir(COD)( $\mu$ -OAc)]<sub>2</sub> [31], Ir(COD)(hfa) [35,36], Ir(COD)(thd) [2,35], [Ir(CO)<sub>2</sub>( $\mu$ -S'Bu)]<sub>2</sub> [37], Ir(COD)(keim) [38], Ir(COD)(hfda) [38], Ir(COD)(amak) [38]. The different ligands were selected to improve the stability and the volatility of the precursors and to decrease its melting point. Compare to the previous family, the deposition temperature is slightly higher due to the chelate ligand that stabilizes the precursor.

In this work, (methylcyclopentadienyl)(1,5-cyclooctadiene)iridium, Ir(COD)(MeCp), has been selected because it is an air-stable compound that can be used as liquid source. This permits a constant vapor phase delivery rate. We have measured a vapor pressure of 11 Pa/373 K by the transport method in good agreement with the literature data 7 Pa/368 K [31] and 37 Pa/393 K [8].

## 3. Experimental

CVD experiments were achieved in a horizontal, hot-wall reactor 1.2 cm in diameter and 15 cm of isothermal zone. The precursor Ir(COD)(MeCp) was contained in a thermostated bubbler (373 K) and transported using He as carrier gas. Gaseous co-reagent (H<sub>2</sub> and O<sub>2</sub>) was introduced in the gas stream at the entrance of the reactor. The flow rates were monitored using mass flowmeters and the total pressure was automatically controlled using an absolute pressure gauge coupled to a throttle valve control system. Tungsten plates (100×10×1 mm<sup>3</sup>) were used as substrates. They were degreased in hot trichloroethylene and ultrasonically cleaned in ethanol, dried, placed into the reactor after cleaning and subjected to several cycles of vacuum followed by H<sub>2</sub> pressurization. The typical growth conditions are reported in Table 1.

The surface morphology and the thickness of the coatings were analyzed by SEM. Their microstructure was determined by XRD and their surface roughness measured using a profilometer. XPS analyses were carried out using a non-monochromatized Al K $\alpha$  radiation. The relative thickness of the coatings along the sample axis was determined by a nondestructive XRD method consisting measuring the intensity of the

Ir(2 0 0) diffraction peak along the sample. Consistent values of the thickness were obtained after calibration using data determined on cross-sections by SEM because the films are untextured.

## 4. Results and discussion

### 4.1. Ir growth under $H_2$ atmosphere

Deposition of Ir films under  $H_2$  ambience is very sensitive on the residence time ( $\tau$ ) and the decomposition temperature. For  $\tau=0.05$  s and  $T\leq 573$  K the precursor sweeps out the reactor without decomposition. Deposition starts at 573 K for  $\tau=0.05$  s. Under these transport conditions and increasing the temperature to 673 K the precursor is totally decomposed near the entrance of the reactor resulting in an abrupt gradient of the film thickness. The growth rate reaches a peak at approximately  $0.7\text{ }\mu\text{m}$  at the entrance of the reactor and falls down to zero after a few centimeters. The Ir films are dense, untextured and constituted of small grains ( $\sim 200$  nm). Their surface roughness is similar to that of the W substrate ( $1\text{--}1.5\text{ }\mu\text{m}$ ). No evidence for impurities was found by XPS analysis. The mean growth rate in the isothermal zone is relatively low because the Ir(COD)(MeCp) flow rates obtained using a bubbler were only in the range  $0.05\text{--}0.10$  sccm, which is 50–100 times lower than the values used in direct liquid injection process [9,32,33]. The main problem using  $H_2$  as co-reagent in this hot-wall CVD reactor is due to the high reactivity of the gas mixture, which makes difficult to control the growth and to deposit uniform thicknesses over several centimeters long.

### 4.2. Ir growth under $O_2$ atmosphere

Ir films grown in presence of  $O_2$  with a low thickness ( $\leq 100$  nm) exhibit a surface morphology similar to those deposited under  $H_2$ . However, the structure of the thickest films ( $\geq 1\text{ }\mu\text{m}$ ) tends to be columnar on W substrate, leading to a more nodular surface morphology. This structure has a low density boundaries between the columns and individual columns are constituted of small crystallites. XRD patterns reveal the films are polycrys-

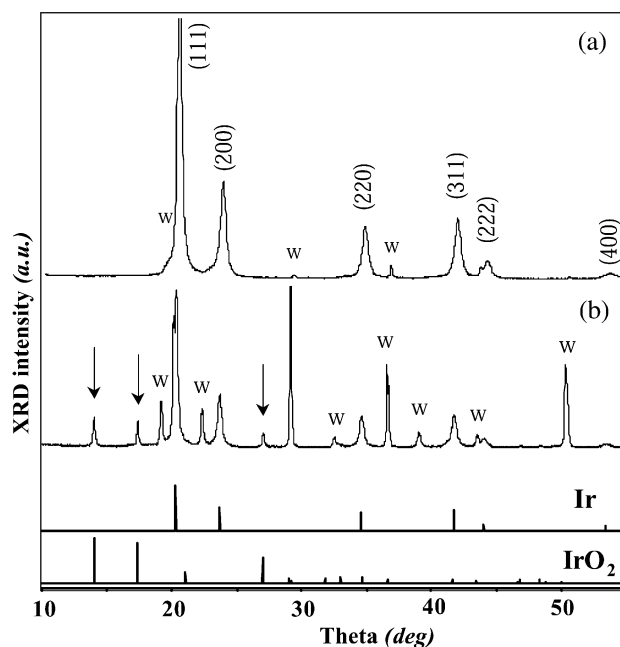


Fig. 1. XRD patterns of Ir coatings deposited at 573 K under  $O_2$  atmosphere as a function of the  $O_2$ /Ir(COD)(MeCp) mole ratio: (a) ratio = 60; (b) ratio = 1000. Peaks noted W originate from the tungsten substrate. Ir and  $IrO_2$  patterns from JCPDS files are given for comparison.

talline and despite the columnar growth, no evidence for a preferential orientation was found (Fig. 1). The mean crystallite size determined from the Scherrer's formula is approximately 35 and 45 nm for films deposited at 573 and 623 K, respectively. This confirms the columns are constituted of small crystallites. For films grown at 573 K, decreasing the pressure from 13.3 to 6.7 kPa decreases the crystallite size from 35 to 15 nm. Ir films deposited using a low  $O_2$  partial pressure exhibit a high purity. After cleaning the surface contamination by  $Ar^+$  sputtering for only 5 min, no impurity was detected on the XPS spectra. XRD patterns of coatings deposited using a high excess of oxygen ( $O_2$ :Ir(COD)(MeCp)=1000) clearly reveal a mixture of Ir and  $IrO_2$  (Fig. 1). For a mole ratio  $O_2$ :Ir(COD)(MeCp)  $\leq 135$ , co-deposition of oxide was not observed. Oxidation of Ir has been reported at high

Table 1  
Typical MOCVD conditions used for the deposition of Ir thin films

Parameters	$H_2$ as co-reagent	$O_2$ as co-reagent
Deposition temperature (K)	573–673	573–623
Total pressure (Pa)	1.3–13.3	6.7–13.3
Total flow rate (sccm)	250	250–900
Carrier gas (He) flow rate (sccm)	50	50–130
Co-reagent flow rate (sccm)	200	0.4–100
Ir(COD)(MeCp) mole fraction	$1.6 \times 10^{-4}$ – $3.6 \times 10^{-4}$	$5.8 \times 10^{-5}$ – $2.2 \times 10^{-4}$
Co-reagent/Ir(COD)(MeCp) ratio	2220–5000	4.5–1000
Residence time (s)	0.05–0.50	0.11–0.50

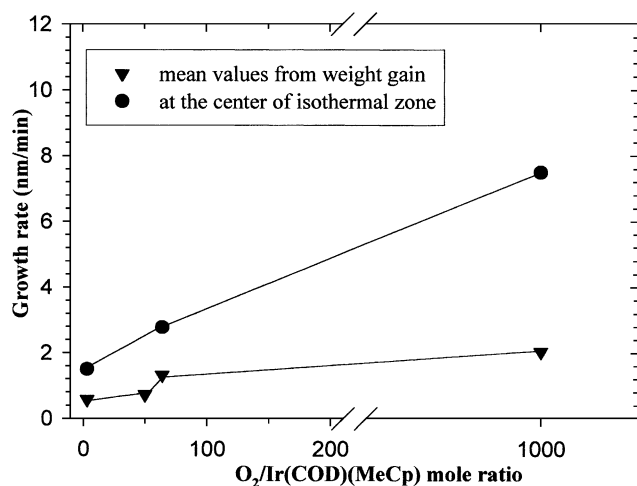


Fig. 2. Influence of the reactive gas phase composition on the growth rate of Ir coating deposited at 573 K. The mean values (▼) were determined from weight gain measurements and the values at the center of the reactor (●) were measured on cross-sections.

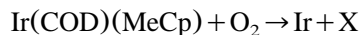
O<sub>2</sub> partial pressure and  $T > 873$  K [32]. Furthermore the deposition of IrO<sub>2</sub> was also reported using the gas mixture Ir(acac)<sub>3</sub>/O<sub>2</sub> at high O<sub>2</sub> flow rate and  $T \geq 873$  K [18]. From this last work, we can deduce that the formation of IrO<sub>2</sub> is possible at 873 K for an atomic ratio in the reactive gas phase O:Ir > 9. In our case, the Ir source is different and the deposition temperature is lower ( $\leq 623$  K) resulting in a significantly higher value of the critical ratio O:Ir. This is in agreement with experimental results since no oxide was identified for O<sub>2</sub>:Ir(COD)(MeCp)  $\leq 135$ .

Under the conditions reported in Table 1, the growth rate is relatively low and typically varies from 0.6 to 4.1 nm/min for a given position in the reactor ( $\sim 2$  cm). As for the deposition under H<sub>2</sub>, the growth rate depends on the temperature and the residence time. In addition, Fig. 2 shows it increases with the O<sub>2</sub> partial pressure in agreement with previous reports [8,32,33]. A thickness gradient was observed along the reactor. For high temperature and/or low residence time, the growth rate is maximum at the entrance of the reactor and rapidly decreases downstream. A better thickness uniformity can be obtained by adjusting these parameters but this is detrimental to the conversion rate of the precursor and, subsequently, to the mean growth rate.

#### 4.3. Optimization of the growth using a kinetic model

In absence of O<sub>2</sub>, Ir(COD)(MeCp) decomposes at  $T > 760$  K to produce MeCpH and COD [8,33]. When O<sub>2</sub> is used as co-reagent, it oxidizes the ligands producing CO, CO<sub>2</sub> and H<sub>2</sub>O and decreases the decomposition temperature to 465 K [33]. In addition to these by-products, we have analyzed in a cold trap at the outlet of the reactor, the presence of acetone and furan. This

indicates the mechanism is complicated and we will only consider the overall reaction:



where X represents all the organic by-products. The deposition rate increases with the partial pressure of both the Ir source and the oxygen and it was reported that the growth rate is approximately first-order in O<sub>2</sub> partial pressure at 550 K [33]. Consequently, we assume the growth rate of the overall CVD reaction is:

$$G = k p[\text{Ir(COD)(MeCp)}] p[\text{O}_2] \quad (1)$$

where  $k$  is the rate constant ( $k = k_0 \exp(-E_a/RT)$ ). A simple plug-flow model was used to calculate the growth rate [39]. We assume the reactor operates in a kinetic regime. It is divided into successive cylindrical parts and a mass-balance is calculated in each zone using the kinetic (Eq. (1)). The Ir(COD)(MeCp) concentration at the entrance of the zone  $i$  corresponds to the amount calculated at the outlet of the zone  $i-1$ . The reaction rate in each zone is the amount of precursor consumed by the reaction divided by the residence time of the reactive species. Due to the high excess of O<sub>2</sub>, its partial pressure was assumed constant along the reactor. The coated surface areas were both the flat substrate and the reactor wall. Preliminary CVD experiments were carried out to validate this model and to determine a set of kinetic data. Fig. 3 shows a good fitting between theoretical and experimental data for two values of the residence time. An activation energy  $E_a = 98 \text{ kJ mol}^{-1}$  and a pre-exponential factor  $k_0 = 5.8 \times 10^{14}$  were determined.  $E_a$  is approximately 30% higher than the value recently reported for a cold-wall reactor [8]. It is probable that in our hot-wall CVD reactor there is a more significant contribution of gas phase reactions, which increases the apparent activation energy.

The model confirms clearly that the thickness gradient is due to depletion of the Ir source. The thickness

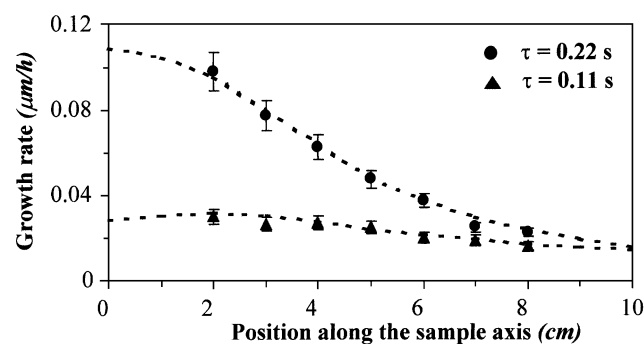


Fig. 3. Experimental (symbols) and theoretical (dotted curves) values of the growth rate of Ir coatings versus the position in the isothermal zone along the reactor for different residence time of gas species:  $\tau = 0.22$  s (●);  $\tau = 0.11$  s (▲). The residence time was adjusted by changing the total pressure from 13.3 to 6.7 kPa ( $T = 573$  K).

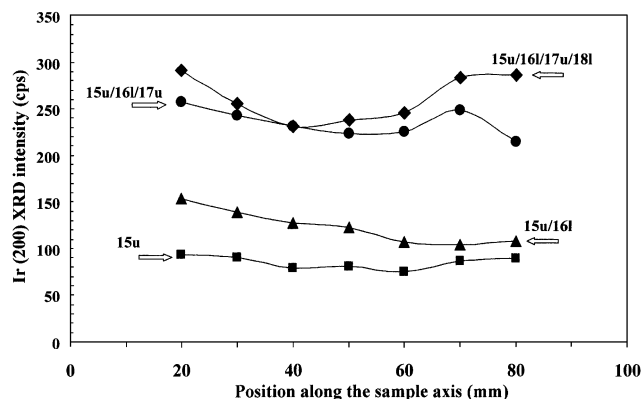


Fig. 4. Variation of the relative thickness of an Ir coating along the sample axis. The coating is constituted of four layers grown at 573 K under 6.7 kPa using a mole ratio  $O_2/Ir(COD)(MeCp)=62$ . The sample was turned above and below as well as fore and aft to get an uniform coating on the upper and lower faces of the W plate. The arrows indicate the direction of the gas stream at each step of the process. The letters *u* and *l* in the code of the run mean *upper* and *lower* face, respectively.

uniformity along the reactor is improved by decreasing the deposition temperature and the residence time. However, the yield of the process decreases rapidly with these parameters. This was confirmed by experimental measurement of the yield at 573 K, which decreases approximately from 37 to 15% by decreasing  $\tau$  from 0.22 to 0.11 s. Satisfactory thickness uniformity was obtained along the sample at 573 K under 6.7 kPa and using a mole ratio  $O_2:Ir(COD)(MeCp)=62$ . Samples were prepared under these conditions for oxidation tests (not reported). However, the growth rate on the lower face of the substrate is lower than on the upper one and the deposition is not uniform on the edges of the samples due to the contact with the reactor wall. Consequently, the samples were prepared by a multi-step process. They were turned above and below as well as fore and aft at each step to obtain uniform multilayer coatings. Fig. 4 shows a coating constituted of four Ir layers on a W plate 100 mm long. SEM analysis of cross-section confirms the good thickness uniformity of this coating along the sample. A good conformal coverage of the surface roughness is observed (Fig. 5). Interestingly, the Ir layers grown on Ir surfaces do not exhibit a columnar structure. Their density is higher than that of the layer grown directly on the W surface. The structure of these multilayer coatings is more favorable for a protection against oxidation at high temperature.

## 5. Conclusion

Deposition of pure Ir coatings were achieved in a hot-wall MOCVD reactor on both faces of W plates 100 mm long using  $Ir(COD)(MeCp)$  as Ir source. In presence of  $H_2$  as co-reagent, the high catalytic activity of

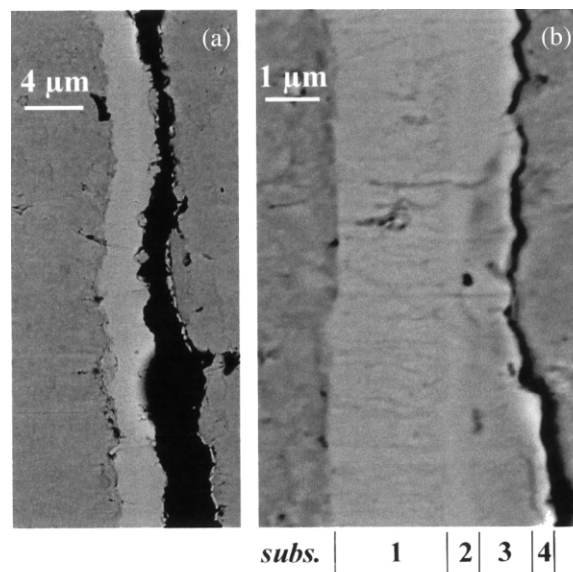


Fig. 5. SEM images of cross-sections of an Ir coating deposited on W plate at 573 K. The coating is approximately 3  $\mu m$  thick and constituted of four layers with different thicknesses.

Ir growing surface makes difficult the control of the growth rate along the reactor. Oxygen is particularly efficient to eliminate C contamination of the layers and to enhance the growth rate. However, co-deposition of Ir and  $IrO_2$  has been observed using high  $O_2$  partial pressure. A simple kinetic model has been used to optimize the thickness uniformity along the reactor. Typical growth conditions are: 573 K, 6.7 kPa and a mole ratio  $O_2:Ir(COD)(MeCp)=62$ . Under these conditions, the residence time of the reactive species in the isothermal zone is short (0.11 s) and the yield of the process is low. As a result, the economical practicability of the process is limited because it strongly depends on the cost of the Ir source. The behavior as oxidation barrier of multilayer Ir coatings deposited by this process on W plates is currently under investigation.

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