

# Study of diamond film deposition by thermogravimetry

Thermo Fisher Scientific, Process Instruments, Newington, USA

## Introduction

Deposition of diamond films involves many variables, thus optimization of the process requires many time consuming tests using expensive equipment. The ultimate goal of these tests is full control of the process to produce fast growth of mono-crystalline diamond on non-diamond substrates. Growth rate control requires an insight into the kinetics of the deposition process. Presently, point-by-point information is not available, as only the final growth is measurable.

Thermogravimetry, however, provides a potential for continuous monitoring of the deposition by recording weight, time, and temperature simultaneously. Additionally, the thermogravimetric (TG) instrument can control the environment as well as the temperature in Hot Filament Chemical Vapor Deposition (HFCVD) or Laser-Enhanced CVD (LEGVD). As a consequence TG's are excellent instruments for studying the kinetics of diamond film deposition involving HFCVD and LEGVD.

## Equipment

A Thermo Scientific TG-171 Experimental Station was used for this study of HFCVD deposition of carbon films. A Thermo Scientific TG-131 Experimental Station could have been used, as well. The TG-171 has a temperature range from ambient to 1100 °C. The basic features that make these TG's suitable for CVD studies are:

- capability to incorporate hot filament coils and optical measurement devices
- adaptability to peripherals for vacuum control and auxiliary heating.
- Large sample volume and mass capacity
- high weight sensitivity
- corrosive resistant balance and contamination-free system

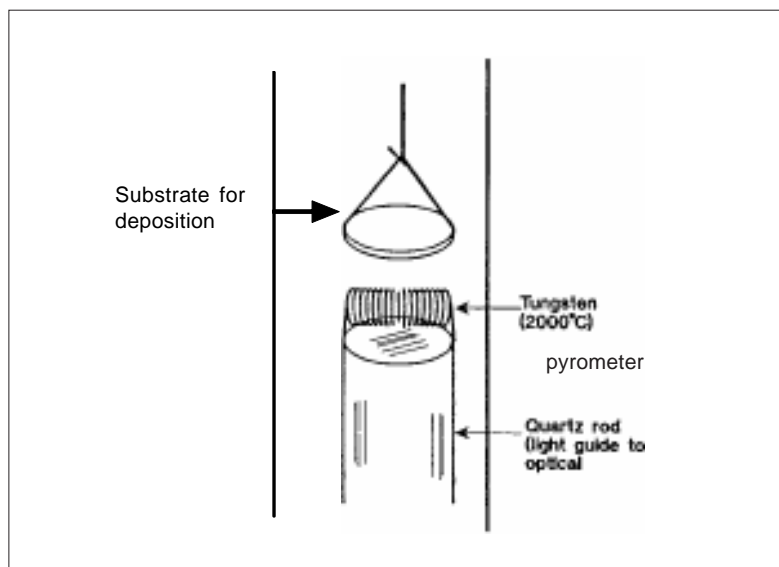


Figure 1

- computer-controlled gas switching
- computerized data acquisition and analysis.

To the basic TG unit a 20 mm long by 2 mm GD tungsten coil of .18 mm wire (from an automotive bulb) was added to provide a hot filament. This coil was positioned 5 mm below a quartz substrate, 25 mm in diameter and 1.5 mm thick. The temperature of the coil was controlled manually with a variac to 2000 °C. This temperature was measured by optical pyrometry via a solid quartz rod that served as a light guide. The arrangement of the above setup is illustrated in Figure 1.

The system pressure control was maintained dynamically as shown in Figure 2. A Baratron vacuum gauge with an MKS low pressure controller regulated continuously a variable solenoid valve for reactant gases which compensated for the pressure loss through a calibrated orifice to a vacuum pump. The steady pressure of 30 mbar was maintained.

The TG-171 that was used in this study contained a 38 mm quartz

tube for the heating rates and for maintaining isotherms. The system provided automatic programming.

## Procedure

The temperature of the tungsten coil was set at 2000 °C. The quartz substrate had an initial weight of 1.08 g. A 0.5% methane and 99.5% hydrogen mixture was admitted to the system and the pressure was stabilized to a constant dynamic value of 30 mbar. With gas flowing the temperature was raised to 900 °C where the isotherm was maintained. Deposition was measured continuously by recording the weight of the substrate. The precision of the weight readings was  $\pm 10$  micrograms.

The experiment was repeated at a lower tungsten coil temperature of 1900 °C. In all repeats the same temperature program and pressure conditions were maintained.

After the deposition experiments, the quartz substrate with deposited films was cooled to ambient temperature and then subjected to flowing air. The samples were not removed from the reactor tube, and immediately, linear

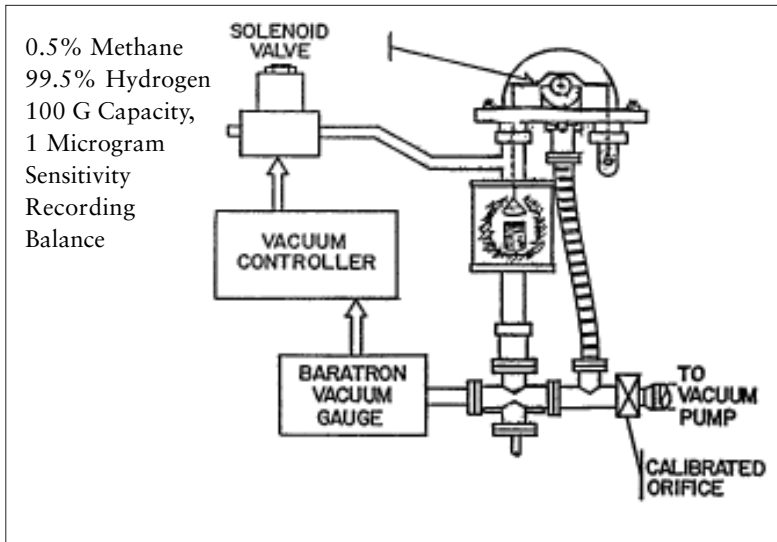


Figure 2

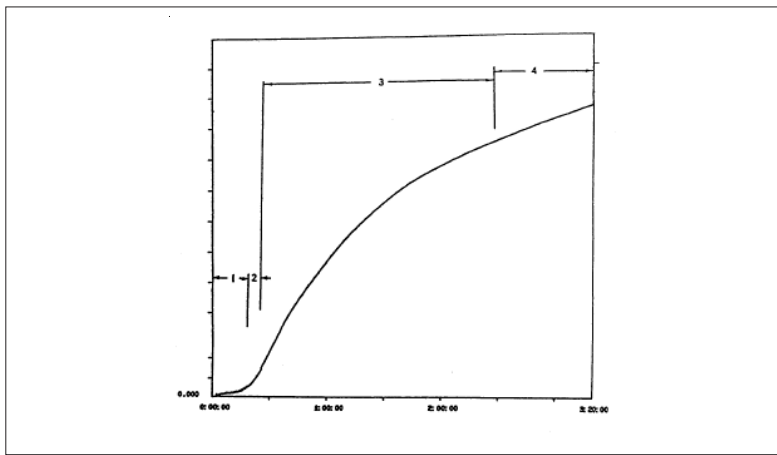


Figure 3

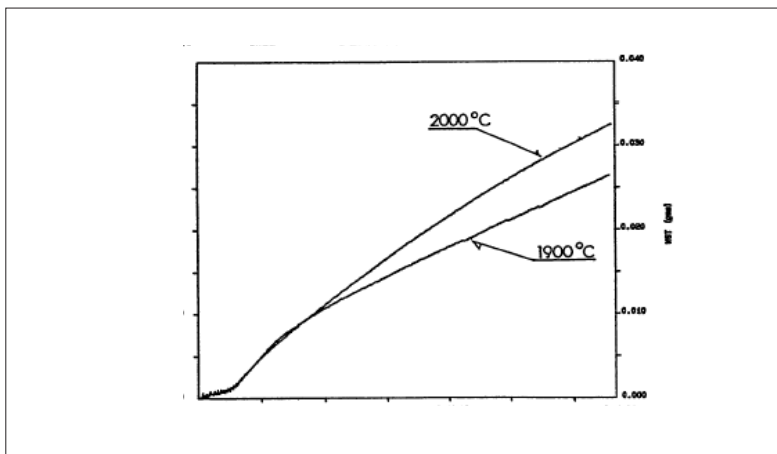


Figure 4

heating (2 °C/min) from room temperature to 2000 °C, was applied to study the rate of oxidation of the deposited layer, as a way of an immediate, relative characterization of the obtained product.

## Results

The results are displayed graphically in Figures 3 and 4.

In Figure 3 the filament temperature of 2000 °C was established before the experiment was started. Figure 4

shows the influence of filament temperature on deposition rate with a lower filament temperature of 1900 °C.

## Discussion

On Figure 3 four areas are indicated. The initial area (1) shows a slow weight gain during the heating period to 900 °C. This weight gain can be attributed possibly to the generation of nuclei. Area (2) shows recorded growth which can be attributed possibly to generation and growth of

nuclei. Area (3) shows a long period of weight gain with a gradual slowing under the isothermal condition of 900 °C. This growth could be attributed to crystal growth. During this period the surface area for deposition is decreasing thus slowing the growth rate even though the crystals are increasing in size. In area (4) the weight gain is linear which is indicative of a completely covered substrate. In this area the surface area is constant with a resultant average growth rate of 4.2 microns/hour. The actual kinetic analysis of the curve was not done here, but with weight and time being measured simultaneously the basis for calculation is there. The actual experiment (as indicated on the time line) took only 3 hours and 20 minutes.

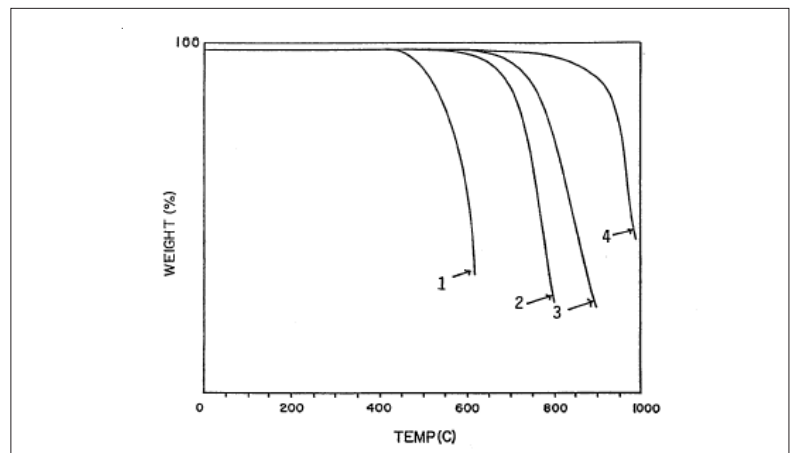
Figure 4 shows the influence of the single variable (filament temperature), with all the other parameters of the process un-changed. In a short space of time the dependence of deposition rate on filament temperature as well as practical minimum and maximum temperatures could be determined, if one wished. The significance of the filament temperature dependence is beyond the instrumental method objective of this application note.

Figure 5 shows a method of characterizing the deposited carbon. Curve (1) is carbon black deposited from a torch which compares with the literature value for graphite. Curve (4) is natural diamond from the literature. Curve (2) is carbon deposited at 1900 °C and curve (3) is carbon deposited at 2000 °C. Thermal oxidation by controlled heating rates in flowing air at a constant rate indicate a feasible simplified method of indicating the phase of the deposited carbon to verify the effects of parameter changes immediately without resorting to X-ray or Raman investigations with subsequent sample handling. The differences in thermal oxidation rates are significant and they may be used for a characterization of the preceding disposition.

## Conclusion

Thermogravimetry is a suitable method for investigating parameters in the deposition of HFCVD diamond films. It also provides a quick method of characterizing these films in place.

*Ref. (1) P.D. Gigl, IDA Seminar, Toronto, 27 Sept 1989.*



*Figure 5*

1. Graphite-carbon black;
2. 1900 °C Deposition;
3. 2000 °C Deposition
4. Natural Diamond

**Thermo Fisher Scientific  
Process Instruments**

**International/Germany**

Dieselstr. 4,  
76227 Karlsruhe  
Tel. +49(0)721 40 94-444  
info.mc.de@thermofisher.com

**Benelux**

Tel. +31 (0) 76 5 87 98 88  
info.mc.nl@thermofisher.com

**China**

Tel. +86 (21) 68 65 45 88  
info.mc.china@thermofisher.com

**France**

Tel. +33 (0) 1 60 92 48 00  
info.mc.fr@thermofisher.com

**India**

Tel. +91 (22) 27 78 11 06  
info.mc.in@thermofisher.com

**United Kingdom**

Tel. +44 (0) 1785 81 36 48  
info.mc.uk@thermofisher.com

**USA**

Tel. 603 436 9444  
info.mc.us@thermofisher.com

**[www.thermo.com/mc](http://www.thermo.com/mc)**

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