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CHEMICAL VAPOR DEPOSITION STATISTICAL PARAMETRIC STUDY

W.C. Robinson, F.H. Patterson
J.D. Fleming and C.W. Gorton

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W. C. Robinson, F. H. Patterson,
J. D. Fleming, and C. W. Gorton

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CHEMICAL VAPOR DEPOSITION STATISTICAL PARAMETRIC STUDY

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J. D. Fleming,² and C. W. Gorton²

ABSTRACT

Factors affecting the chemical vapor deposition of tungsten are being evaluated in a statistically designed parametric study. Eighty-one experiments were required in the $\text{WF}_6\text{-H}_2$ deposition system to provide a third-order polynomial correlation between the response parameters and the independent system parameters over the experimental range of 450 to 820°C, 9 to 20 torrs, 60 to 370 cm^3 WF_6 per minute, and 752 to 5240 cm^3 H_2 per minute. The system parameters were H_2/WF_6 ratio, total flow rate, temperature, and pressure. The initial response parameters were determined for an internal deposit in a 15-in. length of a 0.807-in.-ID copper mandrel. The application and limitations of utilizing the resulting curves for systems of different size and geometry will be discussed. The deposition rate of tungsten at hydrogen fluoride mole fractions of 0.02, 0.05, 0.10, and 0.20 was also determined for each experiment and correlated with the system parameters. These data in conjunction with theoretical consideration of the system give indications of the rate-controlling process in portions of the experimental range. The agreement between theory and experiment and a preliminary interpretation of the deposition mechanism at various conditions will be presented.

INTRODUCTION

Chemical vapor deposition is being investigated at Oak Ridge National Laboratory as a possible fabrication method for hardware that is otherwise difficult to fabricate. These items, including fuel, tubing, coatings, and special parts, are often of an intricate shape. Furthermore, very close control of total thickness, efficiency, and thickness uniformity are often necessary for successful fabrication of the desired component. The

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qualitative effects of the experimental variables on uniformity, deposition rate, and efficiency are generally known by operating CVD engineers. However, the variables are not independent and most hardware is therefore produced by a trial-and-error adjustment of experimental variables until a satisfactory but not necessarily optimum set of conditions is found for the production of that particular part. Operation is further plagued by the occasional occurrence of rough nodular growths. The conditions that lead to these nodules are also qualitatively known, but again there seems to be a combination of variables that may produce them with no one variable being controlling. Therefore, one cannot predict definitely if nodules will occur on a part but only if they are likely to occur.

Finally, there is the irritating lack of knowledge as to whether the rate-controlling mechanism in CVD deposits is adsorption, or diffusion, or chemical reaction, or if each controls in different experimental regions.

The tungsten deposition process was selected for examination for two reasons and for two purposes. The reasons were (1) the tungsten process is a relatively simple CVD process with two initial components, and therefore the variables can be held to a minimum; and (2) tungsten deposition is a very widely used and practical process, so that the results of the study could be of maximum direct benefit to CVD operations. The purposes were to (1) optimize the tungsten deposition process in a chosen system with respect to each of the three response variables: total deposition, deposition efficiency, and thickness uniformity; and (2) attempt to understand the process, including the rate-controlling mechanisms and, if possible, develop a theoretical approach that accurately predicts the engineering response variable from first principles.

EXPERIMENTAL APPARATUS

A schematic of the experimental equipment used in this investigation is shown in Fig. 1. The apparatus was deliberately limited to the simplest equipment possible for the deposition of tungsten. The usual techniques for enhancing thickness uniformity, such as induced temperature gradients, gas preheaters, and mandrel manipulators, were not included. These would

Fig. 1. Deposition Apparatus.

prohibit accurate evaluation of the effects of experimental variables on the deposit homogeneity. The equipment consists of a 16-in. deposition chamber, a scavenger furnace and chamber, a vacuum pump, a cold trap, and a water scrubber to remove hydrogen fluoride. The WF_6 flow is monitored by a Hastings flowmeter, but the actual flow rate was calculated by weight change of the WF_6 cylinder. The hydrogen flow was measured by a rotameter. The tungsten was deposited in a 0.807-in.-ID copper tube.

STATISTICAL PROGRAM

The controllable variables of a standard deposition process are temperature, pressure, time, total flow rate, and inlet composition. Time was held constant for all runs in the investigation, and an experimental design was developed to evaluate the effects of the the other variables on chosen response parameters. The design is concerned not with what the response is but only if it is a function of the experimental variables. In the tungsten deposition system the mole fraction of only one component

is specified to fix the composition of the inlet gas stream. Therefore only four independent variables are needed. The ranges of these four variables are listed below.

Temperature, °C	450 to 820
Pressure, torrs	9 to 20
WF ₆ Flow Rate, cm ³ /min	60 to 370
H ₂ Flow Rate, cm ³ /min	750 to 5200

The complete design required 81 experiment units, which made up a third-order rotatable design. This allows one to describe the response surface with a cubic polynomial equation. The feature of rotatability guarantees that the precision of the estimates derived from the experiment will be unaffected by the orientation of the response surface in the space of the four design variables.

The conditions for the 81 experiments are listed in Tables 1, 2, and 3. The experiments were divided into 3 blocks or phases of 27 experiments each. Each block of 27 experiments comprises a complete second-order rotatable design. Phase 1 covers the extremes in the experimental region, phase 2 the center, and phase 3 the intermediate parts.

PROCEDURE AND EXPERIMENTAL RESULTS

The experiments were performed in the order specified by the statistical design. The experimental results are given in Tables 4, 5, and 6. We could not achieve some combinations of flow rate and pressure proposed in Table 1 with the available pumping capacity. Also, our WF₆ flow rate was determined by a weight difference after the experiment since the Hastings flowmeter was not accurate, and we sometimes deviated from the desired tungsten gas ratio.

The deposit thickness of each tube was determined by an x-ray attenuation technique and checked by manual measurement and x-ray metallographic techniques. The initial measurements were made at nine points in the 15-in. length, at locations specified by a Gaussian integration technique. Later the x-ray attenuation method was modified to produce a continuous trace of the deposit thickness. Examples of the nine point measurements and of a 1/2-in. increment measurement from a continuous trace are given in Table 7.

Table 1. Experimental Design for Investigating
Deposition Rates, Phase 1

Run	Temperature (°C)	Pressure (torrs)	Gas Ratio (% WF ₆)	Flow Rate (cm ³ /min)
1	713.92	9.301	5.573	2405.6
2	635.00	12.500	6.000	3600.0
3	635.00	12.500	7.000	3600.0
4	713.92	15.700	6.427	2405.6
5	713.92	9.301	6.427	2405.6
6	713.92	15.700	5.573	4794.4
7	635.00	12.500	5.000	3600.0
8	713.92	15.700	6.427	4794.4
9	713.92	9.301	6.427	4794.4
10	635.00	12.500	6.000	3600.0
11	713.92	15.700	5.573	2405.6
12	556.08	15.700	5.573	2405.6
13	556.08	9.301	6.427	4794.4
14	556.08	15.700	6.427	4794.4
15	556.08	9.301	5.573	2405.6
16	635.00	12.500	6.000	6400.0
17	635.00	12.500	6.000	800.0
18	556.08	15.700	6.427	2405.6
19	820.00	12.500	6.000	3600.0
20	556.08	9.301	6.427	2405.6
21	556.08	9.301	5.573	4794.4
22	635.00	20.000	6.000	3600.0
23	713.92	9.301	5.573	4794.4
24	635.00	5.000	6.000	3600.0
25	556.08	15.700	5.573	4794.4
26	635.00	12.500	6.000	3600.0
27	450.00	12.500	6.000	3600.0

Table 2. Experimental Design for Investigating
Deposition Rates, Phase 2

Run	Temperature (°C)	Pressure (torrs)	Gas Ratio (% WF ₆)	Flow Rate (cm ³ /min)
1	635.00	12.500	6.000	3600.0
2	713.92	12.500	5.573	3600.0
3	713.92	12.500	6.000	4794.4
4	556.08	12.500	6.000	2405.6
5	713.92	15.700	6.000	3600.0
6	635.00	15.700	6.427	3600.0
7	635.00	9.301	6.427	3600.0
8	635.00	12.500	6.427	2405.6
9	556.08	12.500	6.000	4794.4
10	635.00	12.500	6.427	4794.4
11	635.00	12.500	5.573	2405.6
12	635.00	9.301	6.000	2405.6
13	635.00	15.700	6.000	4794.4
14	635.00	12.500	6.000	3600.0
15	713.92	9.301	6.000	3600.0
16	713.92	12.500	6.427	3600.0
17	635.00	15.700	5.573	3600.0
18	556.08	15.700	6.000	3600.0
19	556.08	12.500	6.427	3600.0
20	635.00	12.500	5.573	4794.4
21	635.00	9.301	6.000	4794.4
22	556.08	9.301	6.000	3600.0
23	635.00	9.301	5.573	3600.0
24	713.92	12.500	6.000	2405.6
25	556.08	12.500	5.573	3600.0
26	635.00	15.700	6.000	2405.6
27	635.00	12.500	6.000	3600.0

Table 3. Experimental Design for Investigating
Deposition Rates, Phase 3

Run	Temperature (°C)	Pressure (torrs)	Gas Ratio (% WF ₆)	Flow Rate (cm ³ /min)
1	507.06	12.500	6.000	1663.7
2	635.00	12.500	6.692	1663.7
3	762.94	12.500	6.000	5536.3
4	635.00	7.313	5.308	3600.0
5	635.00	17.687	6.692	3600.0
6	635.00	12.500	6.000	3600.0
7	635.00	12.500	6.000	3600.0
8	635.00	12.500	5.308	5536.3
9	507.06	12.500	6.000	5536.3
10	762.94	12.500	5.308	3600.0
11	635.00	7.313	6.692	3600.0
12	635.00	7.313	6.000	1663.7
13	635.00	17.687	5.308	3600.0
14	762.94	12.500	6.692	3600.0
15	635.00	12.500	6.692	5536.3
16	507.06	7.313	6.000	3600.0
17	635.00	17.687	6.000	5536.3
18	762.94	12.500	6.000	1663.7
19	507.06	12.500	5.308	3600.0
20	507.06	17.687	6.000	3600.0
21	635.00	17.687	6.000	1663.7
22	762.94	7.313	6.000	3600.0
23	635.00	7.313	6.000	5536.3
24	635.00	12.500	5.308	1663.7
25	762.94	17.687	6.000	3600.0
26	635.00	12.500	6.000	3600.0
27	507.06	12.500	6.692	3600.0

Table 4. Experimental Variables and Results, Phase 1^a

Run	System Pressure (torrs)	Metered Flow (cm ³ /min)		WF ₆ Used (g)	WF ₆ Flow (cm ³ /min)	Available Tungsten (g)	Total Deposited (g)	Total Efficiency (%)	Deposition in 15-in. Section	
		WF ₆	H ₂						Weight (g)	Efficiency (%)
1	9.3	134	2272	515	129	317.9	311	97.8	292	91.8
2	12.5	216	3384	960	241	592.6	399	67.3	370	62.4
3	12.5	252	3348	1000	250	617.3	397	64.3	358	58.0
4	15.7	155	2251	610	153	376.5	382	100.0	350	92.8
5	9.3	155	2251	640	160	395.0	370	93.7	349	88.3
6	15.7	267	4527	1030	258	635.8	595	93.6	561	88.2
7	12.5	180	3420	740	185.5	456.8	394	86.2	368	80.5
8	15.7	308	4486	1200	301	740.7	692	93.5	673	90.8
9	14.0	308	4486	1200	301	740.7	670	90.4	630	85.0
10	12.5	216	3384	950	238	950.0	586	69.9	378	64.0
11	15.7	134	2272	510	128	314.8	308	97.8	272	86.3
12	15.7	134	2272	525	132	324.1	168	51.8	153	47.2
13	11.3	308	4486	1200	301	740.7	162	21.9	141	19.0
14	15.7	308	4486	1235	309	762.3	170	22.3	147	19.3
15	9.3	134	2272	560	140	345.7	136	39.3	122	35.3
16	12.5	384	6016	1420	356	876.5	532	60.1	483	55.1
17	12.5	48	752	240	60	148.1	135	91.1	127	85.8
18	15.7	155	2251	625	156	385.6	193	50.0	172	44.6
19	12.5	216	3384	900	225	555.5	524	94.3	475	85.4
20	9.3	155	2251	600	150	370.4	137	37.0	115	31.1
21	12.3	267	4527	1070	266	660.5	171	25.9	148	22.4
22	20.0	216	3384	925	231	571.0	472	82.7	441	77.2
23	9.3	267	4527	1100	275	680.0	609	89.6	570	83.9
24	12.3	216	3384	900	225	555.5	400	72.0	362	65.1
25	15.7	267	4527	995	267	614.2	179	29.1	158	25.7
26	15.3	216	3384	900	225	555.5	440	79.2	399	71.8
27	12.5	216	3384	900	225	555.5	40	7.2	23	4.1

^a See Table I for design variables.

Table 5. Experimental Variables and Results, Phase 2^a

Run	System Pressure (torrs)	Metered Flow (cm ³ /min)		WF ₆ Used (g)	WF ₆ Flow (cm ³ /min)	Available Tungsten (g)	Total Deposited (g)	Total Efficiency (%)	Deposition in 15-in. Section	
		WF ₆	H ₂						Weight (g)	Efficiency (%)
1	12.5	216	3384	900	225	555.5	406	73.1	371	66.8
2	12.5	200	3400	840	210	518.5	486	93.7	461	88.9
3	12.5	288	4506	1060	266	654.3	594	90.8	557	85.1
4	12.5	150	2356	540	135	333.3	166	49.8	147	44.1
5	15.7	216	3384	850	213	524.7	516	98.3	489	93.2
6	15.7	231	3369	875	219	540.1	416	77.0	382	70.7
7	9.3	231	3369	900	225	555.5	323	58.1	296	53.3
8	12.5	155	2251	525	132	324.1	308	95.0	276	85.2
9	16.5 → 35.0	288	4506	1100	276	680.0	207	30.4	183	26.9
10	12.5	308	4486	1200	301	740.7	404	54.5	367	49.5
11	12.5	134	2272	525	132	324.1	308	95.0	292	90.1
12	9.3	150	2356	560	140	345.7	315	91.1	291	84.2
13	15.7	288	4506	1215	304	750.0	400	53.3	364	48.5
14	12.5	216	3384	910	228	561.7	356	63.4	326	58.0
15	13.2	216	3384	880	220	543.2	519	95.5	484	89.1
16	12.5	231	3369	940	235	580.2	544	93.8	515	88.8
17	15.7	200	3400	825	206	509.2	405	79.5	379	74.4
18	15.7	216	3384	875	219	540.1	173	32.0	159	29.4
19	12.5	231	3369	910	228	561.7	161	28.9	148	26.3
20	14.4 → 18.0	267	4527	1055	264	651.2	501	76.9	461	70.8
21	11.2	288	4506	1120	281	691.3	468	67.7	433	62.6
22	9.6	216	3384	890	223	549.4	137	24.9	125	22.7
23	9.3	200	3400	850	213	524.7	374	71.3	344	65.6
24	12.5	150	2356	550	138	339.5	337	99.3	312	91.9
25	12.5	200	3400	875	219	540.1	173	32.0	156	28.9
26	15.7	150	2356	525	132	324.1	323	99.7	306	94.4
27	12.5	216	3384	930	233	574.1	379	66.0	346	60.3

^aSee Table II for design variables.

Table 6. Experimental Variables and Results, Phase 3^a

Run	System Pressure (torrs)	Metered Flow (cm ³ /min)		WF ₆ Used (g)	WF ₆ Flow (cm ³ /min)	Available Tungsten (g)	Total Deposited (g)	Total Efficiency (%)	Deposition in 15-in. Section	
		WF ₆	H ₂						Weight (g)	Efficiency (%)
1	12.5	100	1564	445	111	274.7	88	32.0	76	27.7
2	12.5	111	1553	475	119	293.2	279	95.1	261	89.0
3	14.0	332	5204	1325	332	817.9	734	89.7	689	84.2
4	10.6	191	3409	900	225	555.5	363	65.3	331	59.6
5	17.6	241	3359	1200	300	740.2	500	67.5	458	61.9
6	12.5	216	3384	900	225	555.5	405	72.9	374	67.3
7	12.5	216	3384	825	207	509.2	391	76.8	349	68.5
8	13.4	294	5242	1075	269	663.6			397	59.8
9	14.0	332	5204	1225	307	756.1	175	23.1	149	19.7
10	12.5	191	3409	775	194	478.4	474	99.1	440	92.0
11	9.4	241	3359	975	244	601.8	354	58.8	324	53.8
12	7.3	100	1564	475	119	293.2	254	86.6	233	79.5
13	17.7	191	3409	845	211	521.6	442	84.7	414	79.4
14	12.5	241	3359	925	232	571.0	543	95.1	509	89.1
15	14.5	370	5166	1335	335	824.0	410	49.7	372	45.1
16	9.0	216	3384	865	217	533.9	64	12.0	56	10.5
17	17.7	332	5204	1225	307	756.1	450	59.5	412	54.5
18	12.5	100	1564	475	119	293.2	264	90.0	218	74.3
19	12.5	191	3409	775	194	478.4	84	17.5	75	15.7
20	17.7	216	3384	900	225	555.5	95	17.1	84	15.1
21	17.7	100	1564	450	113	277.8	274	98.6	256	92.1
22	8.8	216	3384	875	219	540.1	515	95.3	483	89.4
23	14.0	332	5204	1275	320	787.0	415	52.7	386	49.0
24	12.5	88	1576	400	100	246.9	235	95.2	218	88.3
25	17.6	216	3384	850	213	524.7	506	96.4	464	88.4
26	12.5	216	3384	850	213	524.7	405	77.2	374	71.3
27	12.5	241	3359	1025	256	632.7	90	14.2	81	12.8

^aSee Table III for design variables.

Table 7. Deposit Thickness as a Function of
Position Along Mandrels^a

Distance from Section End (in.)	Deposit Thickness (in.)
<u>Measured Values^b</u>	
0.2388	0.0039
1.2298	0.0054
2.8997	0.0072
5.0681	0.0088
7.5000	0.0094
9.9319	0.0094
12.1003	0.0089
13.7702	0.0079
14.7612	0.0070
<u>Read from Continuous Scan</u>	
0.5000	0.0044
1.0000	0.0051
1.5000	0.0058
2.0000	0.0064
2.5000	0.0069
3.0000	0.0073
3.5000	0.0078
4.0000	0.0081
4.5000	0.0085
5.0000	0.0088
5.5000	0.0090
6.0000	0.0091
6.5000	0.0093
7.0000	0.0093
7.5000	0.0094
8.0000	0.0094
8.5000	0.0095
9.0000	0.0095
9.5000	0.0095
10.0000	0.0094
10.5000	0.0094
11.0000	0.0093
11.5000	0.0092
12.0000	0.0090
13.0000	0.0085
13.5000	0.0082
14.0000	0.0078
14.5000	0.0073
15.0000	0.0068

^aFrom phase 3, run 27.

^bFor statistically selected locations.

STATISTICAL RESULTS

Initially the three response variables were correlated and plotted as functions of the four experimental variables selected according to two models. Along with temperature and pressure, model 1 used total flow rate and WF_6 percentage in the inlet gas, while model 2 used flow rates of the two reactant gases. Each response was measured for the center 15 in. of the 16-in. mandrel. Typical graphs of these responses are plotted in Figs. 2 through 7.

Figure 2 shows an example of the total deposition pressure-temperature contours calculated according to model 1. It is one graph from a sequence in which total flow rate and WF_6 percentage were varied. One could similarly plot the response contours as functions of any two experimental parameters for selected values of the other two; temperature

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Fig. 2. Total Deposition Contours for a Total Inlet Gas Flow of 4000 cm³/min and 5.5% WF_6 in the Inlet Gas.

Fig. 3. Total Deposition Contours for Inlet Flow Rates of 2500 cm³/min H₂ and 200 cm³/min WF₆.

Fig. 4. Deposition Efficiency Contours for a Total Inlet Gas Flow of 4000 cm³/min and 5.5% WF₆ in the Inlet Gas.

Fig. 5. Deposition Efficiency Contours for Inlet Flow Rates of 2500 cm³/min H₂ and 200 cm³/min WF₆.

Fig. 6. Range-to-Mean Thickness Ratio Contours for a Total Inlet Gas Flow of 4000 cm³/min and 5.0% WF₆ in the Inlet Gas.

Fig. 7. Range-to-Mean Thickness Ratio Contours for Inlet Gas Flow of 4000 cm³/min H₂ and 150 cm³/min WF₆.

and pressure are used in these examples since they are the most completely independent variables in our system. Figure 3 shows a similar example of total deposition plotted according to model 2. Figures 4 and 5 show examples of the deposition efficiency calculated for the two models. This quantity is the weight of deposit in the 15-in. length expressed as a percentage of the weight of tungsten introduced as WF₆. Figures 6 and 7 illustrate the range of deposition thickness in the 15-in. length divided by the mean deposition thickness in that length, plotted for both models.

Up to this point, all our correlations are with the inlet gas conditions. As the gas reacts passing through the mandrel, its composition and flow rate vary; WF₆ and hydrogen are consumed and hydrogen fluoride appears. With a simple stoichiometric balance, the average composition and flow rate at any point can be calculated from the

initial conditions and the mass of tungsten deposited up to that point. Applying a Gaussian integration technique to the thickness data, we calculated the mass of tungsten deposited up to each of nine selected points along the mandrel. From it, in turn we calculated the average composition of the gas stream and the component flow rates at each point. Finally, by interpolation we obtained the average gas composition, flow rate, mandrel position, and deposit thickness at points at which the hydrogen fluoride mole fraction in the gas had reached 0.02, 0.05, 0.10, and 0.20. The thicknesses obtained were checked by comparison with the continuous scan data. Since the experiments were all for the same duration, the deposit thickness is a measure of the point deposition rate. We correlated these with the experimental values, calculated for the extent of reaction along the mandrel. Figure 8 shows an example of this type of correlation.

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Fig. 8. Deposit Thickness Contours for a Total Gas Flow of 4000 cm³/min and 5.0% WF₆ in the Gas Stream at Points Where the Hydrogen Fluoride Mole Fraction Reached 0.05.

DISCUSSION AND INTERPRETATION

The total weight of deposit, deposition efficiency, and thickness uniformity all depend on the length of the heated substrate and are therefore not directly relatable to deposition mechanisms. Their value is that they represent a correlation between controllable experimental variables and the deposit product. Even though the results are not quantitatively applicable to another system of different size or geometry, they show a trend with experimental conditions that should be independent of the system used. Thus, with our results available, a very few experiments with another apparatus should suffice to establish the relationships for that apparatus reasonably well. We believe that systems of a different size but similar geometry will have an analogous correlation between deposit and experimental variables. Therefore, a complete set of the curves generated in this correlation between the listed responses and experimental variables will be published.³

Examination of diffusion and laminar flow theory indicates that the curves cannot be applied directly even to systems of cylindrical geometry if they are of a different size. Even though one can introduce exactly the same mass velocity of each component and the same H_2 -to- WF_6 ratio, the curves will not be quantitatively analogous because the response parameters will be a function of the physical dimensions and scaling parameters (e.g., the Reynolds Number and total length-to-diameter ratio).

One further observation is necessary in regard to theoretical consideration of these "engineering" curves. Most of the curves with total deposition or efficiency as a response show a double-valued function. The theoretical equations presently derived do not predict or even allow a double-valued function, although our data definitely are double-valued. This behavior is a function of the apparatus and not a fundamental phenomenon. Any other than an ideal system will have the same characteristics. The double-valued function results from predeposition

³F. H. Patterson and W. C. Robinson, Jr., Statistically Designed Chemical-Vapor Deposition Experiment, (to be published).

in the mandrel ahead of the measured 15-in. length at the higher mandrel temperatures. At temperatures around 700°C the observed efficiencies in the 15-in. section begin to approach 100%. At higher mandrel temperatures the gas lines leading into the mandrel become hot enough (despite thermal shielding) to allow deposition, and deposition begins in them. This reduces the apparent efficiency or total deposition in the 15-in. length, although all the available tungsten is deposited, and creates the double-valued function. Therefore, to optimize efficiency on a given piece of hardware requires a mandrel temperature in the range indicated or the use of special heating or injection techniques.

The deposition thicknesses at hydrogen fluoride concentrations of 0.02, 0.05, and 0.1 mole fraction of the gas stream monotonically increase with hydrogen fluoride concentrations at all values of temperature and pressure.

There were not enough data at 0.20 mole fraction to correlate meaningfully. The monotonic increase is contrary to theory and is believed to be caused by the temperature gradient imposed on the mandrel by the inlet gas stream. The fact that this temperature gradient, which should be small in our apparatus, is still the rate-controlling factor at hydrogen fluoride concentrations as high as 0.10 mole fraction indicates that the hydrogen fluoride effect on the deposition rate is small. Obviously the correlation needs to be made at higher hydrogen fluoride concentrations if possible and at low flow rates to minimize the effect of cooling by the inlet gas. Curves showing this are being prepared but are not available at the time of this writing. Since the present data indicate that there is a temperature gradient effect in the mandrel up to hydrogen fluoride concentrations of 0.1 mole fraction, the usual activation energy plots of deposition rate vs the reciprocal of the absolute temperature were not made from Fig. 8 and/or the other graphs of this series. The temperature was measured on the outside of the copper mandrel near the center of the 15-in. section, so it would not indicate accurately the gas-phase temperature until the internal gradient no longer existed. The surprising length of thermal gradient here means that previous Arrhenius-type plots for determination of activation energy may be in error.

To understand the data generated by this program, we are trying to derive an equation for predicting deposition efficiencies from theoretical considerations. To keep the number of variables at a minimum as well as to obtain a simple closed-form analytical expression, several simplifying assumptions were made. This approach was considered reasonable, since only the form of the equation was desired and not an accurate analytical prediction of deposition efficiency. The vapor deposition process is assumed to involve at least five different steps,⁴ any one of which could govern the rate of deposition. These processes are (1) diffusion of the reactants to the heated surface, (2) adsorption of reactants onto the surface, (3) reaction at the surface, (4) desorption of gaseous products from the surface, and (5) diffusion of gaseous products into the gas stream. The present equation considers only the processes of diffusion and kinetics, with the further assumption that the reaction is first order with respect to WF_6 . The derivation involves a mass balance, which includes the effect of the decreasing bulk mass fraction of WF_6 as well as diffusion to the tube wall and subsequent reaction. The equation is

$$E = 1 - \exp - \left\{ \frac{C_1}{Q_{WF_6} + 2Q_{H_2}/298} \left[1 - \frac{1}{1 + (P/T_w)\exp(C_2 - C_3/T_w)} \right] \right\} \quad (1)$$

where

E = deposition efficiency as a fraction,

Q_{WF_6} = WF_6 flow rate (cm^3/min),

Q_{H_2} = H_2 flow rate (cm^3/min),

p = measured system pressure (torrs),

T_w = measured system deposition temperature ($^{\circ}K$).

The details of this derivation will be presented at a later date.

⁴J. D. Fleming, W. C. Robinson, Jr., and C. F. Leitten, Jr., Thermochemical Analysis of Vapor Plating Processes, ORNL-TM-1454 (July 1966).

The applicability of this equation was tested by obtaining a least-squares estimate for the constants C_1 , C_2 , and C_3 using all 81 data points. The results of this approach are:

Constant	Least-Squares Estimate	Approximate Standard Error
C_1	788	102
C_2	20.2	1.2
C_3	15,120	897

An idea of the fit of Eq. (1) may be obtained from Fig. 9, which is a plot of all of the data taken for a pressure of 12.5 torrs and a temperature of 635°C. The solid curve is a plot of Eq. (1) for a hydrogen flow rate of 3350 cm³/min. Some of the data points do not correspond to this hydrogen flow rate but were plotted also, since Eq. (1) indicates that for the analytical model chosen the efficiency is not sensitive to the hydrogen flow rate. It is well to keep in mind that the solid curve shown in this figure was obtained using Eq. (1) with the constants C_1 , C_2 , and C_3 obtained by a statistical analysis of all of the data.

Fig. 9. Deposition Efficiency Vs WF₆ Flow Rate.

CONCLUSIONS AND FUTURE WORK

The effects of the experimental variables on three response variables, total deposition, deposition efficiency, and deposit thickness uniformity, were defined for deposition of tungsten inside a cylindrical mandrel of 0.807-in. ID. These complete results are presented elsewhere. The same evaluation will be made using other response parameters including mechanical properties, fluorine content, and microstructure. One cannot apply the obtained results directly to other sizes or shapes, but an attempt will be made to define the relationship between the experimental variable effects on responses in different sizes and geometries.

The effect of concentration of hydrogen fluoride byproduct on deposition rate is quite small compared to the temperature effect. A long thermal gradient is present in standard deposition mandrels. To evaluate the hydrogen fluoride effect on deposition rate, we will have to examine hydrogen fluoride mole fractions higher than 0.10.

An equation that was developed from theoretical considerations is a reasonable representation of the data in our experimental range. This indicates that diffusion and kinetics are the rate-controlling processes in most of our experimental range. Application of equations developed from considerations of separate rate-controlling processes indicates that diffusion is the controlling process in the low-pressure high-temperature region of our experimental range. The constants in the present equation will be refined by a fit to only the data in the range expected to be controlled by diffusion or kinetics, and an absorption term will be added to the equation.

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