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EVALUATING THE INFLUENCE OF GROWTH PARAMETERS ON CVD DIAMOND DEPOSITION USING FACTORIAL ANALYSIS

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Abstract - The deposition of diamond films by low pressure CVD methods has been demonstrated using a number of thermal and plasma assisted CVD techniques. Addition of oxygen to the methane-hydrogen feedstock has been reported to improve the quality of diamond deposited and decrease the temperature at which diamond deposition is feasible. Oxygen also effects the growth rate and possibly the uniformity of the film.

In this paper an experimental design methodology, factorial analysis, is presented which is, in principle, applicable to any CVD process. The factorial analysis identifies the most influential growth parameters and any interactions between independently variable parameters. The analysis has been applied to diamond growth using CH₄-O₂-H₂ mixtures in a microwave assisted CVD process. The effect of oxygen addition on growth rate and film quality is discussed.

1. Introduction

The chemical vapour deposition of diamond films has been demonstrated by a wide range of methods including thermal filament, DC discharge, rf and microwave plasma assisted CVD, oxyacetylene and plasma torch /1/. Growth conditions for the deposition of diamond requires substrate temperatures to be monitored between 700 and 1000°C using a gas feedstock of 0.3-5% methane diluted in hydrogen.

Other parameters such as the excitation source (plasma or filament temperature), its distance from the substrate, flow rates and pressure also influence the growth rate and the quality of the deposited film. Some general conclusions may be drawn from the extensive range of studies that have been made in an attempt to 'optimise' the diamond growth process. Firstly, the amount of amorphous-graphitic carbon that is co-deposited with the diamond increases with methane concentration. The amorphous-graphitic carbon content can be reduced and hence the quality of the diamond film increased at higher substrate temperatures up to some threshold value of approximately 1000°C. A compromise between growth rate and film quality occurs as the growth rate decreases with decreasing methane partial-pressure.

It has been proposed that the addition of oxygen to the methane-hydrogen feedstock has the effect of reducing the temperature at which good quality diamond films can be grown ie. below 700°C /2/. This is advantageous in the coating of temperature sensitive substrates, with the possibility of opening up new application areas such as hard coatings on polymeric materials. It has also been postulated that oxygen additions permit the deposition of high quality films using extended methane concentrations which would overcome the sacrifice in deposition rate.

Hirose and Terasawa /3/ have observed qualitative improvements in film quality and growth

rate using a range of oxygen containing precursors such as alcohols, aldehydes and ketones. Subsequently, Kawato and Kondo /4/ reported experiments using a similar thermal filament CVD reactor and feed stocks of $\text{CH}_4 - \text{H}_2 - \text{O}_2$ mixtures. These authors observed that the addition of 0.4% oxygen to 1.6-4% methane /hydrogen increased both growth rate and diamond purity, compared to experiments performed without oxygen. A more quantitative evaluation of the effect of oxygen additions was performed by Saito et al /5/, who used $\text{CH}_4 - \text{H}_2 - \text{O}_2$ mixtures in a microwave plasma to deposit diamond thin films. Enhanced growth rates of 1-5 $\mu\text{m/hr}$ were reported and maximum growth rate as achieved when the $\text{H}_2/\text{O}/\text{CH}_4$ ratio was between one-third and a half. These deposition parameters produced better crystallinity and reduced non-diamond impurities. These authors also investigated the etching of diamond and graphite using microwave discharges of $\text{H}_2 - \text{H}_2\text{O}$ mixtures /5/. Addition of water vapour to the discharge was found to double the etch rate of graphite. This observation was used to infer that the primary role of the oxygen containing addition is the preferential etching on graphite carbon which is co-deposited with the diamond hence improving the quality of the film.

Liou et al /2/ have also used microwave assisted CVD to investigate the influence of oxygen additions to diamond forming plasmas of methane/hydrogen mixtures over the range of substrate temperatures from 300^o-1000^oC. In the absence of oxygen the amorphous-graphitic content of the deposited films was found to increase above 900^oC. Addition of a few percent of oxygen or less, was found to improve film quality, growth rate, and to possibly extend the deposition region. At temperatures below 500^oC the successful growth of diamond was attributed to the etching of graphite deposits by oxygen. Below 500^oC a white soot was deposited in the absence of oxygen.

In this paper we present the results of a statistical experimental design method, factorial analysis /6,7/, which has been applied to the microwave assisted CVD deposition of diamond films from $\text{CH}_4 - \text{H}_2 - \text{O}_2$ mixtures. The design method provides a quantitative ranking of the most important parameters and interactions between them.

2. Experimental Details

2.1 The MACVD reactor and substrate pretreatment

The schematic design of an MACVD reactor is shown in figure 1 and consists of a 1kW 2.45GHz microwave source, heated platen capable of holding substrates up to 3" in diameter. Pressure is monitored in a side-arm using an absolute pressure capacitance manometer. In this experiment no external heating was used and the substrate temperature was measured via a chromel-alumol thermocouple attached to the backface of the molybdenum substrate holder and also by an optical pyrometer. Gas flows were controlled by rf suppressed mass flow controllers which were premixed before admission into the reactor. Films were deposited onto 30mm silicon wafers which had been polished mechanically for one hour using a 1 μm grade diamond polishing paste. The substrates were cleaned in methanol, acetone and a 1.1.1 trichloroethylene vapour degreasing bath prior to weighing. The substrates were mounted into a fixed substrate holder to ensure constant positioning of the wafers. Deposition times were 22 hours and the substrate platen was positioned just below the plasma ball during deposition.

2.2 Experimental design using factor analysis

The dependence of diamond film quality and deposition rate on parameters (factors) such as pressure, substrate temperature, methane concentration, oxygen concentration, flow rates (residence time), microwave input power etc, makes CVD diamond growth an ideal experiment for factor analysis. The traditional approach which varies one factor at a time in isolation to monitor the response does not allow the interaction between parameters to be fully assessed. Factorial experiments consist of a series of trials including combinations of parameters at set levels. In the simplest case, as used here, the factor-levels are either high or low value.

Therefore a full factorial experiment involving four factors at each of two-levels would require

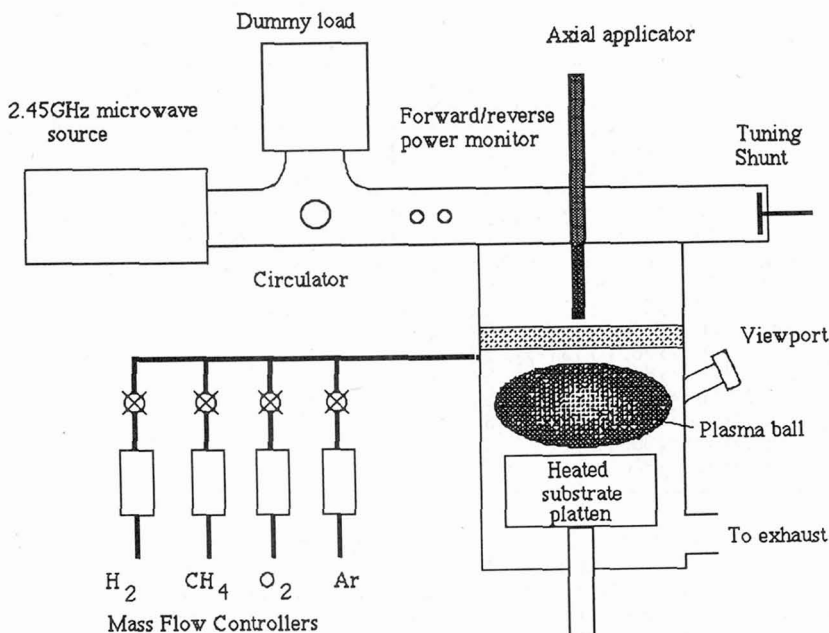


Figure 1. Schematic diagram of the microwave CVD reactor.

2^4 or 16 trials to be performed. The outcome of each combination produces a 'response' which is used to estimate the effect of each factor. In this paper we have chosen to study four factors, pressure P (at 20 and 50 mbar), microwave power M (at 500 and 800 W), methane flow rate C (at 1 and 3 sccm), and oxygen flow rate O (at 0.5 and 1.5 sccm). The combination of factors for the full factorial experiment are shown in Table 1(a). Under each factor are 8 runs with the factor at a high (+) level and 8 runs at a low (-) level. The 'factor-effect' is defined as a change in the average response (weight gain) arising from the change in factor-level combinations, i.e.

$$\text{effect} = (\text{mean response at high level}) - (\text{mean response at low level})$$

The full factorial would provide information concerning 4 main (individual) factors, 6 two-factor interactions, 4 three-factor interactions and one four-factor term. The level of multi-factor effect is found by multiplying the level of its component factors e.g. the term PCO would be high (+) if $P(+1) \times C(-1) \times O(-1)$ and low (-) if $P(-1) \times C(-1) \times O(-1)$ for instance.

The number of experiments that have to be performed can be halved if certain information can be sacrificed. If this is done the same factors and their effects can be investigated, however it is no longer possible to identify the effect of each individual term and 'confounding' occurs. Depending upon which 8 runs are selected from the full factorial several factors will have the same high and low levels in each run and so it is impossible to attribute the response to either uniquely. The experiment is referred to as a fractional or half factorial experiment ($1/2(2)^4$). Table 1(b) shows the interactions that can be estimated by this method. The systematic choice of combinations used here is designed to ensure that the main effects are confounded with multi-factor effects having negligible values. In general, effects including two, three or four factors are likely to have increasingly smaller values if the factors are independently variable which is a prerequisite of factorial analysis experimental design.

In these experiments the response was determined by: the weight gain of each substrate due to

Table 1 Experimental designs for (a) full ($(2)^4$) factorial and (b) the half ($1/2(2)^4$) factorial used in "randomised" order to avoid the introduction of systematic errors. (+)/(-) denote high / low factor levels.

(a)					(b)				
	P	M	C	O		P	M	C	O
Run 1	20 (-)	500 (-)	1 (-)	0.5 (-)	Run 1	50 (+)	800 (+)	1 (-)	0.5 (-)
Run 2	20 (-)	500 (-)	1 (-)	1.5 (+)	Run 2	50 (+)	500 (-)	3 (+)	0.5 (-)
Run 3	20 (-)	500 (-)	3 (+)	0.5 (-)	Run 3	50 (+)	500 (-)	1 (-)	1.5 (+)
Run 4	20 (-)	500 (-)	3 (+)	1.5 (+)	Run 4	50 (+)	800 (+)	3 (+)	1.5 (+)
Run 5	20 (-)	800 (+)	3 (+)	0.5 (-)	Run 5	20 (-)	500 (-)	1 (-)	0.5 (-)
Run 6	20 (-)	800 (+)	3 (+)	1.5 (+)	Run 6	20 (-)	800 (+)	3 (+)	0.5 (-)
Run 7	20 (-)	800 (+)	1 (-)	0.5 (-)	Run 7	20 (-)	500 (-)	3 (+)	1.5 (+)
Run 8	20 (-)	800 (+)	1 (-)	1.5 (+)	Run 8	20 (-)	800 (+)	1 (-)	1.5 (+)
Run 9	50 (+)	500 (-)	1 (-)	0.5 (-)					
Run 10	50 (+)	500 (-)	1 (-)	1.5 (+)					
Run 11	50 (+)	500 (-)	3 (+)	0.5 (-)					
Run 12	50 (+)	500 (-)	3 (+)	1.5 (+)					
Run 13	50 (+)	800 (+)	1 (-)	0.5 (-)					
Run 14	50 (+)	800 (+)	1 (-)	1.5 (+)					
Run 15	50 (+)	800 (+)	1 (-)	0.5 (-)					
Run 16	50 (+)	800 (+)	1 (-)	1.5 (+)					

the deposit; or more importantly for the assessment of diamond formation, by a product of the weight gain and a ratio of measured Raman signal intensities due to diamond and non-diamond phases (see below). When the magnitude of the effects are compared with the overall average response those factors having a more significant response can be identified as those with magnitudes greater than the average. Those interactions with a measured effect less than the overall average can be considered as less significant than experimental variability.

3. Results and Discussion

The mean deposit weight responses of two replica sets of experimental combinations are shown in Table 2. Corresponding Raman spectra of the deposited material are shown in figure 2. The average weight gain response (0.85975) indicates that there are five significant factor effects namely; pressure P + MCO (1.352); methane flow C + PMO (1.3255); the interaction PC + MO (1.048); oxygen flow O + PMC (-1.0045); the interaction PM + CO (-0.9805). The three interactions including main effects (pressure, methane and oxygen flows) are associated with three factor effects (eg MCO) which are unlikely to make a significant contribution to the magnitude of each effect. If this is true then the weight gain response is governed by pressure, methane and oxygen flow rates. The surprising observation is, perhaps, that pressure has such a significant effect within the parameter ranges used (see also reference 9/).

Clearly, as the methane partial pressure increases deposition and hence weight gain increase. This has been observed widely both in practice and from prediction by modelling the surface and gas-phase kinetics of diamond deposition. The weight gain response does not discriminate between the purity of the deposited film in terms of diamond (sp^3 -bonded) and graphitic (sp^2 -bonded) carbon. The Raman spectra show from runs 3 and 8 that at a ratio of 1: 3 methane to oxygen atoms the deposit is either negligible or becomes predominately graphitic. As the oxygen flow rate is decreased (from the sign of the effect) weight gain again increases. Oxygen may have several roles in the diamond deposition process including: preferentially etching of graphite co-deposited with the diamond; suppression of the formation of polycyclic aromatic hydrocarbons which are suggested to be responsible for the formation of non-diamond deposits 8/; and as a homogeneous catalyst for the generation of hydrogen and diamond-forming hydrocarbon radicals.

The weight gain response is also positive in the case of increasing pressure. In practice a maximum has been observed in the deposition rate as a function of pressure. Frenklach and

Table 2. Main and multi-factor terms with measured experimental responses.

Run	Main effects				Two - factor effects						Three - factor effects				Four - factor effects	Weight	Weight*Ir
	P	M	C	O	PM	PC	PO	MC	MO	CO	PMC	PMO	MCO ^a	PCO ^b	PMCO		
1	+	+	-	-	+	-	-	-	-	+	-	-	+	+	+	0.35	0.35
2	+	-	-	-	-	+	-	-	+	-	-	+	-	+	+	4.44	4.07
3	+	+	-	+	-	-	+	+	-	-	+	+	-	-	+	0.35	0.00
4	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	1.01	0.89
5	-	-	-	-	-	-	-	-	-	-	-	-	-	-	+	0.07	0.07
6	-	+	+	-	-	-	+	+	-	-	+	-	+	+	+	0.59	0.51
7	-	-	+	+	+	-	-	-	-	+	+	-	-	+	+	0.06	0.06
8	-	+	-	+	-	+	-	-	+	-	+	-	+	+	+	0.02	0.00

Superscripts a,b,c,d,e,f and g denote pairs of confounded factors.

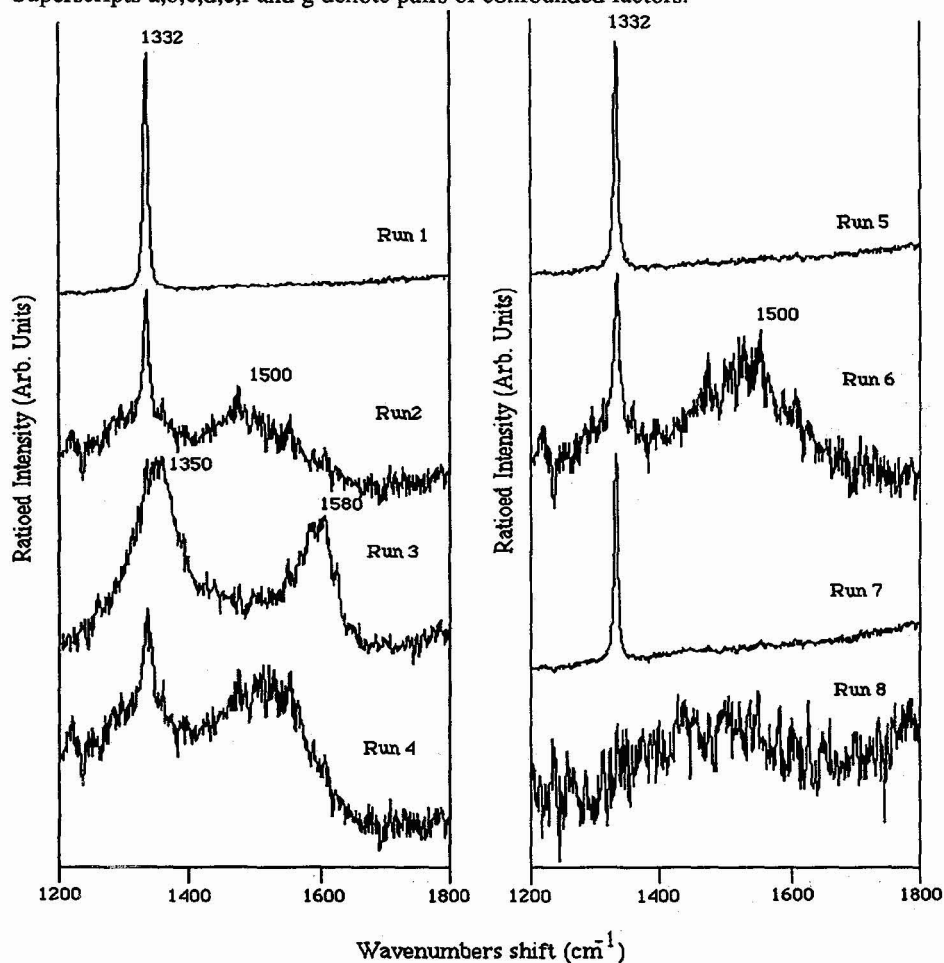


Figure 2. Raman spectra of particles or films deposited in the half-factorial runs.

Wang /8/ as suggested on the basis of theoretical modelling that the corresponding substrate temperatures for maximum deposition rate shifts to higher levels with increasing pressure. The reactor pressure will influence the collisional mean free path and hence collisional frequencies of the reactive intermediates. The subsequent reactions will influence the generation of hydrogen, hydrocarbon and oxygen-containing radicals which undoubtedly effects the deposition rates.

The physical significance of the interaction effects PC + MO and PM + CO are unclear and the effects could be unconfounded by completing the other half of the factorial combinations. As both pressure P and methane flow C are significant main effects in their own right it would be reasonable to suspect that PC might be a dominant interaction in the PC + MO factor but in the absence of further experiments this cannot be assumed. Both pressure and methane concentration may clearly influence the generation of diamond forming precursors however most of the thermodynamic modelling studies deal with the effect of temperature rather than pressure. In the case of the interaction PM + CO it might also be expected that the term CO is predominant and probably reflects the balance between oxygen and carbon either in the suppression of graphite forming precursors or the competitive deposition - etching of carbonaceous deposits.

The weight gain response does not discriminate between diamond and graphite growth and therefore a response which allows for this is required. Raman spectroscopy is a quantitative analytical technique and provides distinct spectral features attributable to diamond and non-diamond carbon phases. On this basis, the relative intensities of Raman peaks of diamond and graphite could be used to normalise the weight gain response. It should be noted however that the Raman cross-sections for diamond and graphite vary by as much as 50-60 times. Another important parameter is the absorption coefficient of the two phases which influences the volume of material sampled. Typically, the incident radiation might probe up to microns in diamond and only several tens of nanometres in graphite. Consequently, it must be assumed that any heavily absorbing graphite phases are homogeneously distributed with the deposited diamond otherwise the normalisation of the weight gain response would be erroneous. The weight gain response was multiplied by the ratio $I_r = I_d / (I_d + I_g)$ where I_r represents the measured ratio of Raman peak intensities due to diamond (d) and graphite (g) respectively. Estimation of the integrated peak area is impeded by a degree of overlap between the diamond single phonon scattering signal and the graphite line. Another potential source of error is accurate estimation of the graphite E line intensity which is superimposed on a monotonically varying fluorescence background. Peak fitting of Raman signals from carbon films has been the subject of several papers and we have chosen to simply take the integrated area of the peaks in the regions $1300-1350\text{cm}^{-1}$ and $1400-1650\text{cm}^{-1}$ to represent the appropriate intensities due to diamond and graphite.

When the response is measured as the product of weight gain and Raman intensity ratio (Table 2) the same five factors show significant effects with the exception that the effect of the methane concentration becomes more significant than the pressure effect. The results show that although oxygen additions have a significant effect on the quality of diamond grown within this range of experimental parameters (C:O of 0.33 to 3), it should be noted that, not surprisingly, the methane concentration but also the pressure are more significant. This observation indicates that other deposition parameters other than the oxygen partial pressure should be considered carefully while considering the quality of diamond films grown using oxygen additions.

4. Conclusions

For a given parameter space it has been shown that pressure can have a more significant effect on diamond growth rate and quality than oxygen concentration. This may be significant when comparing literature reports concerning the growth of diamond films at extended methane concentrations (>1.5%) or at low temperatures using $\text{CH}_4 - \text{H}_2 - \text{O}_2$ mixtures. The procedure of factorial analysis has proven to be an efficient and objective way of quantitatively ranking the

significance of parameters and combinations of effects on the growth of diamond thin films.

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