

AD-A104 582

SRI INTERNATIONAL MENLO PARK CA
THE CHEMICAL VAPOR DEPOSITION OF IRIIDIUM.(U)
JUL 81 J B MOONEY, R T REWICK, D L HAYNES

F/G 9/1

N00014-79-C-0580

UNCLASSIFIED

NL

1 of 1
ADA
04-82

END

DATE

FILMED

10-81

DTIC

AD A104582

DTIC FILE COPY



LEVEL

THE CHEMICAL VAPOR DEPOSITION OF IRIIDIUM

Final Report

June 1981

By: John B. Mooney, Senior Research Chemist
Engineering Sciences Laboratory

Robert T. Rewick, Physical-Inorganic Chemist
Daniel L. Haynes, Chemist
Thomas E. Gray, Chemist
David M. Vandenberg, Chemist
Physical Chemistry Department

Prepared for:

Scientific Officer, NRL Code 5220
Naval Research Laboratories
4555 Overlook Avenue
Washington, D.C. 20375

Attn: Mr. Howard Lessoff

Contract/N00014-79-C-0880

SRI Project 1013

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution unlimited

SRI International
333 Ravenswood Avenue
Menlo Park, California 94025
(415) 326-6200
Cable: SRI INTL MPK
TWX: 910-373-1246

81 7 31 06E

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER	2. GOVT ACCESSION NO. <i>AD-A104</i>	3. RECIPIENT'S CATALOG NUMBER <i>582</i>	
4. TITLE (and Subtitle) THE CHEMICAL VAPOR DEPOSITION OF IRIIDIUM <i>12</i>		5. TYPE OF REPORT & PERIOD COVERED Final Report	
7. AUTHOR(s) J.B. Mooney, R.T. Rewick, D.L. Haynes, T.E. Gray, D.M. Vandenberg		6. PERFORMING ORG. REPORT NUMBER SRI Project 1013	
9. PERFORMING ORGANIZATION NAME AND ADDRESS SRI International 333 Ravenswood Avenue Menlo Park, California 94025		8. CONTRACT OR GRANT NUMBER(s) Contract N00014-79-C-0880	
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Research Laboratories 4555 Overlook Avenue Washington, D.C. 20375		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
14. MONITORING AGENCY NAME & ADDRESS (if diff. from Controlling Office)		12. REPORT DATE July 1981	13. NO. OF PAGES 28
		15. SECURITY CLASS. (of this report) Unclassified	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this report) DISTRIBUTION STATEMENT 1 Approved for public release; Distribution Unlimited			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from report)			
18. SUPPLEMENTARY NOTES			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The preparation of iridium films for thermionic cathodes by chemical vapor deposition was studied. The deposition from $\text{IrCl}_3/\text{H}_2/\text{CO}$ atmospheres was very inefficient; however, iridium was deposited from $\text{IrF}_3/\text{H}_2/\text{CO}$ at 465°C & 25°C with reasonable efficiency. The majority of the deposits were porous or loose powders. An attempt to deposit iridium on a substrate designed to produce a microporous film was unsuccessful because of the poor throwing-power of the process.			

DD FORM 1 JAN 73 **1473**
EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

ABSTRACT

The preparation of iridium films for thermionic cathodes by chemical vapor deposition was studied. The deposition from $\text{IrCl}_3/\text{H}_2/\text{CO}$ atmospheres was very inefficient; however, iridium was deposited from $\text{IrF}_6/\text{H}_2/\text{CO}$ at $465^\circ\text{C} \pm 25^\circ\text{C}$ with reasonable efficiency.

The majority of the deposits were porous or loose powders. An attempt to deposit iridium on a substrate designed to produce a micro-porous film was unsuccessful because of the poor throwing-power of the process.

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	<i>on file</i>
By	
Distribution/	
Availability Codes	
Dist	Special
<i>A</i>	

CONTENTS

ABSTRACT.....	11
LIST OF ILLUSTRATIONS.....	1v
LIST OF TABLES.....	v
I INTRODUCTION.....	1
II EXPERIMENTAL DETAILS.....	3
A. Apparatus.....	3
B. Materials.....	7
III RESULTS.....	9
A. Deposition from IrCl_3	9
B. Deposition from IrF_6	9
C. Effect of Temperature.....	11
D. Substrate Type.....	15
E. IrF_6 Exposure.....	16
F. Effect of Carrier Gas Composition and Flow Rate.....	17
G. Effect of Low Pressure.....	18
H. Nature of the Deposit.....	18
I. Elemental Analysis.....	22
J. Deposition on Silicon Microstructures.....	22
IV DISCUSSION.....	24
A. Iridium Deposition from IrCl_3	24
B. Iridium Deposition from IrF_6	24
REFERENCES.....	26

ILLUSTRATIONS

1	Schematic Diagram of Iridium Chemical Vapor Deposition Apparatus.....	4
2	Chemical Vapor Deposition Apparatus.....	5
3	Assembled Apparatus with Vaporizer in Place.....	6
4	Sticking Efficiency for Iridium Deposition on Copper from IrF_6 as a Function of Temperature.....	15
5	Dendrite Iridium Deposit (Run 33 in Table 4).....	20
6	5000X SEM Photograph of Iridium Deposit on Copper Substrate (Run 16 in Table 3).....	20
7	5000X SEM Photograph of Iridium Deposit on Copper Substrate (Run 5 in Table 3) Before Removal.....	21
8	2000X SEM Photograph of Iridium Deposit (Back Side, Run 5 in Table 3) After Removal from Copper Substrate.....	21
9	Deposition on Silicon Microstructure.....	23

TABLES

1	Preparation of IrF_6	8
2	Summary of Iridium Deposition Results Using IrCl_3	10
3	Initial Iridium Deposition Results from IrF_6	12
4	Iridium Deposition Results from IrF_6	13

I INTRODUCTION

This report summarizes the results of an investigation of a method for the production of thin films of iridium by chemical vapor deposition (CVD) with the objective of controlling crystallographic orientation.

The need for ultra-long-life ($> 10^6$ hour) traveling wave tubes for satellite communications has stimulated a resurgence of interest in dispenser cathodes (Schroff, 1978; Longo, 1978; Smith, 1978). The conventionally accepted types are made of porous tungsten impregnated with barium calcium aluminates (Levi, 1955; Brodie and Jenkins, 1956). The emission capability of the dispenser cathode gradually decreases during its lifetime at a rate strongly dependent upon the cathode's operating temperature (Longo, 1978). Related experiments have shown that this decay is associated with a decline in the rate at which barium is supplied to the surface (Brodie and Jenkins, 1957a; Rittner et al., 1957) and with changes in the physical-chemical structure of the cathode surface. Scanning electron micrographs have shown that not only does the chemical composition of the pore ends and the bulk material undergo alteration, but the crystal structure of the tungsten (Maloney, 1978; Sickafus, 1978) is also affected. Emission micrographs of the cathode surface show a marked patchiness (Brodie and Jenkins, 1957b; Tuck, 1978), with the more intense emission originating at the pore endings--at least at the beginning of life.

Recently, there have been studies of iridium as a base metal for dispenser cathodes, at the Naval Research Laboratory (NRL) (Thomas et al., in press) and at Varian (Falce, 1978). The various properties of iridium that can influence cathode operation were discussed by Thomas et al. They found that, as with other materials (Weissman and Kinter, 1963), crystallographic orientation influences the thermionic work function, and, in randomly oriented, large-grained films, is responsible for

"patchy" emission. Oriented polycrystalline films can be produced by vapor deposition (Thomas et al., in press; Bauer, 1962; Powell et al., 1966; Yang and Hudson, 1967; McMurray et al., 1965).

Our investigation revealed that the deposition of iridium using IrCl_3 as a source was very inefficient even in the presence of H_2/CO . IrF_6 was a more efficient source, and we could deposit iridium layers over a substrate temperature range of 400°C to 500°C , with a sharp peak in the deposition efficiency at $465^\circ \pm 25^\circ\text{C}$.

Depositions up to $50\text{-}\mu\text{m}$ thick were obtained. The depositions were porous and often nonadherent powders. No evidence of preferred orientation was found.

II EXPERIMENTAL DETAILS

A. Apparatus

A schematic view of the stainless-steel-and-glass iridium chemical-vapor-deposition apparatus is shown in Figure 1. The volatile iridium source could be supplied from either the IrCl_3 or IrF_6 vaporizer as shown. The carrier gas, consisting of either argon (Ar), hydrogen (H_2), or carbon monoxide (CO), or mixture, was metered through the appropriate vaporizer from calibrated flowmeters. Deposition experiments were usually conducted at atmospheric pressure, but a Cartesian diver pressure regulator was sometimes used to investigate subambient conditions. The substrate, consisting of a freshly etched or cleaned metallic specimen, was placed on a graphite susceptor containing a thermocouple well and centered in position between radio frequency (RF) induction coils (Lepel Model 1-2.5). The flow stream containing volatilized iridium struck the heated surface of the specimen through a cone-shaped glass impinger located about 1.5-mm above the specimen surface. The wall temperature of the reactor was maintained by a hot-air gun for IrCl_3 experiments and by cold water for IrF_6 experiments. A photograph of the assembled apparatus with the IrF_6 vaporizer in place is shown in Figures 2 and 3. Volatile iridium species were generated from IrCl_3 by flowing the carrier gas (mixtures of argon, carbon monoxide, and hydrogen) through a heated sample of the powder in the vaporizer shown in Figure 1. The exact nature of the volatile iridium species was unknown, but an iridium carbonyl chloride such as IrCOCl_2 was a likely candidate. To avoid deposition of iridium on cold wall surfaces, the lines following the IrCl_3 vaporizer were heated.

The vaporizer containing IrF_6 was transferred to the vapor phase by passing the carrier gas (usually a mixture of argon and carbon monoxide) through the U-tube maintained at low temperature. The mass flow rate of

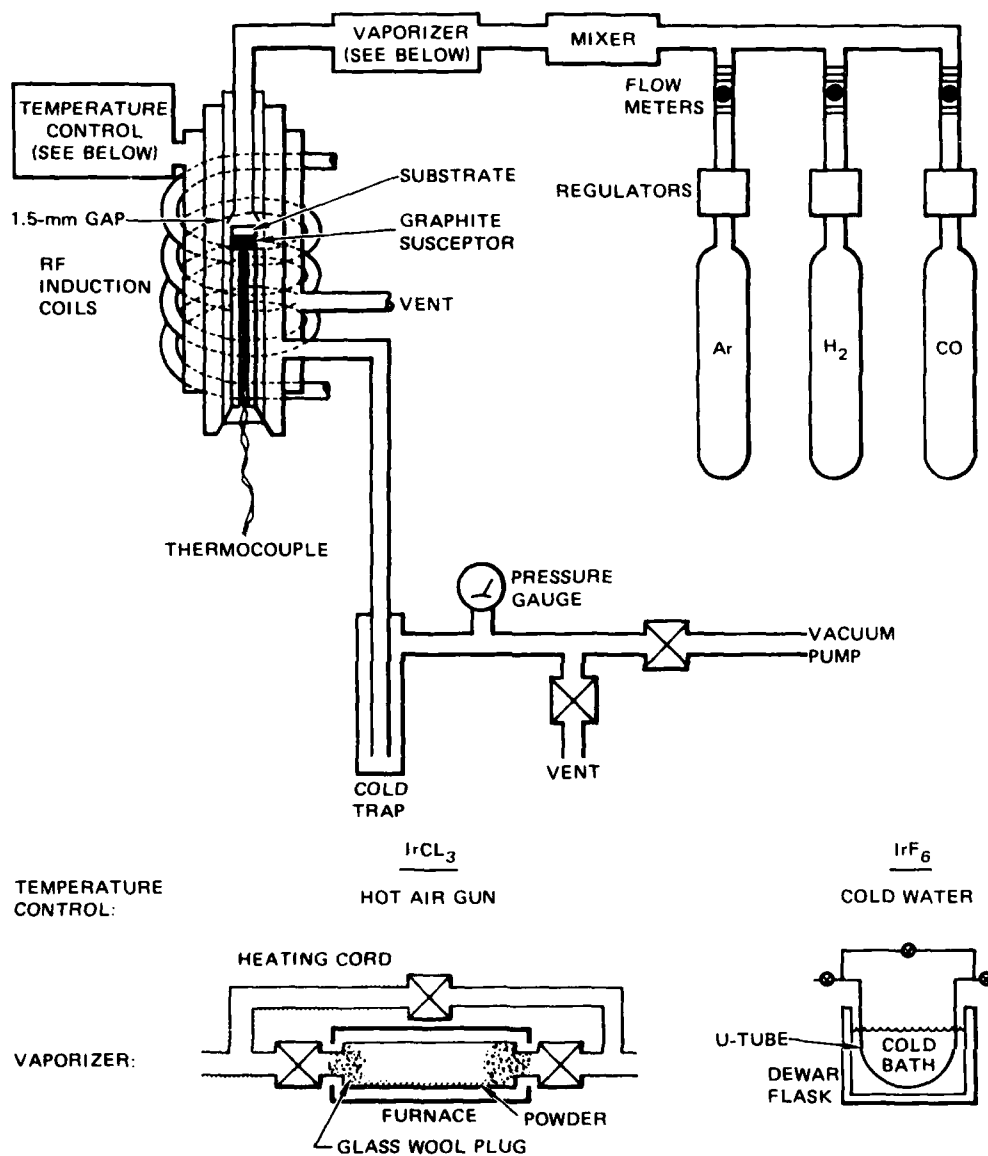


FIGURE 1 SCHEMATIC DIAGRAM OF IRIDIUM CHEMICAL VAPOR DEPOSITION APPARATUS

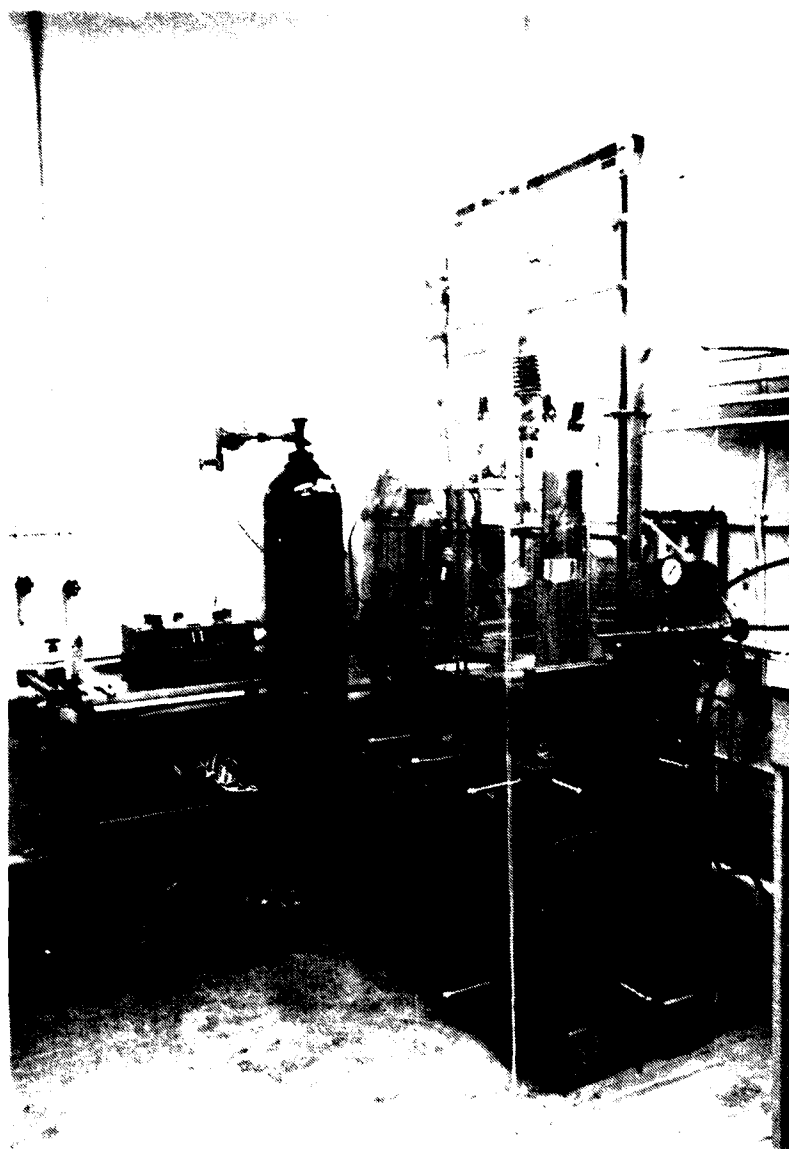


FIGURE 2 - CHEMICAL VAPOR DEPOSITION APPARATUS

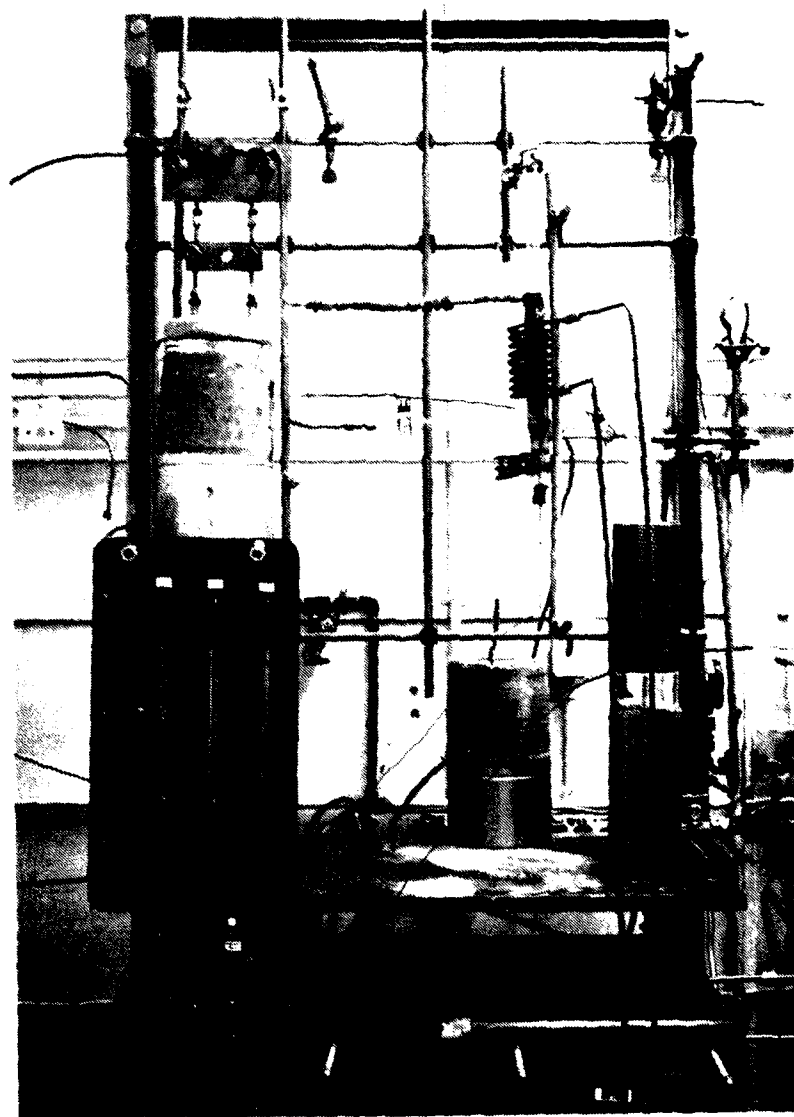


FIGURE 3 ASSEMBLED APPARATUS WITH VAPORIZER IN PLACE

IrF_6 can be estimated from the volumetric flow rate of the carrier gas and the known vapor pressure/temperature relationship for IrF_6 . Since vapor saturation was not achieved under our flow conditions, we calculated the actual IrF_6 mass flow rate by weighing the U-tube before and after the deposition experiment. To avoid losses of IrF_6 to hot wall surfaces, the reactor walls were cooled with cold water.

B. Materials

Amorphous IrCl_3 was obtained from Alpha Products in sealed glass ampules. All transfers of the powder were conducted in the inert atmosphere (N_2) of a dry box. To prepare IrF_6 , a section of 0.030-inch (0.75 mm) diameter iridium wire (99.5 percent purity from Englehard Industries) was burned in elemental fluorine (280 torr) in a Monel[®] vessel maintained as -196°C . Under these conditions, combustion of iridium proceeds to IrF_6 in greater than 90 percent conversion (Table 1). The volatile product was then distilled into the tared U-tube and stored at -78.5°C . During a deposition experiment, the U-tube was attached to the CVD apparatus and maintained at the desired temperature with a slush bath, usually $\text{LN}_2/\text{acetonitrile}$ (-46.5°C).

The suitability of a variety of metallic substrates for the deposition of iridium was investigated during the course of this study. The materials included molybdenum, copper, iridium-coated copper, silicon, SiO_2 -coated silicon, and copper-coated silicon. In general, the specimens were 0.625-inch (1.5625 cm) diameter disks, about 0.005 to 0.010-inch (0.125 to 0.25 mm) thick, and cleaned by standard acid etching or polishing techniques. Each sample was weighed to ± 0.2 mg before and after the experiment to determine the weight of iridium deposited. The nature of the deposit on selected specimens was characterized by scanning electron microscopy (SEM), X-ray fluorescence (XRF), and X-ray diffraction (XRD) analysis.

Table 1
PREPARATION OF IrF_6
($\text{Ir} + 3\text{F}_2 \rightarrow \text{IrF}_6$)

Run	Reactants			Product	
	Fluorine (mole)	Iridium* (mole)	Iridium Consumed* (wt%)	IrF_6 (mole)	Conversion† (wt%)
1	0.0510	0.0161	88.8	0.0130	91.2
2	0.0597	0.0162	92.6	0.0126	84.5
3	0.0594	0.165	93.6	0.0117	76.0
4	0.0616	0.0166	93.5	0.0146	94.2
5	0.0598	0.0165	93.2	0.0142	92.4
6	0.0595	0.0167	(51.2)‡	0.0060	(69.5)‡
7	0.0599	0.0165	93.1	0.0143	93.0
8	0.0608	0.0163	93.1	0.0167	110.3
9	0.0603	0.0165	93.7	0.0137	88.7
10	0.0600	0.0164	93.5	0.0140	91.4
11	0.0603	0.0164	93.2	0.0144	94.2
12	0.0436	0.0123	91.0	0.0105	93.4
Average			92.7		91.8

* 0.030-inch diameter wire (99.5 percent purity).

† Based on weight of iridium consumed.

‡ Wire broke (not included in average).

III RESULTS

A. Deposition from IrCl₃

The important parameters concerning the efficient deposition of iridium from IrCl₃ included vaporizer and substrate temperatures and carrier-gas composition and flowrate. The results from these studies, summarized in Table 2, demonstrate that no more than about 2.5 mg of iridium can be deposited on a molybdenum or copper substrate in the form of isolated iridium patches as detected by SEM/XRF surface analysis. Specifically, we observed that conditions that fostered the generation of a volatile iridium species (150°C to 200°C in the presence of H₂/CO) also fostered the reduction of IrCl₃ to the metal. In nearly all attempts to volatilize iridium from IrCl₃ in the presence of H₂/CO, but especially with hydrogen, theoretical conversion of the chloride to finely divided pyrophoric iridium metal was observed. The small fraction of volatile iridium species generated during reduction to the metal, responsible for the iridium deposits observed on the molybdenum and copper substrates, appeared to decompose on wall and substrate surfaces heated above 300°C.

B. Deposition from IrF₆

Our experimental approach to optimizing conditions for the deposition of iridium from IrF₆ has entailed a detailed evaluation of these parameters: substrate type, temperature, pressure, IrF₆ concentration, flow rate, and presence of hydrogen and CO in the carrier stream. Results from these studies are described below.

Table 2
SUMMARY OF IRIIDIUM DEPOSITION RESULTS USING IrCl₃

Run Number	Sample*	Carrier Gas		Temperature Conditions (°C)				Run Time (h)	Sample Weight Change (mg)	Parameter Studied	Notes
		Gas Composition (volume percent)	Flow Rate (cm ³ /min)	IrCl ₃	Transfer Lines	Reactor Wall	Sample				
1	Mo	30 CO/70 Ar	200	150 [†]	175	175	880	5.0	-0.8	Impinger	1
2	Mo	30 CO/70 Ar	200	249	175	175	895	5.1	+1.3	IrCl ₃ Temp.	1
3	Mo	60 CO/40 Ar	200	250	175	175	830	5.0	-0.7	Co Conc.	
4	Mo	33 CO/67 H ₂	200	175	175	180	885	5.0	+0.6		
5	Cu	33 CO/67 H ₂	200	173	175	185	880	5.0	+0.1	Cu Sample	2
6	Cu	30 CO/70 Ar	200	245 [†]	175	180	885	5.0	-0.4	Repeat No. 2	
7	Cu	30 CO/70 Ar	200	247	175	170	530	5.0	-0.8	Sample Temp.	
8	Cu	30 CO/70 Ar	200	250	175	150	337	5.0	0	Sample Temp.	1,3
9	Cu	30 CO/70 Ar	500	242 [†]	175	170	350	5.0	-0.6	Flow Rate	3,4
10	Cu	30 CO/70 Ar	200	245 [†]	175	175	346	5.1	+0.2	Repeat No. 8	3
11	Cu	28 CO/69 Ar/3 H ₂ O	200	250 [†]	175	175	345	5.3	+2.4	Effect of H ₂ O	3,5
12	Cu	28 CO/69 Ar/3 H ₂ O	200	145	150	165	302	5.0	+1.1	Sample Temp.	2,3,6
13	Cu	28 Cu/69 Ar/3 H ₂ O	200	152 [†]	163	163	296	5.2	-0.1	Repeat No. 12	3,6

* Metal disk 0.625-inch (15.9 mm) diameter × 0.005-inch (0.127 mm) thick.

[†] Fresh IrCl₃ sample.

NOTES:

1. SEM/XRF Analysis isolated particles of iridium.
2. IrCl₃ reduced to iridium metal.
3. Silver-colored coating on sample.
4. SEM/XRF Analysis isolated particles of iridium; high nickel, iron.
5. SEM/XRF Analysis higher concentration of iridium particles; high chlorine.
6. SEM/XRF Analysis nearly uniform iridium film; some particles.

C. Effect of Temperature

Initial screening experiments to optimize deposition temperature were conducted in the range 308°C - 915°C on a copper substrate. Above 700°C, the amount of iridium deposited (above 30 mg) was essentially independent of temperature, flow rate, or IrF₆ concentration. Below 700°C, temperature played a dramatic role on the amount of adherent iridium deposited. The relationship between temperature and iridium deposition is best compared to the deposition efficiency of IrF₆, which is defined as substrate weight gain/total IrF₆ exposure. As shown in Table 3, initial IrF₆ exposures were not constant and varied over a large range; this deficiency was corrected in later experiments. Initial results suggested that maximum iridium deposition efficiency occurred over a narrow temperature range; at ~489°C, nearly 20 percent of the exposed IrF₆ was deposited as iridium on the copper substrate. A ± 10°C variation from this temperature reduced the deposition efficiency to less than 5 percent. In these early experiments, the reported temperatures are that of the graphite susceptor. More accurate temperature measurements of the substrate surfaces were achieved by positioning the thermocouple to contact the sample. Temperature measurements at this position (Table 4) were about 20°C to 40°C cooler than those given in Table 3.

As shown in Table 4, we focus on temperature conditions near 450°C to optimize iridium deposition efficiency from IrF₆. The results, plotted in Figure 4, demonstrate a narrow range temperature dependence for maximum efficiency, which peaks at about 465°C.

Because of the high radiant output from the heated graphite susceptor, reactor wall temperatures were difficult to control by air cooling, and varied between about 40°C to 190°C. Because the hot walls provided another sink for IrF₆ decomposition, more efficient cooling was provided by flowing tap water through the cooling jacket, which maintained the wall surface at about 18°C.

Table 3
INITIAL IRIIDIUM DEPOSITION RESULTS FROM IrF₆

Run Number	Substrate	Carrier Gas		IrF ₆		Temperature (°C)		Substrate Weight Gain* (mg)	Sticking Efficiency† (%)	Nature of Deposit (see notes)	
		Gas Composition (vol. %)	Flow Rate (cm ³ /min)	Temp. (°C)	Total Exposure (sec)	Mass Flow Rate (mg/h)	Sample (Graphite Susceptor)			Visual	SEM XRD
1	Ir/Cu	82 Ar/18 CO	73	-78.5	1266	60	474	32.6	2.6	Black	1
2	Ir/Cu	82 Ar/18 CO	73	-78.5	135	8	308	2.0	1.5	Spotty black	
3	Ir/Cu	82 Ar/18 CO	73	-78.5	21	1	504	0.9	4.3	No visible deposit	
4	Ir/Cu	82 Ar/18 CO	73	-46.5	317	79	470	4.3	1.4	Fairly uniform grey with some black patches	2
5	Cu	82 Ar/18 CO	73	-46.5	501	123	493	84.1	16.8	Adherent, grey	3
6	Cu	82 Ar/18 CO	73	-46.5	380	91	308	5.0	1.3	Grey/black, hygroscopic	4
7	Cu	82 Ar/18 CO	73	-46.5	122	31	415	2.1	1.7	Adherent, light grey	
8	Cu	82 Ar/18 CO	73	-46.5	---	---	577	0.3	---	Adherent, silver	5
9	Cu	82 Ar/18 CO	73	-46.5	1559	390	613	6.6	0.4	Loose, dark grey	6
10	Cu	82 Ar/18 CO	73	-46.5	1928	473	443	12.5	0.6	Loose, dark grey	
11	Cu	82 Ar/18 CO	73	-46.5	183	46	732	10.9	6.0	Light coating, lumps	
12	Cu	73 Ar/27 CO	73	-46.5	916	250	488	18	7.8	Loose, silver/black	7
13	Cu	100 Ar	50	-46.5	113	28	499	2.9	2.6	Loose, grey/black	
14	Cu	82 Ar/18 CO	73	-78.5	-13	-0.8	512	-0.1	--	No visible deposit	
15	Cu	82 Ar/18 CO	73	-78.5	3019	163	553	86.5	2.9	Loose, grey/black	
16	Cu	82 Ar/18 CO	73	-46.5	1128	282	489	224.4	19.9	Adherent, grey/black	8
17	Cu	82 Ar/18 CO	73	-46.5	227	56	580	6.1	2.7	Loose, grey/silver	10
18	Cu	82 Ar/18 CO	73	-46.5	125	31	486	7.6	6.1	Adherent, grey/black	11

* Adherent deposit.

† Weight gain/Total IrF₆ exposure.

NOTES:

1. Clusters and needles of iridium.
2. Mostly 1- μ m particles with some 7.5- μ m lumps.
3. Mostly 2.5- μ m particles with some 10- μ m clusters.
4. Broad-peaked iridium pattern (small particle size); unknown impurity.
5. Very thin coating, perhaps film.
6. Coating too thin to measure iridium pattern.
7. Thin film with cracks.
8. Thick film with cracks.
9. Strong iridium with sharp peaks; no evidence for preferred orientation.
10. Nonhomogeneous film surface with some larger clusters.
11. Mostly 4- μ m particles with some larger clusters.

Table 4
IRIDIUM DEPOSITION RESULTS FROM IrF₆

Run Number	Substrate	Carrier Gas		IrF ₆			Sample (At Surface)	Reactor Walls	Substrate Weight Gain (mg)	Sticking Efficiency (%)	Nature of Deposit (see notes)		SDM	XRD
		Gas Composition (vol. %)	Flow Rate (cm ³ /min)	Temp. (°C)	Total Exposure (mg)	Mass Flow Rate (mg/h)					Visual			
17	Cu	60 Ar/40 CO	100	-46.5	520	130	490	18	47.1	9.1	Coherent gray/black film, some fell off when removing disk from apparatus	1		
20	Cu/Si	60 Ar/40 CO	100	-46.5	412	103	484	18	34.6	16.6	Silver/gray spotty deposit plus powder. Sample does not cover entire disk.			
21	Cu	60 Ar/40 CO	100	-46.5	415	204	435	18	46.2	11.1	Nonuniform silver/gray deposit plus loose powder.			
22	Cu	60 Ar/40 CO	100	-46.5	388	97	413	18	1.9	0.5	Light covering, silver/black adherent plus fine powder.			
23	Cu	60 Ar/40 CO	100	-46.5	285	70	474	18	2.7	0.9	Silver/black adherent + loose powder.			
24	Cu	60 Ar/40 CO	100	-46.5	194	48	533	18	0	0	Thin silver/black adherent plus loose powder.			
25	Cu	60 Ar/40 CO	100	-46.5	155	39	330	18	3.8	2.5	Thin metallic silver deposit; no loose powder.			
26	Cu	82 Ar/18 CO	73	-46.5	166	42	437	18	0	0	No change of color of Cu disk, so little if any deposited.			
27	Cu	82 Ar/18 CO	73	-46.5	315	74	436	15	35.6	11.3	Dark to light grey, mostly adherent, small amount of loose particulate.			
28	Cu	82 Ar/18 CO	73	-46.5	315	79	469	15	-1.5	--	Center of disk dark blue/purple small amount loose particles.			
29	Cu	82 Ar/18 CO	73	-46.5	398	96	402	15	1.4	0.4	Very thin dark purple film; adherent.			
30	Cu	82 Ar/18 CO	73	-46.5	358	95	419	15	45.8	12.8	Light to dark grey adherent film.	2		8
31	Cu	82 Ar/18 CO	73	-46.5	295	74	370	15	8.3	2.8	Medium grey to metallic silver; adherent. Some loose particulate.	3		
32	Cu	82 Ar/18 CO	73	-46.5	217	54	402	15	11.2	5.2	Light to medium grey adherent.			
33	Cu	82 Ar/18 CO	73	-46.5	230	53	450	16	33.6	14.6	Medium grey, uniform and mostly adherent, small amount of loose particles.	4		
34	Cu	82 Ar/18 CO	73	-46.5	129	29	478	16	26.2	20.3	Dark grey, uniform and mostly adherent. Moderate amount of loose particles.	5		
35	Cu	82 Ar/18 CO	73	-46.5	214	54	506	15	11.1	5.2	Patchy dark grey, adherent.			
36	Cu	82 Ar/18 CO	73	-46.5	194	48	485	15	13.3	6.9	Dark grey, adherent.			
37	Cu	88 Ar/12 CO	75	-46.5	188	47	478	16	2.2	1.2	Medium to dark grey adherent with no loose particulate.			
38	Cu	82 Ar/18 CO	73	-23	831	208	470	19	46.2	5.6	Mostly uniform dark grey adherent with large amount of loose particulate.	6		
39	Cu	82 Ar/18 CO	73	-78.5	0	0	464	15	0	0	Uniform shiny silver, adherent--very thin.			

Table 4 (concluded)

Run Number	Substrate	Carrier Gas		IrF ₆			Sample Area (At Surface)	Reactor Walls	Substrate Weight Gain (mg)	Sticking Efficiency (%)	Nature of Deposit (see notes)	
		Gas Composition (vol %)	Flow Rate (cm ³ /min)	Temp. (°C)	Total Exposure (mg)	Mass Flow Rate (mg/h)					Visual	SEM / XRD
40	Cu	82 Ar/18 CO (0.30 atm)	?	-46.5	1278	399	485	14	24.5	1.9	Medium to light grey adherent, heavier on one side of disk, small amount of loose particulate.	
41	Cu	82 Ar/18 CO (0.096 atm)	?	-78.5	-56?	0	472	14	0	0	Cu discolored yellow and grayish with rough texture.	
42	Cu	82 Ar/18 CO	?	-78.5	20	5	468	14	0.4	2.0	Cu discolored with thin medium grey adherent. Darker spot in middle. Very small amount loose particulate.	7
43	Cu	82 Ar/18 CO	?	-64	107	27	466	14	0	0	Very uniform light to medium grey adherent. Very small amount of loose particles. Very thin deposit.	
44	Cu	82 Ar/18 CO (0.30 atm)	?	-63.5	20	5	467	14	0.1	0.5	Cu discolored magenta. Very small amount loose particulate.	
45	Cu	82 Ar/18 CO	73	-78.5	10	0.67	480	14	0	0	No deposit. No particulate.	
46	Cu	82 Ar/18 CO	73	-46.5	595	50	472	13	33.4	5.6	Dark grey adherent. Small amount loose particulate and a few lumps.	
47	Cu	82 Ar/18 CO	73	-46.5	441	37	486	13	56.7	12.9	Dark grey in middle surrounded by light grey. Lumpy with moderate amount of loose particulate.	
48	Cu	82 Ar/18 CO	73	-46.5	457	38	465	13	69.8	15.3	Dark grey, lumpy adherent with light grey spot in middle. Large amount loose particulate.	
49	Cu	82 Ar/18 H ₂	73	-46.5	138	34.5	449	13	0	0	No adherent. Large amount loose flakes.	
50	Cu	82 Ar/18 CO	220	-46.5	811	162	471	13	32.1	4.0	Dark grey adherent. Smooth on outside, rough in middle. Moderate amount loose particulate.	
51	Cu coated contoured silicon	82 Ar/18 CO	73	-46.5	820	68	465	13	10.5 (corrected to normal disk area)	1.3	Spotty light and dark grey adherent. Large amount loose particulate.	
52	Cu with Ir wire	82 Ar/18 CO	73	-46.5	197	49	485	13	0.4	0.2	Uniform medium grey adherent. More shiny around edges and next to Ir wire. Small amount loose particulate.	

* Adherent deposit.

† Weight gain/Total IrF₆ exposure.

‡ Large amount loose powder.

§ Reactor cleaned.

NOTES:

1. Very large aggregate lumps ~80 µm.
2. Approximately 5 µm spears.
3. Film appearance with some ~2 µm lumps.
4. Large lumps ~30 µm and small lumps ~3 µm.
5. Very rough texture; particles ~30 µm.
6. Very rough texture; particles ~20 to 50 µm.
7. Film appearance with some ~10 µm lumps.
8. Well-crystallized pure Iridium; no preferred orientation.

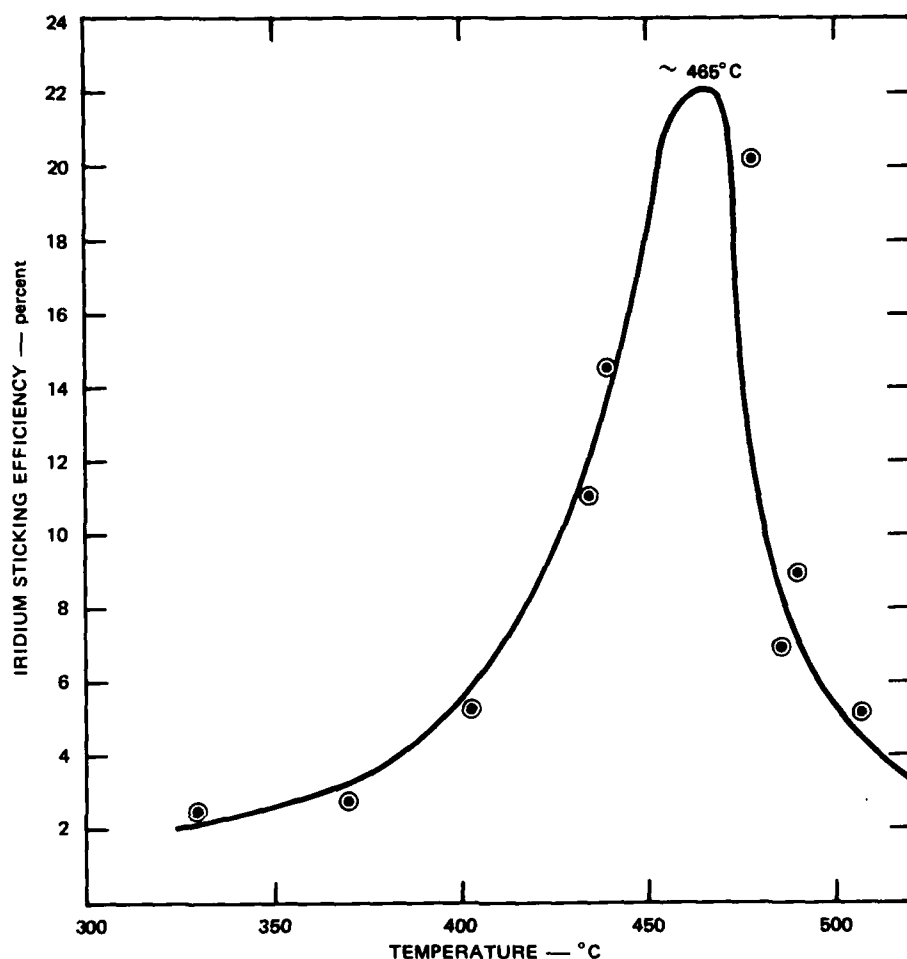


FIGURE 4 STICKING EFFICIENCY FOR IRIIDIUM DEPOSITION ON COPPER FROM IrF_6 AS A FUNCTION OF TEMPERATURE

D. Substrate Type

Several substrate materials for the deposition of iridium from IrF_6 were investigated. These included copper, molybdenum, quartz, and iridium-coated copper disks [0.625-inch (1.5625 mm) diameter x 0.0005 inch (0.125 mm) thick], and copper-coated and SiO_2 -coated silicon specimens.

For all samples except the copper and iridium surfaces, a substrate weight loss was observed during exposure to IrF_6 . This can probably be ascribed to IrF_6 attack to form volatile substrate species such as MoF_6 , $\text{Mo}(\text{CO})_6$, and SiF_4 . For the copper substrate, initial reaction probably forms a passivation coating of nonvolatile CuF or CuF_2 , which have melting points in excess of 900°C .

E. IrF_6 Exposure

The gas phase concentration of IrF_6 in the carrier stream was varied by changing the temperature of the vaporizer. The total IrF_6 mass flow rate was calculated from a knowledge of exposure time and the weight of the vaporizer before and after a deposition experiment. During initial experiments (Table 3), poor temperature control of the vaporizer resulted in a large variation of the IrF_6 mass flow rate: 168 ± 149 (standard deviation) mg/h at -46.5°C . We speculate that the reason for the variation was nonuniform cooling of the solid IrF_6 residing in the upper portion of the exit arms of the U-tube vaporizer. The IrF_6 vaporizer was loaded with the gas stream entering the arm of the U-tube that eventually became the exit during the deposition process. Since the IrF_6 readily condenses at -78°C , it collected near the entrance. Consequently, the temperature of the vaporizer was sensitive to the depth of the coolant on that region of the U-tube. The difficulty was eliminated by reversing the direction of loading to correspond to the direction of vaporization, such that the IrF_6 had to flow through the U-tube to enter the reactor and thermal uniformity was assured, and more uniform mass flow rates were achieved: 62 ± 21 (standard deviation) mg/h at -46.5°C .

By adjusting the temperature of the IrF_6 vaporizer and the time for the experiment, total exposures were varied from ~ 20 to 3,000 mg IrF_6 , and mass flow rates from ~ 1 to 470 mg/h. (Tables 3 and 4.) The results of this study showed that the quantity and quality of iridium deposited by CVD under these conditions is not strongly influenced by the rate at which IrF_6 is supplied to the substrate surface. While larger IrF_6

exposures result in the deposition of more iridium, the deposition efficiency remained essentially constant for a given temperature. In fact, the deposition efficiency curve constructed from the wide range of IrF_6 exposures given in Table 3 is essentially the same as the curve from a narrower range of exposures in Table 4 (Figure 4).

F. Effect of Carrier Gas Composition and Flow Rate

Carrier gas effects were investigated using mixtures of argon, CO, and hydrogen supplied through calibrated flowmeters. Initial results (Table 3) demonstrated that the presence of CO aids in achieving an adherent iridium deposit on a copper substrate. For example, in a carrier stream of pure argon, a "sticking efficiency" of 2.6 percent was observed (Run 13); at nearly the same temperature in the presence of (18 CO)/(82 argon) volume percent (vol%), 16.6 of the IrF_6 was deposited on the substrate (Run 5). Hydrogen is apparently too strong a reducing agent; in the presence of (18 hydrogen)/(82 argon) vol%, a large amount of nonadherent iridium powder was formed on the surface of the substrate (Run 49).

The nature of the iridium deposit on a copper substrate is affected by the concentration of CO in the CO/argon carrier stream. In the presence of 40 vol% CO, most of the deposit is in the form of loose powder, probably generated during gas phase reduction of IrF_6 above the substrate surface. When the CO concentration is lowered to 12 vol%, deposition efficiency is poor and little powder forms. While the effect of CO was not optimized over a broad range of concentrations, it appeared that iridium was deposited in the presence of 18 vol% CO in argon in the form of an adherent coating.

The effect of total gas-flow rate was not extensively studied. Most deposition experiments were conducted at a volumetric flow rate of $73 \text{ cm}^3/\text{min}$. Lowering the flow rate to $50 \text{ cm}^3/\text{min}$ appeared to have little effect on deposition efficiency and quality of the iridium deposit.

At a high flow rate of $220 \text{ cm}^3/\text{min}$, however, a reduction in deposition efficiency from about 20 to 4 was observed.

G. Effect of Low Pressure

Chemical vapor deposition studies are frequently conducted at low pressure to achieve desirable results. In the present study we evaluated 0.30- and 0.1-atm conditions using a Cartesian diver manostat and a deposition temperature near the maximum shown in Figure 4. While the composition of the carrier gas was adjusted to the ratio (18 CO)/(82 argon), it was not possible to measure the total volumetric flow rate at subambient pressure. Under these conditions we observed little if any iridium deposit on the copper substrate (Table 4, Run 40-44).

H. Nature of the Deposit

To evaluate the effectiveness of our experimental approach to optimizing the deposition of iridium from IrF_6 on a copper substrate, the deposit was analyzed in terms of

- Sticking efficiency
- Weight of adherent deposit
- Visual appearance
- Scanning electron microscopy and X-ray fluorescence analysis
- X-ray diffraction analysis.

Sticking Efficiency--Evaluation of parameters to maximize the amount of iridium deposition was most easily expressed in terms of the sticking efficiency for IrF_6 . In our work, sticking efficiency was influenced most by temperature and to a lesser degree by carrier-gas composition and flow rate. The repeatable observation of a narrow-range temperature dependence for iridium deposition, peaking at about 465°C (Figure 4), was a significant result from our study.

Weight of Adherent Deposit--In several cases, particularly in the presence of a high concentration of CO and hydrogen, a large amount of

loose iridium powder was found on the substrate surface. Powder formation probably occurs in the gas phase and is not a function of the nature of the surface. All results are reported in terms of the weight of adherent iridium deposit and not loose powder, which can easily be removed by tilting the sample. Under optimized conditions of temperature ($\sim 465^{\circ}\text{C}$) and carrier-gas composition [(18 CO)/(82 argon) vol%], more than 200 mg of adherent iridium was deposited on a 198 mm^2 copper disk in 4 hours. Presumably, larger amounts could be deposited over longer time periods.

Visual Appearances--As shown in Tables 3 and 4, the visual appearance of the iridium deposits from IrF_6 ranges in color from silver to black, suggesting a variety of particle sizes. In general, thinner deposits tended to be more silver/grey in color, but no particular hue could be related to a given parameter such as temperature, flow rate, or gas composition.

Microscopic Examination--Selected iridium deposits were examined by scanning electron microscopy (SEM). Most samples appeared to be dendritic (Figure 5) in nature, but occasionally a film was formed (Figure 6). The variation in morphology of the iridium deposits suggest that deposition is quite sensitive to subtle changes in experimental conditions, which we were not able to control repeatably. We speculate that temperature control to better than $\pm 5^{\circ}\text{C}$ may be required to achieve consistent morphology. SEM analysis further suggests that the initial layers of iridium deposited on copper appear as a thin film, followed by particulate or dendritic growth. This conclusion was reached by examining the iridium interface of a particulate-type deposit (Figure 7) after removal from the copper substrate. Figure 8 is a SEM photograph of the copper side of the iridium deposit, which appears film-like in nature. It is possible, however, that acid treatment used to remove the iridium deposit from the substrate may have produced the effect shown.

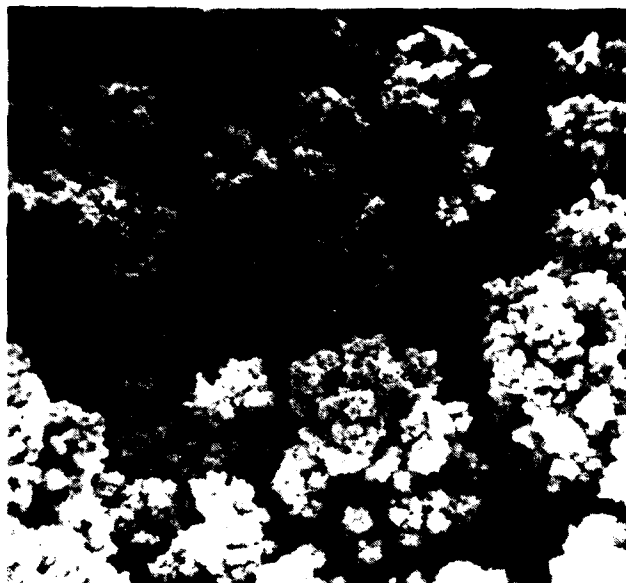


FIGURE 5 DENDRITE IRIIDIUM DEPOSIT (RUN 33 IN TABLE 4)



FIGURE 6 5000X SEM PHOTOGRAPH OF IRIIDIUM DEPOSIT ON COPPER SUBSTRATE (RUN 16 IN TABLE 3)

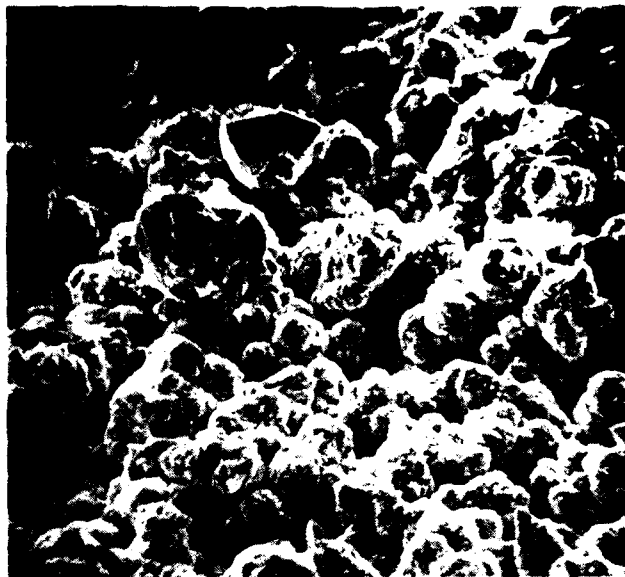


FIGURE 7 5000 $\times$ SEM PHOTOGRAPH OF IRIIDIUM DEPOSIT ON COPPER SUBSTRATE (RUN 5 IN TABLE 3) BEFORE REMOVAL



FIGURE 8 2000 $\times$ SEM PHOTOGRAPH OF IRIIDIUM DEPOSIT (BACK SIDE, RUN 5 IN TABLE 3) AFTER REMOVAL FROM COPPER SUBSTRATE
XRF analysis shows minor copper contamination

I. Elemental Analysis

X-ray fluorescence and diffraction analyses of selected deposits demonstrated the presence of essentially pure iridium with occasional trace contamination from aluminum and chlorine. X-ray diffraction analysis showed no preferred crystallographic orientation for any of the deposits studied.

J. Deposition on Silicon Microstructures

We attempted to deposit a microporous film on a silicon substrate supplied by Richard Thomas of NRL. The structure was prepared by anisotropic etching of a $\langle 110 \rangle$ silicon wafer to produce a pattern of ridges about 60- μm high, 14- μm long, and 1- μm wide, spaced 6 μm apart in rows separated by 30 μm . The pattern is apparent in Figure 9, which also shows the nature of the resultant deposit. The substrate was coated with copper by vacuum evaporation prior to iridium deposition. The dendritic growth, similar to that shown in Figure 5, totally dominated the deposition process.

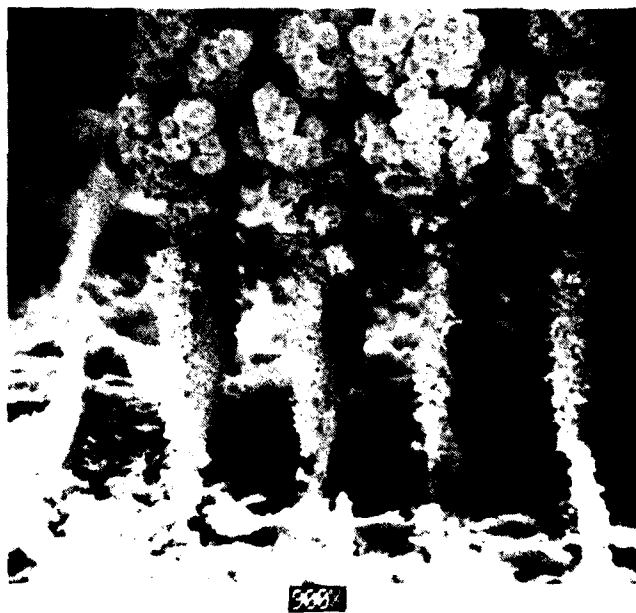


FIGURE 9 DEPOSITION ON SILICON MICROSTRUCTURE

IV DISCUSSION

A. Iridium Deposition from IrCl_3

A computer-assisted literature search for thermodynamic and vapor pressure properties of IrCl_3 produced little pertinent data on which to base volatilization and deposition experiments. Powell (1962) suggested that the volatilization and decomposition temperatures of IrCl_3 are too close to permit efficient use of this material in vapor deposition reactions, but that metal carbonyl halide compounds are stable and amenable for CVD work. Macklin and Withers (1967) reported on the deposition of iridium from IrCl_3 , but presented little data on the nature of the volatile iridium species or the amount of iridium deposited. We speculate that for iridium carbonyl chloride species, such as IrCOCl_2 may be formed in the presence of IrCl_3 and CO (Powell, 1962). Our results, however, suggest that (IrCOCl_3) generated from IrCl_3 and CO is not an efficient transport reagent for iridium CVD work, because of the narrow-range temperature limits for its formation and decomposition.

B. Iridium Deposition from IrF_6

A review of the work of Macklin and Withers (1967) suggested that IrF_6 is the best halide for depositing iridium coatings. The hexafluoride, which has a sublimation pressure of 1 atm at 53°C , is the most volatile source of the metal (vapor pressure = 248 torr at 25°C , 77 torr at 0°C , and 7 torr at -40°C), but is quite sensitive to decomposition. This sensitivity creates a handling and storage problem that requires careful attention to cleanliness and the avoidance of reducing agents. In practice, it is nearly impossible to avoid the slow decomposition of the hexafluoride to iridium metal or IrF_6 species. In our work, IrF_6 was prepared and stored in fluorine-passivated apparatus, and between runs maintained at -78.5°C .

While Macklin and Withers (1967) reported that iridium deposition rates up to 0.5 mil/h ($13\text{ }\mu\text{m/h}$) were observed using IrF_6 , they report little data to support this claim. We estimate from their work that the iridium layer deposited on a graphite surface is about $2.3\text{ }\mu\text{m}$ thick.

During the course of our investigation, we were able to achieve deposits considerably thicker than previously reported. For example, the thickness of the film-like deposit shown in Figure 6 is calculated from its weight and surface area to be about $50\text{ }\mu\text{m}$ and was deposited at about $13\text{ }\mu\text{m/h}$ (in agreement with the rate reported by Macklin and Withers). Other deposits, which are probably porous in nature, were generally greater than $10\text{ }\mu\text{m}$.

The narrow-range temperature dependence for iridium deposition from IrF_6 (Figure 4) has not been previously reported. We speculate that the temperature dependence curve could be refined with more-accurate and precise temperature measurement and control than is possible with the present apparatus.

Sladek (1971) mathematically described the temperature region in chemical vapor deposition for the transition from film to particle formation. In Sladek's scheme, the transition occurs rather suddenly at critical values defined as M^* and T_o^* , and (in general) film formation is favored at lower temperatures. We do not have sufficient critical information concerning the physical/chemical properties of IrF_6 to calculate M^* and T_o^* for a theoretical approach to the problem. It seems clear, however, that this approach would not predict a maximum in the sticking efficiency curve (Figure 4) and that this effect is indeed unique to chemical vapor deposition of iridium from IrF_6 .

REFERENCES

- Bassous, E., 1978: "Fabrication of Novel Three-Dimensional Microstructures by Anisotropic Etching of <100> and <110> Silicon," IEEE Trans. on Electron Dev., Vol. ED-25, No. 10, pp. 1178-1185.
- Bauer, E., 1962: "Fiber Texture," Trans. 9th AVS Vac. Symp., p. 35 (McMillan Co., New York).
- Brodie, I., and R.O. Jenkins, 1956: "Impregnated Barium Dispenser Cathodes Containing Strontium or Calcium Oxide," J. Appl. Phys., Vol. 27, No. 4, pp. 417-418 (April).
- Brodie, I., and R.O. Jenkins, 1957a: "Evaporation of Barium from Impregnated Cathodes," J. Electronics, Vol. 2, No. 5, pp. 457-476 (March).
- Brodie, I., and R.O. Jenkins, 1957b: "The Nature of the Emitting Surface of Barium Dispenser Cathodes," Brit. J. Appl. Phys., Vol. 8, No. 1, pp. 27-29 (January).
- Falce, L.R., 1978: "Iridium Cathode Development," Final Report, Varian Associates, N00713-77-C-0186, Naval Research Laboratories.
- Levi, R., 1955: "Improved Impregnated Cathode," J. Appl. Phys., Vol. 26, No. 5, p. 639 (May).
- Longo, R., 1978: "Dispenser Cathodes for Space Applications," Tri-Service Cathode Workshop, Naval Research Laboratories, Arlington, Virginia (January).
- Macklin, B.A., and J.C. Withers, 1967: "The Chemical Vapor Deposition of Iridium," Proc. Conf. Chem. Vap. Dep. of Refractory Metals, Alloys, and Compounds, Gatlinburg, Tennessee, p. 161.

- Maloney, C., 1978: "SEM and AES Studies on Cathodes," Tri-Service Cathode Workshop, Naval Research Laboratories, Arlington, Virginia.
- McMurray, N.D., R.H. Singleton, K.W. Muszar, and D.R. Zimmerman, 1965: "Tungsten Thermionic Emitter Surfaces Improved by Chemical Vapor Deposition," J. Metals, No. 17, p. 600.
- Powell, C.F., I.E. Campbell, and B.W. Gonser, 1962: Vapor Plating (John Wiley and Sons, Inc. New York).
- Powell, C.F., J.H. Oxley, and J.M. Blocher, Jr., 1966: Vapor Deposition (John Wiley and Sons, New York).
- Rittner, E.S., W.C. Rutledge, and R.H. Ahlert, 1957: "On the Mechanism of Operation of the Barium Aluminate Impregnated Cathode," J. Appl. Phys., Vol. 28, No. 12, pp. 1468-1473 (December).
- Schroff, A.M., 1978: "Lifetimes of Matrix Cathodes," Tri-Service Cathode Workshop, Naval Research Laboratories, Arlington, Virginia (January).
- Sickafus, E., 1978: "Space Dispenser Cathodes," Tri-Service Cathode Workshop, Naval Research Laboratories, Arlington, Virginia (January).
- Sladek, K.J., 1971: "The Role of Homogeneous Reactions in Chemical Vapor Deposition," J. Electrochem. Soc., Vol. 118, No. 4, p. 654.
- Smith, D.H., 1978: "Lifetimes of Impregnated Cathodes," Tri-Service Cathode Workshop, Naval Research Laboratories, Arlington, Virginia (January).
- Thomas, R.E., T. Pankey, J.W. Gibson, and G.A. Haas, in press: "Thermionic Properties of BaO on Iridium," preprint.
- Tuck, R., 1978: "Physical Processes in Dispenser Cathodes," Tri-Service Cathode Workshop, Naval Research Laboratories, Arlington, Virginia (January).

Weinstock, B., 1964: Chem. & Engr. News, p. 86, (21 September).

Weissman, I., and M.L. Kinter, 1963: "Improved Thermionic Emitter Using Uniaxially Oriented Tungsten," J. Appl. Phys., Vol. 34, p. 3187.

Yang, J., and R.G. Hudson, 1967: "Evaluation of Chemically Vapor Deposited Tungsten as Electron Emitters for Nuclear Thermionic Application," Proc. Conf. Chemical Vapor Deposition of Refractory Metals, Alloys, and Compounds, Gatlinburg, Tennessee, p. 329.

