INFLUENCE OF THE FILAMENT MATERIAL ON LOW-PRESSURE HOT-FILAMENT CVD DIAMOND DEPOSITION

S. Okoli, R. Haubner, B. Lux

► To cite this version:

S. Okoli, R. Haubner, B. Lux. INFLUENCE OF THE FILAMENT MATERIAL ON LOW-PRESSURE HOT-FILAMENT CVD DIAMOND DEPOSITION. Journal de Physique IV Proceedings, 1991, 02 (C2), pp.C2-923-C2-930. 10.1051/jp4:19912111 . jpa-00249790

HAL Id: jpa-00249790

<https://hal.science/jpa-00249790>

Submitted on 1 Jan 1991

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

**INFLUENCE OF THE FILAMENT MATERIAL ON LOW-PRESSURE HOT-FILAMENT
CVD DIAMOND DEPOSITION**

S. OKOLI, R. HAUBNER and B. LUX

*Institute for Chemical Technology of Inorganic Materials,
Technical University Vienna, A-1060, Vienna, Austria*

Abstract - The behavior of Re, Ta and W filaments during low-pressure hot-filament CVD diamond synthesis was investigated. With proper matching of the deposition parameters it was possible to produce uniform, well faceted diamond films on cemented carbide substrates using all three filament materials. Carbon layers were formed only on Ta filaments when using 1.0 and 2.0 % CH₄ at filament temperatures below 2200°C. No carbon layer formation was observed on Re and W filaments under these conditions.

Between 2000 and 2400°C the mechanical stability of the Re filaments was superior to that of the Ta filaments as well as that of the W filaments. The W filaments showed the greatest deformation during the carburization.

1. INTRODUCTION

One of the early methods for metastable diamond synthesis was the hot-filament method /1/. As shown by Langmuir /2/ hot solid surfaces can be used to dissociate gas molecules to their atoms by a thermal process. Tungsten filaments heated in hydrogen to 3300 K dissociate great amounts of hydrogen molecules into atomic hydrogen.

In recent years several investigations were carried out using hot-filament techniques to study the effects of different deposition parameters on diamond formation /3-8/. It has been reported that the carburization of the filaments affects the diamond deposition /6/. The carburization behavior of W and Ta filaments has also been investigated /9/.

It was shown repeatedly that carbon layers can be formed on the filaments during diamond deposition. High CH₄ concentrations ($\geq 1\%$) and low filament temperatures ($\leq 2200^\circ\text{C}$) promote this and reduce the efficiency of the filament in decomposing the gas molecules /6,10/. In this paper differences among W, Ta and Re filaments with regard to diamond deposition are examined.

2. EXPERIMENTAL DETAILS

2.1. Experimental set-up

Ta, W and Re wires (non-doped quality, purity: 99.85 % Ta, 99.99 % W and 99.99 % Re) 0.8 mm in diameter and 50 cm long were used. The coils fabricated from these wires were 8 mm in diameter with 18 turns and had a final length of 5 cm. Each such filament was fixed between

two molybdenum electrodes (Fig.1). The power supply was kept constant using an electric power stabilizer. The filament temperature was measured optically using a two-color pyrometer (IRCON pyrometer, model Mirage OR 5 sensor).

Fig.1: Experimental set-up of the hot-filament equipment

2.2. Substrates

The substrates used were cemented carbide inserts supplied by Sandvik Coromant, Sweden. The substrates were used without any surface pretreatment other than ultrasonic cleaning with acetone.

Specification: Type HO5, shape SPUN

Composition : WC (94.5 wt%), Ta(Nb)C (2.0 wt%), Co (3.5 wt%)

2.3. Experimental procedure

The tantalum and tungsten filaments used in these experiments were partially carburized [9]. Since rhenium does not form a stable metal carbide a carburization was not necessary for these filaments.

Filament carburization conditions:

Ta filament: 14 h, 2200°C, 10 torr, 0.5 % CH₄, 30 l H₂/h

W filament: 16 h, 2000°C, 10 torr, 0.5 % CH₄, 30 l H₂/h

Re filament: no carburization treatment

After this the substrates were placed on the substrate holder and the filament-substrate distance was adjusted as required. The reaction chamber was closed and evacuated for 5 minutes. The mixed gas (CH₄/H₂ = 0.5 %) was introduced into the cold reaction chamber. After the flow rate and pressure were set, the diamond deposition was started by heating the filament to the required temperature, which was then kept constant during the run.

To increase or decrease the substrate temperature to the required value, the substrate holder was heated or water cooled. The substrate temperature was measured on the middle substrate (substrate B) by a thermocouple placed in a hole of the substrate (Fig.1).

After the desired deposition time (8 h) the methane flow was turned off and the substrate was allowed to cool to room temperature under pure hydrogen gas.

The deposition parameters used are summarized in Table 1.

2.4. Analysis of the specimens

The diamond deposits so obtained were analyzed using X-ray diffraction and scanning electron microscopy techniques.

The weights of each substrate before and after the deposition were recorded. The film thickness was measured by SEM from the cross section of the substrate. The relationship between the weight increase and the film thickness was determined to be 1 mg $\approx$ 1 μ m.

Table 1: Diamond deposition parameters for testing Ta, Re and W filaments. Only one process parameter was varied at a time.

Wire length	[cm total]:	50	
Filament-substrate distance	[mm]:	10	
Substrate surface temperature [$\pm 10^\circ\text{C}$]:		810	
Deposition time	[h]:	8	
Filament temperature	[$^\circ\text{C}$]:	2200,	2400
Pressure	[torr]:	5, 10, 20,	40, 80
Gas flow rate	[l/h]:	15, 30,	60
Methane concentration	[%]:	0.2, 0.5,	1, 2, 3, 4

↓
Standard condition

3. EXPERIMENTAL RESULTS: Effects on the diamond deposition of different filament materials in connection with various parameters

3.1. Variation of the gas flow rate (15-60 l/h)

Increasing the gas flow rate within the experimental limits (15 to 60 l/h) led to increased diamond crystal density and higher diamond deposition rates for all three filament materials (Fig.2,3)(Table 2). The deposition rates and nucleation densities for the Ta and Re filaments are close to but just slightly higher than those observed for the W filaments (Fig.2,3).

The most important result of increasing the gas flow rate is the greater amount of carbon flowing over the substrates. As shown earlier /6/ the period till layer formation is finished is strongly influenced by the gas flow rate. The residence time of the gas particles in the area of the filament is not that important because of the very high diffusion rate of atomic hydrogen /11,12/. In addition to the rate of supply of nutrient to the growing diamond surface, the surface carbon diffusion rate on the substrate limits the number of nucleation points for diamond crystals /13,14/.

The various filament materials showed no significantly different influence on the quality of the diamond deposition.

Table 2: Influence of filament material on diamond deposition under various gas flow rates
(20 Torr, 2200 $^\circ\text{C}$ filament temperature, 10 mm, 0.5 % CH_4)

gas flow rate [l/h]	Ta filament		W filament		Re filament	
	depos. rate [mg/8h]	crystal density [$10^4/\text{mm}^2$]	depos. rate [mg/8h]	crystal density [$10^4/\text{mm}^2$]	depos. rate [mg/8h]	crystal density [$10^4/\text{mm}^2$]
15	1.3	≥ 10	0.5	<1	1.4	4.5
30	1.9	≥ 10	1.4	3	1.6	6.0
60	2.1	> 10	1.9	3-4	2.1	> 10

3.2. Variation of the gas pressure at 2200 $^\circ\text{C}$ filament temperature

An increase in pressure (10 to 20 torr) led to an increase in the diamond deposition rate (up to 2 mg/8h) (Fig.4,5). However, the crystal quality deteriorated at pressures between 40 and 80 torr. At pressures higher than 80 torr, the diamond crystals were no longer even well faceted (Fig.4)(Table 3).

The total gas pressure in the reaction chamber plays an important role in the formation of the active species responsible for the diamond deposition /15/. At higher pressures (>20 torr), less atomic hydrogen is on the substrate surface due to the lower diffusion rates and the recombination reactions /7/. The optimal substrate surface temperature at which well faceted diamond crystals will be obtained at 0.5 % CH₄ increases with the gas pressure from 760°C (10 torr) to 810°C (20 torr) /8/. The effect of the filament material on the diamond deposition is very slight for changing gas pressures.

Fig.2: Diamond deposition at various gas flow rates (2200°C, 8 h, 10 mm, 810±10°C, 0.5 % CH₄, 20 torr) 10 μm

Fig.3: Influence of the filament materials on diamond deposition at different gas flow rates

Fig.5: Influence of the different filament materials on diamond deposition as a function of the gas pressure

Fig.4: Diamond deposition at various gas pressures for different filament materials (2200°C, 8h, 10 mm, 810°C, 30 l/h, 0.5 %CH₄)

Table 3: Influence of gas pressure on the diamond deposition (2200°C filament temperature, 10 mm, 0.5 % CH₄, 30 l/h)

gas pressure [torr]	Ta filament		W filament		Re filament	
	depos. rate [mg/8h]	crystal density [10 ⁴ /mm ²]	depos. rate [mg/8h]	crystal density [10 ⁴ /mm ²]	depos. rate [mg/8h]	crystal density [10 ⁴ /mm ²]
5	0.7	< 1	0.5	< 1	0.5	< 1
10	1.8	< 10	1.3	< 10	2.0	< 10
20	1.9	> 10	1.4	3	1.6	6
40	2.4	> 10	2.0	> 10	2.3	> 10
80	2.8	> 10	2.1	> 10	2.4	> 10

3.3. Variation of the methane concentration at different filament temperatures

The optimal filament temperature for the deposition of well faceted crystals in a diamond film depended on both the methane concentration and the filament material (Fig.6,7,8)(Table 4). The other diamond deposition parameters showed no significant effects.

Deposition at 2200°C

There is a maximum in the diamond deposition rate when increasing the CH₄ concentration for all three filament materials (Fig.7). Raising the CH₄ concentration produces diamond deposits which are well faceted till the "optimal CH₄ concentration" (maximum growth rate) is reached. At higher CH₄ concentrations the deposits become fine grained and the

growth rate decreases.
The optimal CH₄ concentration as well as the corresponding growth rate are strongly dependent on the filament material (Ta: 1.0% CH₄, 3.5 mg/8h; Re: 2.0% CH₄, 7 mg/8h; W: 2.0% CH₄, 10.5 mg/8h) (Fig.7). At 2200°C the W filament showed the best deposition results.

Fig.6: Influence of CH₄ on diamond deposition at 2200°C using different filament materials (8 h, 10 mm, 20 torr, 30 l/h)

Fig.7: Influence of filament material and CH₄ concentration on diamond deposition at 2200°C filament temperature

Fig.8: Comparison of diamond deposition at Ta and Re filament temperatures of 2200 and 2400°C with different CH₄ concentrations

Deposition at 2400°C

Because of the low mechanical stability of the W filaments diamond deposition was not possible at 2400°C. The experiments using Ta and Re filaments showed a shift of the "optimal CH₄ concentration" for diamond deposition to higher concentrations (Fig.8). The large difference between the filament materials observed at 2200°C is absent. The optimal CH₄ concentration for Ta filaments is ≤ 3% and for Re between 2 and 3%. The maximum diamond growth rate reached was about 12 mg/8h for both filament materials.

Table 4: Influence of CH₄ concentration on the diamond deposition at different filament temperatures (10 mm, 20 torr, 30 l/h)

temp. [°C]	CH ₄ [%]	Ta filament		W filament		Re filament	
		depos. rate [mg/8h]	crystal size [μm]	depos. rate [mg/8h]	crystal size [μm]	depos. rate [mg/8h]	crystal size [μm]
2200	0.5	1.9	> 10	1.4	3	1.6	< 10
	1.0	3.6	5	2.4	5	4.2	3-5
	2.0	1.1	3-3.5	10.0	10	7.0	5-8
	3.0	-	-	8.7	< 1	-	-
2400	0.5	0.9	< 1	-	-	-	-
	2.0	8.4	10	-	-	9.1	5-10
	3.0	12.3	5-10	-	-	11.5	< 1
	4.0	4.3	2- 3	-	-	-	-

4. COMPARISON OF THE FILAMENT MATERIALS

- As already mentioned the filament materials did not fundamentally influence the effects of the other deposition parameters. Increasing the pressure, flow rate, filament temperature and methane concentration increased the diamond deposition rate independently of the filament material.
- The filament materials did however have a strong influence in terms of the maximum CH₄ concentration at which the filament is still active since this depends on the metal's individual thermodynamic characteristics and thus its behavior in the CH₄/H₂ mixture (carbide layer formation).
- The carburization rate of a filament determines its state of deformation. W filaments carburize faster than Ta filaments /9/; as a result W filaments deform more than Ta filaments. Using W filaments for diamond deposition at 2400°C was impossible because of the severe filament deformation.
Since Re does not form a stable metal carbide, carbon has no effect on the filament geometry.
- Mechanical stability values for Re filaments were superior to those of both Ta and W filaments. Ta and W filaments deform geometrically during the carburization.
Re filaments maintain their form for a long time and therefore can be used several times. Because of the carbide formation with both the Ta and W filaments, they can only be used for a few times since they break during sample handling. A very stable filament holder is necessary for a long filament lifetime.
For depositions over large area Re and Ta filaments could yield more uniform films because of the better mechanical stability.
- The economical aspects of Re and Ta filaments cannot be discussed now. Re is more expensive than Ta, but the Re filaments can be used for a longer period than Ta filaments. The real lifetimes of Re filaments were however not tested in our work.

For all three filament materials, the proper matching of the parameters methane concentration and filament temperature made it possible to grow good quality diamond film at growth rates $>1 \mu\text{m/h}$.

5. SUMMARY AND CONCLUSIONS

- Different filament materials needed different CH_4 concentrations for the deposition of well faceted good quality diamond films at high growth rates:

2200°C:	Ta 1.0% CH_4 ,	3.5 mg/8h
	Re 2.0% CH_4 ,	7 mg/8h
	W 2.0% CH_4 ,	10.5 mg/8h
2400°C:	Ta $\leq 3\%$ CH_4 ,	12 mg/8h
	Re $\leq 2\%$ CH_4 ,	12 mg/8h
- For Ta and Re filaments increasing the filament temperature to 2400°C leads to an increase in the deposition rate if the optimal methane concentration at the higher temperature is used. W filaments are not suitable for use at 2400°C due to severe deformation during carburization.
- Re filaments showed a superior mechanical stability over many deposition runs in contrast to Ta and W filaments.
- The general influence of the gas pressure, gas flow rate and filament temperature on the deposition of diamond are similar for all three filament materials, Ta, W and Re.

6. ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support from AB Sandvik Coromant, Stockholm, Sweden and Dr.M.Sjöstrand and Dr.S.Söderberg for the helpful discussion.

7. REFERENCES

1. S.Matsumoto, Y.Sato, M.Kamo, N.Setaka: Jpn.J.Appl.Phys. 21(4) (1982) 183
2. I.Langmuir: J.Amer.Chem.Soc. 34 (1912) 860
3. E.N.Farabaugh, A.Feldman, L.Robins: 2nd Int.Conf.of New Diamond Science and Technology, Washington D.C., Sept.23-27,1990 (in press)
4. J.C.Angus, C.C.Hayman: Science, Vol.241, Aug.1988, 913-921
5. Ching-Hsong Wu, M.A.Tamor, E.W.Kaiser: MRS Fall Meeting, Boston, 1989 (F-3.20)35
6. R.Bichler, R.Haubner, B.Lux: High Temperature-High Pressure, Vol.21 (1989) 576-593
7. R.Litos, R.Haubner, B.Lux: High Temperature-High Pressure, Vol.22 (1990) 99-118
8. S.Okoli: Doctoral Thesis TU Wien (1990)
9. S.Okoli, R.Haubner, B.Lux: 1st Euro.Conf.on Diamond and Diamond-like Carbon Coatings, Sept.17-19, 1990, Crans-Montana (in press)
10. M.Sommer, F.W.Smith: J.Mater.Res. 5(11) (1990) 2433-2440
11. T.Anthony: Proc.NATO ASI, Il Ciocco, Castellveccio Pascoli, Italy, July 22-Aug.3, 1990, Plenum Press
12. T.DebRoy, K.Tankala, W.A.Yarbrough, R.Messier: J.Appl.Phys.68(5) (1990) 2424
13. B.Lux, R.Haubner: Proc.NATO ASI, Il Ciocco, Castellveccio Pascoli, Italy, July 22-Aug.3, 1990, Plenum Press
14. T.Anthony: MRS 1987, Nov.30-Dec.5, N 3.8 Boston, Massachusetts
15. S.Okoli, R.Haubner, B.Lux: J.de Physique, 50,(5)(1989) 159-168