

**RECEIVED BY TIC DEC 26 1973**

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

UCRL - 75121  
PREPRINT

CONF-740103--1



LAWRENCE LIVERMORE LABORATORY  
University of California/Livermore, California

INTERRELATIONSHIPS BETWEEN PROCESS PARAMETERS, STRUCTURE, AND  
PROPERTIES OF CVD TUNGSTEN AND TUNGSTEN-RHENIUM ALLOYS

William R. Holman  
Frank J. Huegel

December 4, 1973

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

This paper was prepared for presentation at the Conference on Structure-Property Relationships in Thick Film and Bulk Coatings, January 28-30, 1974, San Francisco, and for subsequent publication in the Journal of Vacuum Science and Technology.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

GG

INTERRELATIONSHIPS BETWEEN PROCESS PARAMETERS, STRUCTURE, AND  
PROPERTIES OF CVD TUNGSTEN AND TUNGSTEN-RHENIUM ALLOYS\*

William R. Holman and Frank J. Huegel  
Lawrence Livermore Laboratory, University of California  
Livermore, California 94550

ABSTRACT

The development of CVD techniques for fabricating free-standing tungsten and tungsten-rhenium alloy structures is reviewed. Relationships between plating parameters, kinetics, morphology, microstructure, and properties of thick polycrystalline deposits are discussed. It is emphasized that porosity may be grown into the grain boundaries when the deposition rate is controlled by gas phase diffusion, and that fully dense deposits are generally obtained when the rate is limited by a surface process. The origin and control of many of the microstructural features peculiar to CVD are also discussed.

## INTRODUCTION

Results of an internal Lawrence Livermore Laboratory program aimed at the development of CVD processes for fabricating high-strength tungsten and tungsten-rhenium alloys were presented in Refs. 1 through 6. This continuing program has provided techniques for fabricating CVD tubing and other products with tensile properties equal to those of wrought material. It has also resulted in a clearer understanding of some of the interrelationships between process parameters, structures, and properties in bulk CVD deposits.

The program will be reviewed briefly in the following sections, with emphasis on those factors which have been found to influence the microstructure and properties. Earlier discussions on polycrystalline growth processes<sup>1</sup> will be amplified, particularly as they apply to our understanding of the origins of columnar grains, preferred orientation, grain boundary porosity, and other growth-related phenomena. These growth processes all occur on the crystal facets which are exposed at the surface of the growing deposit. In bulk polycrystalline deposits, the grain boundary morphogenesis - "growth" of the boundaries between adjacent crystals - will be treated as the controlling factor in determining many of the properties of the deposit.

## BACKGROUND

Chemical vapor deposition of tungsten by hydrogen reduction of tungsten hexafluoride ( $WF_6$ ) has been the basic CVD process used throughout the program.

Tungsten-rhenium alloys have been produced with essentially the same equipment by co-depositing tungsten and rhenium from a mixture of  $WF_6$  and  $ReF_6$ .

The program at this laboratory was initiated shortly after the feasibility of the "fluoride tungsten"<sup>7</sup> process was reported.<sup>8,9</sup> As a potential technique for fabricating thick, free-standing shapes, this process appeared to offer several advantages over other fabrication methods - if comparable mechanical properties could be obtained. Therefore, the initial objectives of the program included development of techniques for producing tungsten deposits with metallurgical structures which could be expected to exhibit useful mechanical properties. Excellent tensile properties were achieved,<sup>2</sup> but the usefulness of the deposits was limited by the inherent brittleness of unalloyed tungsten at room temperature. Good combinations of strength and ductility were subsequently achieved with rhenium additions,<sup>4</sup> however, and the program has now progressed to the point where co-deposited tungsten-rhenium alloy parts can be produced with mechanical properties equal to those obtained in wrought materials.

Most of the development work has been carried out with an apparatus designed to fabricate short tubes.<sup>1</sup> In this equipment, a flowing mixture of feed gases is directed vertically upward across a rotating tubular mandrel which is heated inductively. The design provides for brushing of the surface during deposition to increase the nucleation rate.

Specimens for mechanical property evaluation are obtained by slicing the coated tube (mandrel) into rings, chemically separating the molybdenum substrate from the deposit, and electropolishing the free-standing CVD ring. Tensile properties of the ring specimens are measured in a ring tensile test apparatus<sup>3</sup>

where the rings are hydraulically expanded while the pressure is measured as a function of change in circumference.

Early tungsten deposition experiments were aimed at producing high-purity deposits with the fully dense, fine-grained, randomly oriented microstructures which are characteristic of strong metal products. Purity was controlled by using standard high-vacuum technology, liquid nitrogen traps on the exhaust, inert materials of construction, and high-purity hydrogen (palladium diffused) for the feed stream and as a gas blanket for those places where shielding from the plating gas was required. Density was found to be influenced by the plating parameters, geometry, and severity of rubbing - as discussed later. Grain size and orientation were modified by rubbing or brushing the surface. This increased the nucleation rate, suppressed the development of columnar grains with a preferred orientation, and produced the desired fine-grained, equiaxed microstructure. Heat treatment below the secondary recrystallization temperature range also improved the microstructure and properties. The room temperature strength was more than doubled by these treatments, but significant ductility was not obtained - regardless of purity, density, grain size or heat treatment.

When it became apparent that CVD tungsten could not readily be produced with any greater ductility than other forms of tungsten, the program was reoriented to include co-deposition of rhenium with the tungsten. This alloy deposition work involved (1) development of equipment for positive displacement metering of premixed liquid fluorides into a throttled flash evaporator prior mixing with hydrogen in the feed line, (2) development of high pumping rate exhaust systems with high conductance hot traps, condensers, and cold traps for handling large gas loads at low pressures, (3) development

of "long-tube" fabrication equipment in which the rotating tubular mandrel is translated horizontally along its axis through the deposition zone.<sup>4</sup> and (4) studies on mechanisms and the interrelationships between plating parameters, deposition rates, deposit compositions, heat treatment, microstructure, and mechanical properties.

## KINETICS

### A. Tungsten

Deposition rate studies on unalloyed CVD tungsten have shown that within the range investigated, there is a maximum plating rate which is a function only<sup>1</sup> of pressure and temperature. This maximum rate is attained when the partial pressure of each reactant and the gas velocity over the substrate surface are both large enough so that the rate-controlling process changes from gas-phase diffusion to one of the processes occurring on the surface (adsorption, desorption, surface diffusion, or a surface reaction). If the partial pressure of either reactant ( $H_2$  or  $WF_6$ ) or the gas velocity is less than a critical value (for a given pressure and temperature), then the rate will be gas-phase-diffusion controlled, and deposition will occur only as fast as the critical reactant can reach (diffuse to) the surface. Under these conditions, any rate up to the maximum can be obtained by adjusting the gas velocity or composition, since these are the variables which control the rate of gas-phase diffusion to the surface.

When the rate is surface controlled, i.e., when gas-phase diffusion is fast relative to the slowest process occurring on the surface and the rate is therefore at the maximum for that particular temperature and pressure, then

the effects of temperature and pressure on the maximum rate are given approximately by the expression<sup>1</sup>

$$R_m = CP^{1/2} \exp \left( - \frac{67,000}{RT} \right),$$

where

$R_m$  is the maximum rate,

$C$  is a constant,

$P$  is the pressure,<sup>10</sup>

$R$  is the gas constant ( $8.31 \text{ J deg}^{-1} \text{ mol}^{-1}$ ),

$T$  is the absolute temperature of the substrate.

Figure 1, taken from Ref. 1, shows the experimental data which lead to this expression. This graph also shows some data points which were obtained at higher temperatures, where the deposition rate had increased to the point where the feed-gas velocity or composition was no longer sufficient to force the process into the surface-controlled regime. At a given pressure, any data point in Fig. 1 which falls below the straight line defined for that pressure by Eq. (1) can be considered as located on a relatively flat dotted curve which breaks away from the line at the temperature above which the maximum rate can no longer be achieved. This point of intersection, the "upper rate break,"<sup>1</sup> will move up or down the line [Eq. (1)] if either the feed-gas velocity or composition is changed. To the left of the break point, i.e., along the dotted curves, the deposition rate is controlled by gas phase diffusion which is obviously not a strong function of the substrate temperature. To the right of the break point, i.e., along the solid curves, the deposition rate is controlled by the rate of the slowest process occurring on the surface. This process is a strong function of substrate temperature as indicated by Eq. (1).



Three theoretical studies analyzing the surface reactions which take place during fluoride tungsten deposition have been published.<sup>5,11,12</sup> The first paper<sup>11</sup> assumed that desorption of HF is the rate determining surface step and showed that this assumption is consistent with the experimental results in Fig. 1. The second paper<sup>5</sup> showed that the experimental results in Fig. 1 are also consistent with activated adsorption of hydrogen as the rate limiting step, and suggested experimental studies on the effects of rate-retarding additives (poisons) as a method for determining which of the two proposed mechanisms is correct. The suggested experiments were carried out<sup>6</sup> and it was concluded that activated adsorption of hydrogen is probably the rate-limiting surface process when tungsten is deposited by hydrogen reduction of tungsten hexafluoride. The third study<sup>12</sup> attempted to treat both gas-phase-diffusion-controlled data<sup>13</sup> and the surface-controlled data given in Fig. 1. It concluded that "none of the models extrapolate accurately between data sets without some forced fitting of the adjustable constants."

#### B. Tungsten-Rhenium

When rhenium is co-deposited with tungsten, the total deposition rate can be treated as the sum of two rates - a pure tungsten rate and a pure rhenium rate. From this viewpoint, the deposit composition is fixed by the relative rates, and the individual rates can be calculated after the total rate and the composition have been determined.

Co-deposition experiments over a very wide range of experimental conditions all indicated that the rhenium rate was always gas-phase-diffusion controlled.<sup>4</sup> Apparently the surface processes involved in the reduction of  $\text{ReF}_6$  are all quite fast (relative to  $\text{WF}_6$  reduction), and the rhenium deposition

rate is therefore limited only by the rate of transport of  $\text{ReF}_6$  to the surface.<sup>14</sup> Applying mass-transport theory, the rhenium rate should be a function of the boundary layer thickness, the concentration gradient across the boundary layer, and the diffusion coefficient. In terms of measurable plating parameters, this has been shown<sup>4</sup> to reduce to the expression

$$R_{\text{Re}} = C(V/P)^{1/2} P_{\text{Re}}$$

where

$R_{\text{Re}}$  is the rhenium rate (total rate  $\times$  fraction Re in deposit),

$C$  is a constant,

$V$  is the gas velocity,

$P$  is the total pressure,

$P_{\text{Re}}$  is the partial pressure of  $\text{ReF}_6$ .

Temperature does not appear in the expression because the inlet gas temperature is constant (ambient) and because temperature variations in the boundary layer (due to heat transfer from the deposit) do not affect the rhenium rate significantly - except at high substrate temperatures.

The insensitivity of the rhenium rate to temperature combined with the large effect of temperature on the maximum tungsten rate [Eq. (1)], both lead to a large variation in the deposit composition with temperature - i.e., as the temperature is lowered, the total rate and the tungsten rate decrease, the rhenium rate remains about the same, and the rhenium concentration in the deposit therefore increases. These effects are illustrated graphically in Fig. 2 (from Ref. 4), where the composition and rates for one set of plating conditions are given as a function of temperature. The graph also shows that in the presence of rhenium the tungsten rate is approximately the same as the rate for unalloyed tungsten at all temperatures in the range

where the rhenium content of the deposit is less than about 25%. At progressively lower temperatures, where the rhenium content is greater than 25%, increasing amounts of a metastable second phase, federite,<sup>1</sup> are found in the microstructure, and the tungsten rate becomes increasingly greater than the value predicted by Eq. 1. The appearance of federite and this "lower rate break"<sup>15</sup> both occur at the temperature where the tungsten rate is about three times the rhenium rate - i.e., at the temperature where the deposit contains approximately 25% Re. This is the optimum composition from a mechanical-property standpoint, since greater rhenium additions result in the appearance of an equilibrium phase (sigma phase) which embrittles the structure. The metastable federite phase is also quite brittle, but it can be transformed to the strong and ductile terminal solid solution by heat treating at high temperatures (above 1200°C). If the federite is deliberately deposited as a dispersion of fine particles in a matrix of solid solution, then the particles will behave as recrystallization nuclei during heat treatment, and a fine-grained, equiaxed, single-phase solid solution structure will develop. This technique has been used to produce strong tungsten-25% rhenium alloy deposits.<sup>4</sup> Yield strengths of approximately  $1.72 \times 10^3$  MPa (250,000 psi) and uniform elongations of 4-5% have been obtained.

#### MORPHOLOGY, MICROSTRUCTURE, AND PROPERTIES

Fully dense, strong tungsten deposits are generally obtained only when the deposition rate is surface controlled. Conversely, when the rate is controlled by gas-phase diffusion, porous deposits with low strength are often observed. Therefore, plating conditions that will ensure surface control

at all points on the surface are generally selected when optimum mechanical properties are desired. On extended surfaces, this may require rather high flow rates and high concentrations to prevent downstream depletion of the feed gas and reversibility to diffusion control. During alloy deposition, downstream depletion of rhenium cannot be avoided since the rhenium rate is diffusion controlled. For this reason, a uniform composition cannot be achieved over a very large area without providing multiple sources or moving either the source and/or the substrate.

Morphology and its relation to the rate controlling process were discussed in Ref. 1, where it was emphasized that the growth of thick tungsten deposits appears to involve three overlapping stages: (1) nucleation and growth of randomly oriented crystals, (2) stable, cooperative growth of columnar crystals with a preferred orientation, and (3) unstable, independent growth of crystals with pores in the grain boundaries. As discussed later, the transition from stage 2 to stage 3 may occur rather early and abruptly under gas-phase-diffusion-controlled conditions. When the rate is surface-controlled, however, stage 2 growth may continue indefinitely.

The transition from stage 1 to stage 2 was considered as resulting from the normal growth of faceted crystals under conditions where a particular crystal habit is adopted.<sup>1,17</sup> In the case of fluoride tungsten, where the (111) (octahedral) facets generally predominate, the randomly oriented crystals which nucleate on the substrate grow on their exposed surfaces as octahedrons. Full eight-sided crystals will not be formed since growth cannot occur in the direction toward (into) the substrate, but four-sided "pyramids" do develop and persist on the growing surface. The line on the substrate along which neighboring crystal surfaces impinge "grows" outward with the deposit to form the grain boundary. If a boundary grows laterally, one crystal is growing at

the expense of its neighbor, and the "overgrown" crystal may not survive. This is illustrated in Fig. 3 where two-dimensional crystals with right-angle facets have been grown schematically from randomly oriented nuclei to form columnar crystals. The grain boundaries in this polycrystalline deposit were allowed to grow with the deposit; their paths were determined by the locus of points where neighboring crystal facets intersected. In drawing this "microstructure," the nuclei were given arbitrary positions and orientations on the substrate and allowed to grow at a constant rate. The surface contour at equal time intervals is given by "isochronal" lines, and the grain boundaries are simply lines connecting the points where neighboring crystals happen to impinge.

It is clear that crystals oriented with facets inclined at nearly equal angles to the substrate survive longer than crystals in which the facets are inclined at different angles - i.e., crystals in which the orientation is such that the tips or corners are growing in a direction nearly normal to the substrate survive longer than crystals in which the tip direction is more inclined. This very simple picture of the origin of columnar growth and preferred orientation appears to explain adequately the structure of fluoride tungsten. Three assumptions are made: (1) A preferred set of crystal facets develops and persists on the exposed surface, (2) all the crystals grow at about the same rate, and (3) nucleation of new crystals is a relatively rare event. Using this model, it was predicted that plating conditions which favor the development of cubic (100) facets should result in a [111] preferred orientation.<sup>1</sup> This was one of the orientations recently reported in CVD chloride tungsten, and the crystals were, in fact, faceted with three-sided pyramids [(100) faces] inclined at approximately equal angles to the surface.<sup>19</sup>

Under different conditions, the [100] orientation was also obtained, but the crystal habit was not obvious in the published electron micrographs.<sup>19</sup>

Further evidence that the model is reasonably correct is given in Fig. 4, where the same schematic procedure is used to show periodic nucleation and growth of new crystals on the surface of one growing crystal. In this example, the new crystals have all been assigned the same orientation to simulate a twinned relationship with the substrate or host crystal. Comparing the sketch (Fig. 4) with a typical microstructure in which periodic nucleation of twins is believed to have occurred (Fig. 5), it is apparent that similar grain boundary shapes were developed in both cases. The fact that parallel boundaries are formed on several crystals which have all nucleated at different times on the surface of the same crystal suggests that the new crystals are crystallographically related to the host -- probably in a twinned relationship. Grains with this twinned appearance have frequently been observed in alloy deposits. The nucleation rate of twins increases and the grain size decreases with increasing rhenium concentration.

Second-stage growth appears to involve a mechanism which stabilized the growth of neighboring crystals so their common boundary remains nearly vertical and neither crystal can grow laterally at the expense of the other. It has been suggested<sup>1</sup> that since the crystals probably grow by the terrace-ledge-kink (TLK) mechanism, the nucleation of new terraces most probably occurs at the energetically favorable grain boundaries. This growth process has been likened to that induced by screw dislocations intersecting close-packed crystallographic planes.<sup>20</sup> In a grain boundary, new terraces would have the same probability of nucleating on each of the two intersecting facets, and straight, vertical boundaries would be expected to form.

Third-stage growth is characterized by the appearance of voids in the boundaries. The voids are formed when crystal facets or crystals without a common boundary impinge at an angle which cuts off the supply of gas to the growing boundary region. This will happen in corners, at the edge of raised areas, or wherever the surface is sufficiently irregular so that the tips of growing crystals can bridge over lower-lying regions. It can also happen on a flat surface if the growth mechanism involves nucleation and growth of terraces from sources other than the grain boundary; i.e., if the plating conditions are such that homogeneous nucleation occurs on the facets, then terraces (or terraces bunched into microscopically visible steps) may grow toward the grain boundaries rather than away from them. The development of voids due to the mismatch between abutting steps which have grown downward into the boundary region is illustrated very schematically in Fig. 6. A void-free boundary growing by the nucleation of terraces in the boundary is sketched in Fig. 7.

Scanning electron micrographs showing growth of steps outward from void-free boundaries (second-stage growth) and inward toward the boundary of porous deposits (third-stage growth) are shown in Figs. 8 and 9. Figure 10 shows development of fully dense layers grown under several surface-controlled conditions, alternating with several porous layers grown under gas-phase diffusion-controlled conditions (temperatures above the upper rate break). These figures emphasize the fact that the microstructure and the structure-sensitive properties of CVD deposits are determined by processes occurring at the growing surface. As discussed below, they also help to visualize and clarify the experimentally observed correlations between rate controlling processes and microstructure.

Under surface controlled conditions, the supply of reactants from the gas phase is always adequate regardless of the deposition rate.<sup>21</sup> This implies that at the gas-solid interface the concentration of unreacted reactants in the gas phase corresponds to saturation over the entire surface of a growing facet. Therefore, the local reaction rate at any point on the surface is not influenced by boundary-layer thickness or local fluctuations in gas composition due to surface irregularities. It is equivalent to the infinite surface diffusion case for PVD deposits<sup>18</sup> where the atoms, after having been accepted, are fully redistributed, and only the thermodynamically most favorable crystal faces will develop. These conditions favor nucleation of terraces at the grain-boundary edges of the facets and, as discussed earlier, result in the second-stage growth of vertical, void-free boundaries.

Under gas-phase-diffusion-controlled conditions, the reaction rate is a function of the total pressure, the partial pressure of the reactants, and the gas velocity [see Eq. (2)]. At local points on the surface of a growing crystal the rate will vary with the rate at which the critical reactant reaches those points. Therefore, the local deposition rate will be greater near the exposed tips of the crystals than in the lower-lying boundary regions where (1) the boundary layer is thicker and (2) the partial pressure of reactants has been reduced by reactions on the surface at higher elevations.

This local depletion of the critical reactant and reduction in deposition rate in the grain boundary region results in the nucleation of terraces at higher elevations on the growing pyramids (Fig. 9) and the development of porous boundaries (third-stage growth). In extreme cases,



repeated nucleation and growth of new, randomly oriented crystals will occur, and a pronounced nodular structure will develop (Fig. 11).

It should be emphasized that third-stage growth results from surface instabilities and therefore does not develop immediately. Under gas-phase-diffusion-controlled conditions, second-stage growth of CVD tungsten will generally persist on smooth substrates for many micrometers (several mils) before third stage growth sets in.<sup>1</sup> This period of grace is exploited in thin-film semiconductor work, where smooth unfaçeted replication of the surfaces and insensitivity of deposition rate to temperature are two practical advantages of operating under diffusion-controlled conditions. "Ridge growth" and "defect growth" problems are disadvantages of operating in this regime, however, and it has recently been found that operating in the relatively narrow transition region between the two regimes (the upper rate break region discussed earlier) will minimize these disadvantages without affecting the advantages.<sup>22</sup>

Many of the structural features or effects which are encountered in chemical vapor deposition can be understood in terms of the above growth processes. A few remarks in several of these areas are given below:

(1) Nodules - There are several sources and types depending on the system, geometry, and plating conditions, but generally they are believed to be nucleated by particles or other foreign matter settling on the surface. The unstable growth conditions which result from gas-phase diffusion control can also lead to the generation of nodules since high points due to surface irregularities will grow at an accelerated rate (the boundary layer is thinner and the concentration of reactants is higher at higher elevations). This accelerated growth will occur rapidly if stray particles act as the initial high points. If the rate is surface controlled, small nodules do not

change their profile significantly or generate porosity. In either case, if the nodule height or angle of intersection with the surface reaches the point where "bridging over" occurs at the intersection, then a conical, porous zone will grow with the nodule.

(2) Brushing - This processing technique generates randomly oriented nuclei on the growing surface and, in effect, perpetuates first-stage growth throughout the deposit.<sup>1</sup> If the contact pressure is excessive, deformation and "rubbed in" porosity will develop as surface material or particles pile up and "bridge over" to form voids. Brushing will often remove small particles or insipient nodules from the surface before they have grown to damaging size.

(3) Federite - Nucleation and growth of finely dispersed federite grains in co-deposited tungsten-rhenium tubing probably occurs as a result of the decrease in  $\text{ReF}_6$  partial pressure with distance as the feed gas flows across the rotating mandrel. Every point on the surface is cyclically exposed to alternating high and low  $\text{ReF}_6$  partial pressures. Since rhenium deposition is diffusion controlled, the rhenium rate at a given point on the surface will fluctuate with the  $\text{ReF}_6$  partial pressure while the surface-controlled tungsten rate will remain relatively uniform. Under proper conditions, the resultant cyclic composition fluctuation will generate alternate federite nucleation and solid solution nucleation or overgrowth. As mentioned earlier, subsequent heat treatment will transform the two-phase deposit into a fine-grained, single-phase structure with good mechanical properties.

(4) Cyclic Efforts - In addition to the above cyclic changes in rhenium concentration, there are smaller and lower frequency variations in composition which occur in synchronism with the periodic metering of premixed liquid fluorides into the flash evaporator.<sup>1</sup> These composition variations

are immeasurably small, but they do produce visible changes in the microstructure, and they are useful in visualizing surface contours at equal time intervals (Fig. 5).

Little work has been reported on periodic changes in plating conditions as a technique for deliberately modifying the microstructure. Cyclic surface contamination and cyclic additions of a few percent carbon monoxide or other hydrocarbons to form thin layers of tungsten carbide have been investigated as techniques for breaking up the columnar microstructure and improving the tensile properties.<sup>23</sup> Alternate layers of a second-phase and periodic contamination of the surface did promote reinitiation of first-stage growth, but the mechanical properties were not improved. A similar technique involving periodic "passivation" of the surface has been patented<sup>24</sup> as a method for improving the tensile strength.

(5) Preferred Orientation - The development of a two-dimensional preferred orientation or fiber texture during the transition from first- to second-stage growth was treated earlier as the normal behavior to be expected of polycrystalline deposits in which a particular crystal habit is adopted. This model explains the transition from a random orientation to a preferred orientation and predicts the orientation if the habit is known. It says nothing about the origin of the crystal habit, however, and simply points out that the preferred habit is the source of the preferred orientation.

The crystal habit developed by chloride tungsten when it is grown with a (110) preferred orientation has not been identified.<sup>19</sup> This orientation is of particular interest for thermionic emitters because of its high vacuum work function. It has never been observed in pure fluoride tungsten, but it is developed in chloride tungsten under a restricted range of plating

conditions.<sup>19,25,26</sup> Apparently the presence of Cl or HCl modifies the relative growth rates of the facets so that a crystal habit is developed in which the direction from the center towards the remotest point on the surface (the direction of fastest growth) is also the direction normal to the (110) plane. This suggestion is supported by a report that the preferred orientation of fluoride tungsten can be changed from [100] to [110] by the addition of Cl to the feed gas.<sup>27</sup> In addition, work at this laboratory has shown the HCl additions poison the surface and drastically reduce the deposition rate of [100] oriented fluoride tungsten.<sup>6</sup> Metallographic evidence that development of the normal octahedral facets was suppressed by the HCl additions was also obtained.

#### SUMMARY

A continuing program on the development of CVD processes for fabricating tungsten and tungsten-rhenium alloys has been reviewed with emphasis on the relationships between kinetics, morphology, microstructure, and properties. It has been shown that dense tungsten deposits with good properties are obtained when the rate-controlling process occurs on the surface. Plating conditions in which the tungsten rate is limited by gas-phase diffusion were shown to result in porous deposits with poor properties. It was also shown that tungsten-25% rhenium alloys can be produced by plating two-phase deposits which are then transformed by heat treatment to form equiaxed, fine-grained, single-phase structures with tensile properties equal to those of wrought material.

Density of polycrystalline deposits, origin of columnar grains, preferred orientation, nodules, federite, cyclic effects, brushing, and other related subjects were discussed in terms of growth mechanisms. It

was shown that many of the structural features peculiar to CVD deposits can be correlated with plating conditions and understood in terms of kinetics and morphology.

#### ACKNOWLEDGMENTS

The authors wish to express their appreciation to Edward Fung and Wayne Cowden for assistance with the experimental work, to Deborah Korte and Wayne Steele for the metallographic work, and to Henry Cheung for consultation.

REFERENCES

- \*Work performed under the auspices of the U. S. Atomic Energy Commission.
- <sup>1</sup>W. R. Holman and F. J. Huegel, Proc. Conference on Chemical Vapor Deposition Refractory Metals, Alloys, and Compounds, Gatlinburg (ANS-AIME, 1967), pp. 127-148.
  - <sup>2</sup>W. R. Holman and F. J. Huegel, *ibid.*, pp. 427-442.
  - <sup>3</sup>W. R. Holman, E. B. Stiles, and E. Fung, *J. Sci. Instrum.* 44, 545 (1967).
  - <sup>4</sup>W. R. Holman and F. J. Huegel, Proc. Second International Conference on Chemical Vapor Deposition, Los Angeles (Electrochemical Society, 1970), pp. 171-191.
  - <sup>5</sup>H. Cheung, Proc. Third International Conference on Chemical Vapor Deposition, Salt Lake City (ANS, 1972), pp. 136-144.
  - <sup>6</sup>F. J. Huegel, E. Fung, H. Cheung, and W. R. Holman, *ibid.*, pp. 145-152.
  - <sup>7</sup>Tungsten formed by the reaction of hydrogen with tungsten fluoride - rather than with tungsten chloride, as in forming "chloride tungsten".
  - <sup>8</sup>W. E. Reid and A. Brenner, NBS Tech News STR-2450 (Jan. 1960).
  - <sup>9</sup>V. A. Nieberlein and H. Kenworthy, USBM Rept. Invest. 5539 (1959).
  - <sup>10</sup>There is good theoretical and experimental evidence to suggest that P should be the partial pressure of hydrogen,<sup>5,11</sup> rather than the total pressure as reported in Ref. 1. Either pressure fits the available experimental data.
  - <sup>11</sup>R. W. Haskell, Proc. Second International Conference on Chemical Vapor Deposition, Los Angeles (Electrochemical Society, 1970), pp. 63-69.
  - <sup>12</sup>L. E. Bracher, Proc. Fourth International Conference on Chemical Vapor Deposition, Boston (Electrochemical Society, 1973), pp. 340.

<sup>13</sup>J. F. Berkeley, A. Brenner, and W. E. Reid, *J. Electrochem. Soc.* 114, 561 (1967).

<sup>14</sup>A possible explanation for the rapid reduction of  $\text{ReF}_6$  might be found in the suggestion that a replacement reaction could be occurring between a rhenium fluoride species and tungsten atoms in the surface.<sup>1</sup>

<sup>15</sup>The presence of federite on the surface apparently lowers the activation energy of the surface process controlling the tungsten rate. A lower rate break has also been reported by other workers.<sup>16</sup>

<sup>16</sup>Yu. N. Tokaev, Yu. N. Golovanov, and A. I. Krasovskii, *Tsvetnye Metally* 10, 61 (1969).

<sup>17</sup>The same reasoning has been applied by van der Drift,<sup>18</sup> whose paper on "Evolutionary Selection, a Principle Governing Growth Orientation in Vapor Deposition Layers" was also published in 1967.

<sup>18</sup>A. van der Drift, *Phillips Res. Repts.* 22, 267 (1967).

<sup>19</sup>G. Wahl and P. Batzies, Proc. Fourth International Conference on Chemical Vapor Deposition, Boston (Electrochemical Society, 1973), pp. 363-374.

<sup>20</sup>J. W. Geus, Chemisorption and Reactions on Metallic Films, edited by J. R. Anderson (Academic Press, New York, 1971), chapter 3, pp. 129-224.

<sup>21</sup>Transport of reactants in the gas phase is rapid relative to the surface process (unspecified) controlling the deposition rate.

<sup>22</sup>J. M. Green, II, T. O. Sedgwick, and V. J. Silvestri, Process for Forming Uniform and Smooth Surfaces, U. S. Patent No. 3,661,636, May 9, 1972; International Business Machine Corp., Armonk, N. Y., assignee.

<sup>23</sup>Unpublished work at this laboratory.

<sup>24</sup>Yu. M. Korolev, V. I. Stolyarov, V. F. Solovyev, A. B. Emelyanov, and A. L. Mosolkov, Method for Deposition for Tungsten Coatings, USSR Patent No. 291,995, February 23, 1971.

<sup>25</sup>L. Yang, R. G. Hudson, J. W. R. Creagh, Proc. Second International Conference on Chemical Vapor Deposition, Los Angeles (1970), pp. 817-837.

<sup>26</sup>F. A. Glaski, *ibid.*, pp. 839-858.

<sup>27</sup>M. Warnecke, F. Imbert, and A. M. Shroff, Eighth Annual Thermionic Conversion Specialists Conference, Carmel, California (IEEE, 1969).

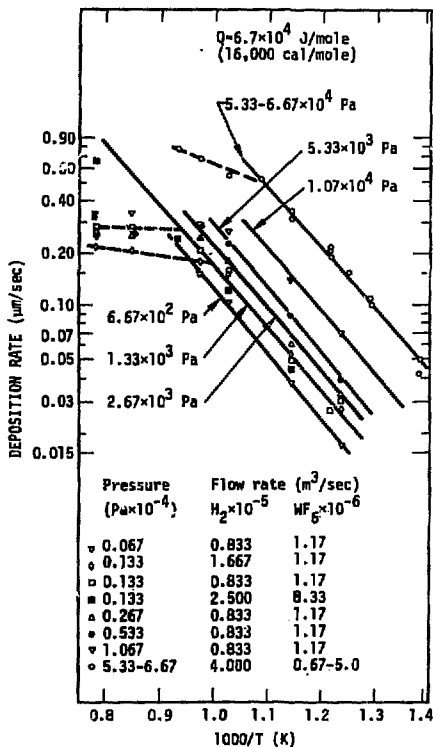


## FIGURE CAPTIONS

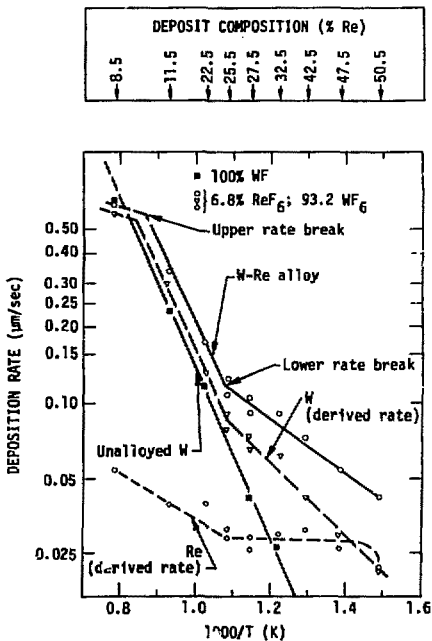
- Figure 1. Effect of plating variables on tungsten deposition rate.
- Figure 2. Effect of temperature on deposition rate and alloy composition.  
(Conditions:  $1.33 \times 10^3$  Pa,  $2.5 \times 10^{-5}$  m<sup>3</sup>/sec H<sub>2</sub>,  $8.33 \times 10^{-6}$  m<sup>3</sup>/sec WF<sub>6</sub> or MF<sub>6</sub>.)
- Figure 3. Growth of two-dimensional crystals from randomly oriented nuclei.  
"Chevron" shaped lines show the surface contour at equal time intervals.
- Figure 4. Nucleation and growth of three twins from one growing crystal face.  
(Compare with typical microstructure, Fig. 5.)
- Figure 5. CVD tungsten-6.5% rhenium alloy deposit. (Compare with Fig. 4.)  
(Conditions: 600°C,  $5.33 \times 10^3$  Pa,  $4.67 \times 10^{-5}$  m<sup>3</sup>/sec H<sub>2</sub>,  $2.33 \times 10^{-6}$  m<sup>3</sup>/sec MF<sub>6</sub>, 10% ReF<sub>6</sub> in MF<sub>6</sub>.)
- Figure 6. Porous grain boundary resulting from growth of steps toward the boundary.
- Figure 7. Dense grain boundary resulting from nucleation of terraces at grain boundary and growth away from the boundary.
- Figure 8. Octahedral facets showing fully dense grain boundaries. (Conditions: 335°C,  $5.1 \times 10^4$  Pa,  $1.67 \times 10^{-5}$  m<sup>3</sup>/sec H<sub>2</sub>,  $2.34 \times 10^{-6}$  m<sup>3</sup>/sec WF<sub>6</sub>. Rate: 0.13 μm/sec.)
- Figure 9. Octahedral facets showing growth of steps toward boundary and resultant porosity. (Conditions: 700°C,  $5.1 \times 10^4$  Pa,  $1.67 \times 10^{-5}$  m<sup>3</sup>/sec H<sub>2</sub>,  $2.34 \times 10^{-6}$  m<sup>3</sup>/sec WF<sub>6</sub>. Rate: 0.51 μm/sec.)

Figure 10. Alloy layers showing grain boundary porosity at temperatures above the upper rate break ( $\sim 700^\circ\text{C}$ ) where the process is gas-phase-diffusion controlled. (Conditions:  $1.33 \times 10^3$  Pa,  $4.67 \times 10^{-5}$  m<sup>3</sup>/sec H<sub>2</sub>,  $2.33 \times 10^{-6}$  m<sup>3</sup>/sec MF<sub>6</sub>, 10% ReF<sub>6</sub> in MF<sub>6</sub>.)

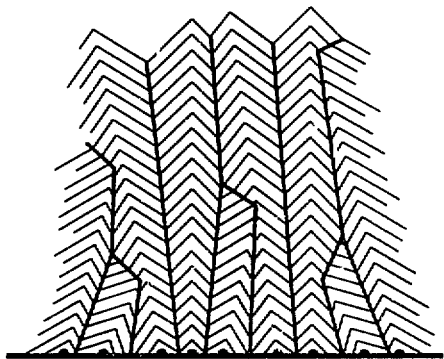
Figure 11. Nodular deposit formed under gas-phase-diffusion controlled conditions. (Conditions:  $600^\circ\text{C}$ ,  $5.1 \times 10^4$  Pa,  $1.67 \times 10^{-5}$  m<sup>3</sup>/sec H<sub>2</sub>,  $3.33 \times 10^{-7}$  m<sup>3</sup>/sec WF<sub>6</sub>. Rate: 0.1  $\mu\text{m}/\text{sec}$ .)



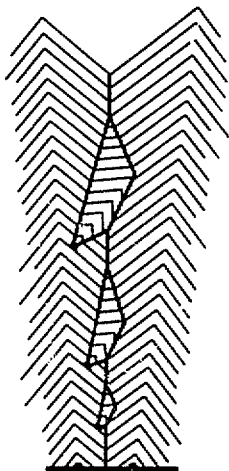
Holman - Fig. 1



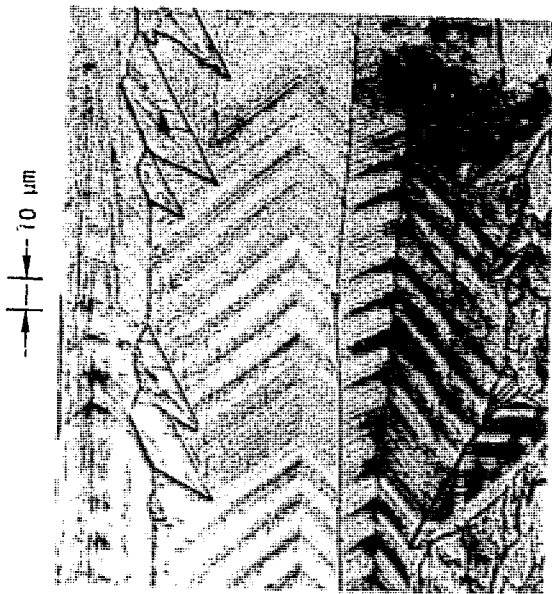
Holman - Fig. 2



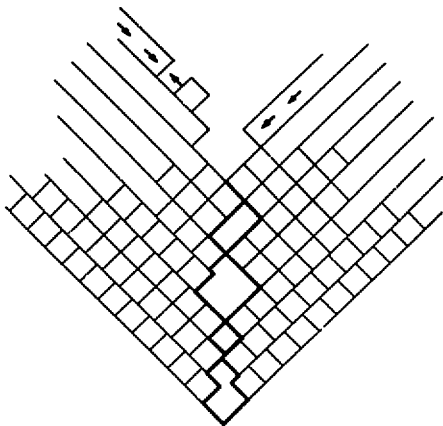
Holman - Fig. 3



Holman - Fig. 4

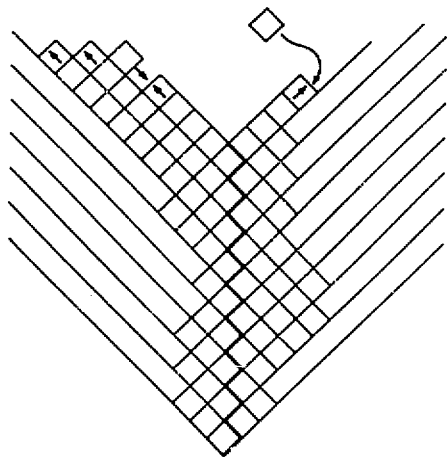


Holman - Fig. 5



Holman - Fig. 6





Holman - Fig. 7

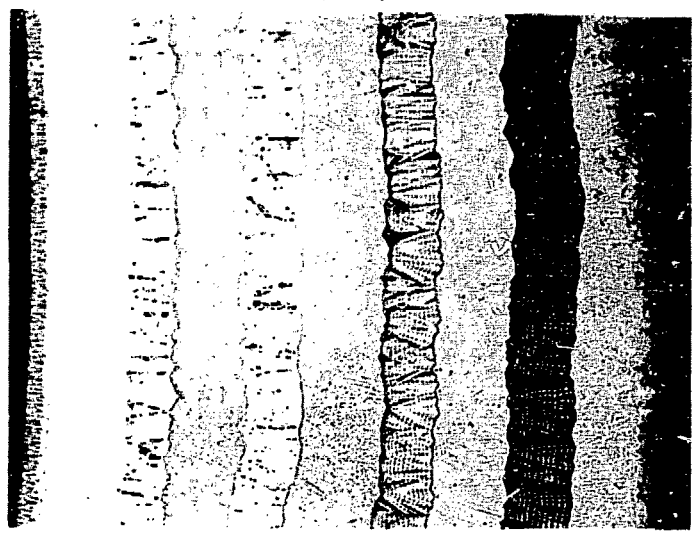


Holman - Fig. 8

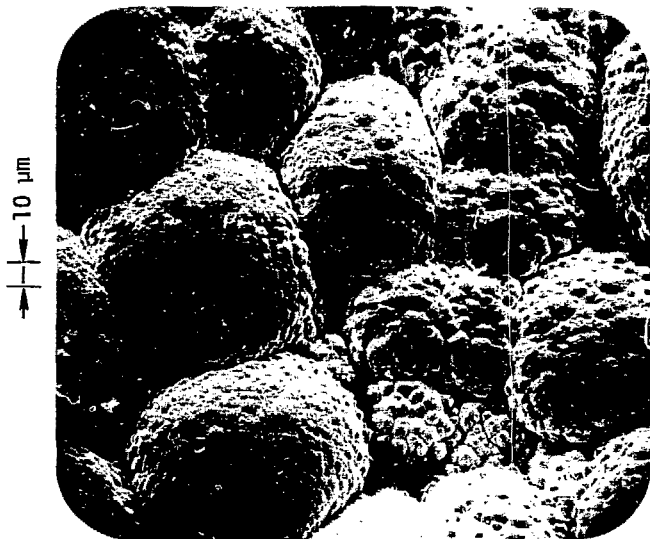


Holman - Fig. 9

100  $\mu\text{m}$



Deposition temp. ( $^{\circ}\text{C}$ )	1000	700	900	600	800	650	500	750	550	675	800
Deposition rate ( $\mu\text{m}/\text{sec}$ )	0.20	0.16	0.19	0.09	0.17	0.13	0.05	0.17	0.07	0.15	0.18
Re	9.5	16.0	10.5	24.0	9.0	19.0	38.0	10.0	27.0	17.0	9.0



Holman - Fig. 11