CHEMICALLY VAPOR-DEPOSITED TUNGSTEN, GRAIN-REFINED AND STABILIZED

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Summary

Efforts to produce chemically vapor-deposited tungsten, having a fine, thermally-stable microstructure, are reviewed. An experimental approach, which involved the reactant thorium acetylacetonate, in addition to hydrogen and WF_6 , was used to prepare tungsten having such a microstructure.

Introduction

In the past 15 years or so, chemically vapor-deposited (CVD) tungsten has found considerable application as a high-temperature structural material. Even wider application would probably be realized if the short-time, elevated temperature strength of this material could be improved. This could be accomplished by producing a fine-grain deposit having considerable resistance to high-temperature grain growth, instead of the more usually found large grain columnar deposit.

One mechanical means of refining the structure of CVD tungsten has been reported [1]. These authors produced short sections of fine-grained, equiaxed fluoride tungsten (tungsten deposited from WF_6) by rubbing the deposit, during its formation, with tungsten wires. In this manner, the energy barrier to nucleation is lowered sufficiently to permit new grains to form. The microstructures of these deposits, however, were stable only up to about 1800 °C [2].

To achieve grain stability at higher temperatures, additions, that are themselves stable, must be made to the deposited structure which will effectively pin the grain boundaries; these additions are of two types.

The first type is comprised of voids or gas-containing bubbles. Since these are formed during post-deposition heat treatment they provide microstructural stabilization but no grain refinement. These voids or bubbles form, mostly at grain boundaries, as the result of the agglomeration of atomic or molecular sized "impurities". Intrinsic "impurities" (those which are formed as the natural result of the deposition of elemental tungsten by the reaction of hydrogen and a tungsten halide) were once thought to be comprised solely of a gas or gases present in the deposition system. For example, fluorine and/or a fluorine-containing gaseous compound such as WF_4 [3] are normally found in fluoride CVD tungsten. More recent evidence [4] suggests, however, that the source of the intrinsic "impurities" is excess vacancies formed during deposition. The coalescence of the gaseous and vacancy "impurities" is believed to provide the bubbles or voids.

No such intrinsic "impurity" stabilization has been reported for chloride CVD tungsten (tungsten deposited from WCl_6). As suggested by Farrell *et al.* [4], the high deposition temperature normally associated with this material (1000 - 1200 °C as compared with 600 - 800 °C for fluoride CVD tungsten) permits increased surface mobility of tungsten atoms, with a presumed consequent reduction in the concentration of excess lattice vacancies. The relative structural instability of chloride CVD tungsten compared with its fluoride counterpart is typified by the grain growth data of ref. 5.

Extrinsic "impurities" (those which are added or formed during deposition as the result of the introduction of a third reactant to produce bubbles or voids) have been used in attempts to stabilize chloride CVD tungsten. Additions of potassium, aluminum, and silicon, in the form of their chlorides, have been made in the expectation that post-deposition annealing would create bubbles containing potassium vapor [6]. A detailed description of this particular means of structural stabilization is given in ref. 7. A further attempt at stabilization by the addition of extrinsic "impurities" (with the attendant purpose of refining the tungsten grain size) utilized the formation and subsequent thermal decomposition of W_2N formed during deposition by the addition of NH_3 gas to the reactant gas stream [8].

In addition to forming voids or bubbles, a second type of grain stabilization has been employed in which a chemically-formed, dispersed, solid phase is co-deposited with the tungsten. In this manner, some stability (and grain refinement) has been achieved by the introduction of gaseous compounds to yield HfN [9], tungsten silicides [10] and carbon (of unidentified form) [11, 12].

In the present work a brief study was made to determine the feasibility of co-depositing fluoride tungsten and ThO_2 to yield a fine grain, dispersion-stabilized microstructure.

Experimental

Initially, undoped tungsten was deposited by the hydrogen reduction of WF_6 onto an inductively-heated molybdenum substrate. The temperature was measured by a thermocouple placed in the annular opening of the substrate. Previous correlations had been made between the annulus temperature and the outer surface (deposition) temperature which was measured with an infrared-radiation sensor unit. The deposition parameters included a hydrogen /WF₆ ratio of 10, a total pressure of 20 Torr and a temperature of 650 °C.

Further deposition to produce an overlay of thoriated tungsten was accomplished without altering the experimental apparatus or opening the system to the air. The alloy deposit was prepared by injecting, alternately, thorium acetylacetonate, Th[$(C_5H_7O_2)_4$], and a mixture of hydrogen and WF₆ for intervals of 10 s and 2 min, respectively. The parameters used during the WF₆-hydrogen injection part of the deposition were identical with those used for the initial deposition of undoped tungsten, except that the system pressure was 80 Torr. During the dopant injection part of the alloy deposition, the parameters included a system pressure of 140 Torr, a flow rate of helium carrier-gas through the thorium acetylacetonate saturator of 1000 cm³/min, saturator and saturator feed-line temperatures of 250 °C and 300 °C, respectively, and a deposition temperature of 1150 °C.

Following sectioning and selective acid dissolution of the molybdenum mandrel, samples of the tungsten (doped and undoped) were analyzed for composition and microstructural stability following high-temperature vacuum annealing for 75 min at temperatures of 2060, 2175 and 2285 °C.

Results

The microstructure of the as-deposited material is shown in Fig. 1. The alternate injections of dopant compound and WF_6 -hydrogen produced a fine-grain, banded structure within the layer of doped tungsten. The undoped tungsten is typical of that formed by conventional CVD practice in that, adjacent to the substrate, the structure is fine, while at a distance from the substrate, fully-developed, coarse, columnar grains are found. From an enlarged view of this duplex (doped and undoped) structure (Fig. 2) it was estimated that within the doped tungsten the short dimension of the grain structure is about 2 μ m or less. This represents an achievement of considerable grain refinement since the grain width of the undoped, fully-developed columnar structure is about 30 μ m.

Following annealing at 2060 °C, the grain size of the undoped tungsten increased to about 80 μ m whilst that of the doped tungsten increased to approximately 10 μ m (Fig. 3). Small voids (bubbles) were found within the doped material (Fig. 4) following this annealing treatment. The more severe thermal treatments of 2175 and 2285 °C produced both increased grain growth in both materials and increased void size in the doped material (Figs. 5 and 6).

The greater void population found near the boundary with the undoped tungsten is felt to be associated with the experimental observation that the initial dopant injection was more voluminous than succeeding ones.

The results of chemical analyses of the doped and undoped material are given in Table 1. Subsequent analysis for thorium, both by X-ray fluorescence and electron microprobe methods failed to detect its presence. The thorium content was judged to be zero.

Discussion

It was the intention of this work to produce a fine-grain, stabilized CVD tungsten by the addition of ThO_2 . The desired result was obtained, but ob-



L 100 Microns

Undoped W

Mo Mandrel

Fig. 1. As-deposited doped and undoped CVD tungsten. $(\times 75)$



Fig. 2. Enlarged view of section of deposit shown in Fig. 1. (× 400)

viously not by the means proposed, since the deposited material was found to contain no thorium. The means by which structural fineness and stability were achieved are analyzed in the following discussion.

Undoped fluoride CVD tungsten possesses, at least within the respective reported ranges for fluorine and oxygen content of $1 \cdot 110$ ppm and $5 \cdot 150$ ppm, a fairly coarse, columnar structure [3, 13 - 16]. The fluorine and oxygen contents found in the doped tungsten of the present work are well within these respective ranges and thus preclude these gases from effecting the observed grain refinement in this material.



Fig. 3. Doped and undoped CVD tungsten following annealing for 75 min at 2060 $^{\circ}$ C. (×100)



Fig. 4. Enlarged view of section of deposit shown in Fig. 3. (×400)

Carbon contents of up to 40 ppm have produced no grain refinement in fluoride-produced CVD tungsten [3, 13 - 16]. Considerable grain refinement has, however, been reported for higher carbon contents -e.g., 100 -150 ppm [11] and 210 - 470 ppm [12]. These observations, along with the demonstrated absence of thorium, suggest that the grain refinement achieved is due to the presence of carbon.

Although present in sufficient amount to strongly influence nucleation behavior, more carbon would need to be present in order to provide a second phase sufficient to effect the observed high-temperature structural stability. Another explanation for this stability must be considered.



Fig. 5. Doped and undoped CVD tungsten following annealing for 75 min at 2175 $^{\circ}$ C. (× 400)



Fig. 6. Doped and undoped CVD tungsten following annealing for 75 min at 2285 $^{\circ}$ C. (×400)

It is a generally accepted observation that in fluoride CVD tungsten, deposited within its normal temperature range of $600 \cdot 800$ °C, the presence of about 10 - 25 ppm of fluorine is desirable [3, 13, 14]. Its presence in these amounts has been related to a certain degree of high-temperature (greater than 1600 °C) grain stabilization caused by the formation of bubbles at grain boundaries. For lesser amounts of fluorine, too few bubbles are formed to provide stabilization. Greater amounts of fluorine have been associated with the high-temperature formation of bubbles of sufficient size and quantity to weaken the structure [15].

Concentration (ppm by weight) Element Undoped W Doped W С 40 160 0 10 32F 10 22Th <400 N.D.

TABLE 1Analytical results for CVD fluoride tungsten

N.D. Not determined.

These observations are borne out by the results of the present work but provide no explanation for the greater stability (greater propensity for bubble formation) of the "doped" tungsten as compared with that of the pure tungsten. Since the deposition temperature for both materials was low (650 °C), one possible explanation is provided by the work of Farrel *et al.* [4], discussed previously. Although the fluorine contents of the two materials are not vastly different, their concentrations of excess lattice vacancies could be. The "doped" tungsten was deposited at the relatively rapid rate of 25 μ m per minute, whilst the rate for pure tungsten was a more typical 12 μ m per minute. Intuitively, one would expect excess lattice-vacancy concentration to vary proportionately with deposition rate and thus be able to provide, during post-deposition annealing, a greater amount of bubbles to the more rapidly deposited "doped" tungsten.

The absence of thorium in the "doped" tungsten was not accounted for. One possible explanation is that the relatively high pressure and temperature chosen for its decomposition resulted in a level of dopant supersaturation sufficient to cause homogeneous gas-phase formation and subsequent entrainment of any and all thorium-bearing products.

Conclusion

Typically, chemically vapor-deposited tungsten is comprised, to a large extent, of coarse, columnar grains. In the present work, tungsten possessing both a fine microstructure and resistance to high-temperature grain growth was chemically vapor deposited by employing the reactants hydrogen, WF_6 , and thorium acetylacetonate. The structural changes effected, however, were not the result of achieving a dispersion of ThO₂ particles as intended. Instead, it was concluded that the fine microstructure resulted from the presence of carbon in the deposit while the microstructure's thermal stability was due to the presence of bubbles or voids, the formation of which was enhanced by a rapid deposition rate.

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